

Survey on Leaching of Coatings Used in Nuclear Power Plants: Letter Report

K. Natesan and R. Natarajan

Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

Paulette Torres, NRC Program Manager

**Prepared for
Office of Nuclear Regulatory Research
U.S. Nuclear Regulatory Commission
Washington, DC 20555-0001
NRC Job Code N6100**



Survey on Leaching of Coatings Used in Nuclear Power Plants: Letter Report

by

K. Natesan and R. Natarajan

Abstract

This letter report presents the result of a survey of open-literature information on the leaching characteristics of coatings used in nuclear power plants. The survey, in general, indicated a complete lack of information on leachability, leaching rate, and potential leaching constituents of nuclear-power-plant coatings. Furthermore, there has been no concerted test program to evaluate the role of coating parameters and the effect of environmental variables (temperature, pH, pressure, etc.) on the long-term chemical performance of the coatings. Most of the testing emphasized evaluation for design-basis accident conditions and for resistance to irradiation.

Contents

Abstract.....	2
1 Introduction	6
1.1 Regulatory Basis for Protective Coatings	6
2 Coating Information	7
2.1 Epoxy Coatings.....	8
2.2 Alkyd Coatings.....	9
2.3 Zinc-rich Coatings.....	9
2.4 Commercial Coatings for Nuclear Application.....	10
3 Research Studies	12
3.1 Basic Chemical Process for Release of Coating Constituents	12
3.2 Coating Evaluation Studies.....	13
4 Summary	20
References	20

Figures

1	Schematic of coating-environment interactions	16
---	---	----

Tables

1	Brief explanation of various types of coating	8
2	Listing of several coatings of Ameron International for nuclear power plant application	10
3	Listing of several coatings of Keeler & Long/PPG for nuclear power plant application	11
4	Descriptions of several coatings of Carboline Company for nuclear power plant application	11
5	Composition of Dimetcote 9	12
6	Composition of Phenolic 305	12
7	Composition of Amercoat 90HS	12
8	Summary of the main factors influencing release	13
9	Resins used for the study	14
10	Total quantities of leached substances from resins	15
11	Leachate analysis of various coatings from several studies	15
12	Coating systems investigated by the SRTC project and those evaluated by the industry coatings PIRT panel	17
13	Coating defects and phenomena of importance	18
14	PIRT summary of several coating constituents used in SRTC study	19
15	Survey results on coating performance from Ameron International	20

Acronyms

ANL	Argonne National Laboratory
ANSI	American National Standards Institute
ASTM	American Society for Testing and Materials
CAS	Chemical Abstract Service
CSS	Containment spray system
DBA	Design basis accident
ECCS	Emergency core cooling system
EPRI	Electric Power Research Institute
LOCA	Loss of coolant accident
MSDS	Materials safety data sheet

NPP	Nuclear power plant
OEM	Original equipment manufacturer
PIRT	Phenomena Identification and Ranking Table
PWR	Pressurized water reactor
SRTC	Savannah River Technology Center
SSC	Structures, systems, and components
USNRC	U.S. Nuclear Regulatory Commission

Acknowledgment

This work is sponsored by the Office of Nuclear Regulatory Research, U.S. Nuclear Regulatory Commission, under Job Code N6100; Program Manager: Paulette A. Torres.

1 Introduction

During a design basis loss-of-coolant accident (DB LOCA) in a pressurized-water reactor (PWR) nuclear power plant, the emergency core cooling system (ECCS) and containment spray system (CSS) provide a recirculation function to cool the containment building and reactor core. However, blockage of the ECCS sump screens by debris generated during the LOCA may degrade ECCS and CSS performance. Therefore, the U.S. Nuclear Regulatory Commission (USNRC) is conducting experiments to assess the transport of debris to the sump screen and resultant increase in pressure drop across the screens. Detailed information on these experiments and programs can be obtained from the USNRC website.

During a LOCA, high-pressure water escaping through a broken pipe essentially scours thermal insulation and protective coatings (i.e., paint) off adjacent piping, equipment, and structures. After creating debris, the water can transport it to the containment sump where it may collect on the sump screen. Precipitants resulting from the chemical reaction of compounds contained in the sump pool may transport to the ECCS sump and interact with other debris to increase the pressure-drop across the sump screen. To determine the contribution of containment coatings to the reactants contained in the sump pool, the USNRC commissioned Argonne National Laboratory (ANL) to conduct a literature search on the leaching characteristics of nuclear power plant coatings. The NRC is also conducting research focused on the possibility of chemical reactions in the sump that could produce additional products. The objective of the chemical effect testing research is to determine if the sump pool environment generates chemical by-products, which contribute to sump clogging. This research is documented in detail in NUREG/CR-6913 (Park et al. 2006) and in NUREG/CR-6914 (Dallman et al. 2006).

1.1 Regulatory Basis for Protective Coatings

At nuclear plants, coatings and paints (1) protect carbon and low alloy steel, and less commonly, galvanized steel, and aluminum surfaces against corrosive environments, (2) protect metallic, concrete, or masonry surfaces against wear during plant operation, and (3) allow for ease of decontamination of radioactive nuclides from the containment wall and floor surfaces. These coatings come in inorganic forms, such as zinc-based paints, and organic forms, such as epoxy coatings.

American National Standards Institute (ANSI) Standards N101.2, "Protective Coatings (Paints) for Light Water Nuclear Reactor Containment Structures," and ANSI N101.4, "Quality Assurance for Protective Coatings Applied to Nuclear Facilities," classify coatings as Service Level 1, Service Level 2, and Service Level 3.

- Service Level 1 coatings are used in areas inside the reactor containment where the coating failure could adversely affect the operation of post-accident fluid systems and thereby impair safe shutdown.
- Service Level 2 coatings are used in areas where coatings failure could impair, but not prevent, normal operating performance. The functions of Service Level 2 coatings are to provide corrosion protection and decontaminability in those areas outside the reactor containment that are subject to radiation exposure and radionuclide contamination. Service Level 2 coatings are not safety related.
- Service Level 3 coatings are used in areas outside the reactor containment where failure could adversely affect the safety function of structures, systems, and components (SSC).

The NRC Generic Letter 98-04 addresses the possible detrimental effects of failed coatings on a plant's ability to recirculate coolant following a LOCA. Therefore, the generic letter is concerned with Service Level 1 coatings. According to RG 1.54, protective coatings that have not been successfully tested in accordance with the provisions in the applicable ANSI or American Society Testing and Materials (ASTM) standards or have not met the acceptance criteria of the standards are considered to be "unqualified." That is, they are assumed to be incapable of maintaining their adhesive properties during a postulated DB LOCA. It is assumed that "unqualified" coatings applied to the interior surfaces of the containment structure and to SSCs inside the containment structure may form debris products under DB LOCA conditions and may need to be evaluated for their potential to clog ECCS sump screens and strainers.

The ASTM standards applicable to qualified nuclear coatings are as follows:

- ASTM D 5144-00, "Standard Guide for Use of Protective Coating Standards in Nuclear Power Plants,"
- ASTM D 3843-00, "Standard Practice for Quality Assurance for Protective Coatings Applied to Nuclear Facilities,"
- ASTM D 3911-95, "Standard Test Method for Evaluating Coatings Used in Light Water Nuclear Power Plants at Simulated Design Basis Accident Conditions," and
- ASTM D5163, "Establishing Procedures to Monitor the Performance of Coating Service Level I Coating Systems in Operating Nuclear Power Plant."

All of these standards are endorsed in RG 1.54 rev. 1.

Protective coatings applied to the interior surfaces of the containment structure and to SSCs inside the containment are considered qualified coatings if they have been subjected to physical property (adhesion) tests under conditions that simulate the projected environmental conditions of a postulated DB LOCA and have been demonstrated to maintain their adhesive properties under these simulated conditions. These tests are typically conducted in accordance with the guidelines, practices, test methods, and acceptance criteria specified in applicable standards for coatings applications, such as those issued by the ANSI or the ASTM.

The purpose of this letter report is to document our survey of the available published information on the leaching characteristics of coatings that have application in PWRs.

2 Coating Information

An exhaustive search on the development of coatings for nuclear applications revealed that the majority of coating activities emphasized DBA compliance. Almost no information has been either developed or published on the leachability and leaching constituents (in water) of the nuclear-power-plant coatings. We have also contacted several nuclear-power-plant coating developers, such as Keeler & Long/PPG High Performance Coatings Division, Ameron International, and Carboline, by telephone and e-mail. The industry response indicated that the coating suppliers as a whole primarily directed their activities towards adhesion characteristics and irradiation resistance, which are the requirements for DBA compliance. The industry responses also indicated that no leaching data were available, at least in the public domain, for any of the coatings applied in nuclear power plants. We have also surveyed studies

that were conducted on leaching of coatings in non-nuclear applications and will discuss all the surveyed results in the following sections.

Numerous coating products are sold for industrial purposes, making it difficult to identify the names, attributes, properties, and limitations of all of them. The most common method of classifying coatings is their generic type, which refers to the chemical attribute, most often the resin type that is unique to a group of coatings. The name for most generic types of coatings is based on the resin (binder) in the formulation.

Coatings that are used in nuclear power plants can be broadly classified into generic coating types such as zinc rich, alkyds, chlorinated rubbers, vinyl, latex emulsions, and epoxies. A brief listing of different types of coating and coating constituents is given in Table 1.

Table 1. Brief explanation of various types of coating

Type of Coating	Coating Constituents	Comments
Epoxy	Two-component system: co-polymer of bisphenol A and epichlorohydrin + a curing agent.	Xylenes and toluenes are used as solvents.
Alkyd	Mainly a mixture of oil/fatty acid, dicarboxylic acid, and polyhydric alcohol.	Alkyd resins can be mixed with nitrocellulose, chlorinated rubber, PVC--copolymers, amino resins, and phenolic and maleic resins
Chlorinated rubber	Derived from natural latex or polyisoprene, chlorinated to contain about 65% chlorine. The binder consists of 65% chlorinated rubber and 35% plasticizer.	Xylenes and alkylbenzenes are used as solvents.
Inorganic zinc	Zinc metal powder mixed with inorganic silicate paint binder.	This binder can be either solvent borne (ethyl silicate) or water borne (alkali silicate).
Vinyl	Most vinyl coatings consist of a resin consisting of a copolymer of PVC and polyvinyl acetate (PVA) in the ratio of 86% PVC to 13 or 14% PVA.	

2.1 Epoxy Coatings

The epoxy resin most commonly used for industrial protective coatings is glycidal ether, which is derived from bisphenol-A and epichlorohydrin. This combination of raw materials yields a series of related compounds that, prior to cross-linking, have an epoxide group at each end of the molecule and an alcoholic hydroxyl group as a mid-chain pendent. Cross-linking takes place preferentially through the terminal epoxy groups, then through the mid-chain hydroxyl groups. The epoxy molecules, particularly those of the bisphenol-A type, are relatively small and must be co-reacted with copolymer curing agents to attain cross-linking properties sufficient to provide a protective coating. The co-polymer cross-linker frequently is called a "catalyst" or "curing agent," and it usually is a polyamine- or polyamide-containing material.

Phenolic modification to the epoxy resin further enhances water resistance, and phenolic-modified epoxies, with amine co-reactants, are perhaps the most popular coating system for freshwater and

saltwater immersion and many aqueous chemical solutions, even at elevated temperatures. Phenolic modification enhances the moisture and heat resistance of the epoxy, but it imparts slightly more brittleness and diminishes alkali resistance.

2.2 Alkyd Coatings

Alkyds are perhaps the most widely used industrial protective coating by virtue of their ease of application, relatively low cost, color stability, and good weather durability in most atmospheric environments. Alkyd resins (binders) are derived as a reaction product of polyhydric alcohols and polybasic acids. The characteristic of the binder and its method of drying and/or curing determine the mechanism of film formation. Many of the natural resins used as binders are derived from exudations from trees or insect secretions. Synthetic binders are generally by-products of chemical refining or manufacturing processes. These resins are man-made and, when refined and modified for coating use, can be used as film formers for protective and decorative coatings.

Alkyds use a polybasic acid derived from a semi-drying or drying oil so that the resin formed can undergo auto-oxidation at any temperature. Alkyd resins are actually polyester resins obtained through a reaction among fatty acids (e.g., acids of tall or soya oil), polyols (e.g., glycerol, ethylene glycol, and neopentyl glycol), and a dibasic acid or anhydride, such as phthalic anhydride, isophthalic acid, and maleic anhydride. The properties of alkyd coatings predominantly are the result of the drying oil used in the manufacture of the alkyd resin.

All alkyd coating systems are initially dried by solvent evaporation and subsequently cured by auto-oxidative cross-linking of the oil constituent. Because of the presence of the drying oil, alkyd coating systems have limited chemical and moisture resistance, cannot be used in highly chemical environments (acid or alkali), and are not resistant to immersion or near-immersion condensing conditions. Alkyd coating systems should not be used in immersion conditions or in environments in which the coating will be subjected to prolonged wetting, dampness, or condensing humidity. Because drying oils are saponified by alkalis, they should not be applied to alkaline surfaces, including galvanized surfaces (as a result of the alkaline nature of zinc hydroxide, a corrosion product of zinc), concrete, mortar, and most cementitious surfaces (as a result of inherent alkalinity due to the lime used as a component of cement).

2.3 Zinc-rich Coatings

Zinc-rich coatings, or zinc-rich primers, are unique in that they provide galvanic protection to a steel substrate. As "rich" in the name implies, the binder contains a large amount of metallic zinc dust pigment. The binder can be an inorganic zinc silicate or an organic resin such as an epoxy, butyl, or urethane. After the coating is applied to a thoroughly cleaned steel substrate, the binder holds the metallic zinc particles together and in contact with the steel. However, Pinney (1998) reported that inorganic zinc coatings have the advantages of excellent solvent, abrasion, and chloride resistance but the disadvantage of failure at high (>10) and low pH (<3), though the reasons for such failures are not given.

In terms of water resistance, laboratory tests by continuous immersion in water have shown that the time to first rust depends on factors such as water temperature, turbulence, water composition, and coating thickness. Based on a study by Kline (1996), the following generalization can be applied:

- Increasing water temperature reduces protection time.
- Flowing water reduces protection time.

- Typical time to first rust ranges from 1-2 years to more than 3 years for a high coating thickness in still distilled water at 100°F and to longer than 5 years in still tap water at 70°F.
- Flowing or agitated water reduces the protection time by about half.

2.4 Chemical Compositions of Typical Containment Coatings

Coatings for nuclear power plant applications are manufactured by Ameron International and by Keeler & Long/PPG. Table 2 lists the available information on the coatings developed by Ameron International. The Keeler & Long/PPG coating systems that are qualified for Service Level 1 in a nuclear power plant are listed in Table 3. Systems used inside containment supplied by Keeler & Long/PPG epoxy, epoxy/epoxy, epoxy/epoxy/epoxy, phenol, and silicone alkyd. Some of the typical coatings developed by Carboline Company and their uses in nuclear plants are listed in Table 4. Tables 5 through 7 show the Materials Safety Data Sheet (MSDS) compositions of three nuclear-power-plant coatings: Dimetcote 9, Phenolic 305, and Amercoat 90HS.

Table 2. Descriptions of several coatings of Ameron International for nuclear power plant application

Amercoat 66:	Polyamide-cured epoxy; not recommended in acid, good in alkali, excellent in salt and water, designed for protection of steel and concrete Dimetcote surfaces against abrasion and nuclear radiation.
66 Resin:	Ti oxide, 15%; Ni, Sb, Ti rutile, 10%; AZO pigment, 40%; xylene, 9%; methyl isobutyl ketone, 17%; methyl N-amyl ketone, 7%; epoxy resin, 25%.
66 Cure:	Xylene, 21%; ethyl benzene, 5%; triethylene tetramine, 5%; polyamide resin, balance.
Amercoat 90:	High-performance epoxy, immersion and nonimmersion use, not recommended in acid, limited in alkali and solvent, excellent in salt and water, designed for protection of steel and concrete surfaces.
Amercoat 90 white resin:	Magnesium silicate, 40%; epoxy resin, 20%; xylene, 16.2%; Ti oxide, 15%; propylene glycol methyl ether, 5%; ethyl benzene 3.8%.
Amercoat 90 cure:	Modified fatty amine, 60%; epoxy resin, 20%; xylene, 17%; ethyl benzene, 4%.
Dimetcote 6:	Inorganic zinc coating (63% solids volume).
Powder:	Zinc dust, 95-100%; zinc oxide, up to 5%.
Liquid:	Ethyl silicate polymer, 35%; xylene, 26%; Ca silicate, 15%; isopropyl alcohol, 9%; ethyl benzene, 6%; amine, 5%; silica (amorphous), 5%.
Amercoat 5105:	Alkyd primer.
5105 Alkyd primer:	Talc, 45%; alkyd resin, 20%; hydrocarbon resin, 10%; heavy aromatic naphtha, 8%; micaceous iron oxide, 6%; Stoddard solvent, 6%.

Table 3. Descriptions of several coatings of Keeler & Long/PPG for nuclear power plant application

System Identification	Coating Systems	Dry Film Thickness (mil)
CARBON STEEL COATING SYSTEMS		
System S-1 Primer Finish	KL65487107 Epoxy White Primer KLE1Series Epoxy Enamel	3.0 – 14.0 2.5 – 6.0
System S-10 Primer Finish	KL65487107 Epoxy White Primer KLD1Series Epoxy High-build Enamel	6.0 – 12.0 3.0 – 6.0
System S-10 Primer/Finish	KL65487107 Epoxy White Primer	8.0 – 18.0
System S-12 Primer/Finish	KL4500 Epoxy Self-Priming Surfacing Enamel	5.0 – 18.0
System S-14 (Floors only) Finish	KL5000 Epoxy Self-Leveling Floor Coating	10.0 – 25.0
System S-15 Primer Finish	KL65487107 Epoxy White Primer KL9600N Hi-Solids Epoxy Coating	2.5 – 6.0 5.0 – 8.0
CONCRETE COATING SYSTEMS		
System KL-2 Curing Compound/Sealer Surfacer Finish	KL4129 Epoxy Clear Curing Compound KL6548S Epoxy Surfacer KLE1Series Epoxy Enamel	0.5 – 1.75 Flush – 50.0 2.5 – 6.0
System KL-8 Curing Compound/Sealer Surfacer Finish	KL4129 Epoxy Clear Curing Compound KL6548S Epoxy Surfacer KLD1Series Epoxy High-build Enamel	0.5 – 1.75 Flush – 50.0 4.0 – 8.0
System KL-9 Curing Compound/Sealer Surfacer Finish	KL4129 Epoxy Clear Curing Compound KL65487107 Epoxy White Primer KLD1Series Epoxy High-build Enamel	0.5 – 1.75 5.0 – 10.0 3.0 – 8.0
System KL-10 Curing Compound/Sealer Surfacer Finish	KL4129 Epoxy Clear Curing Compound KL4000 Epoxy Surfacer KLD1Series Epoxy High-build Enamel	0.5 – 1.75 Flush – 50.0 3.0 – 8.0
System KL-12 Curing Compound/Sealer Surfacer/Finish	KL4129 Epoxy Clear Curing Compound KL4500 Epoxy Self-Priming Surfacing Enamel	0.5 – 1.75 10.0 – 50.0
System KL-14 (Floors only) Primer/Sealer Finish	KL6129 Epoxy Clear Primer/Sealer KL5000 Epoxy Self-Leveling Floor Coating	1.5 – 2.5 35.0 – 50.0

Table 4. Descriptions of several coatings of Carboline Company for nuclear power plant application

Coating Identification	Coating Type – Use	Recommended # of Coats	Dry Film Thickness (mil/coat)
Carboguard 890N	Epoxy – Topcoat	1 or 2	4 to 8
Carbocoat 139	Polyuretane modified alkyd – Topcoat	1	2 to 3
Carbozinc 11SG	Inorganic Zn –Primer	1 to 2	2 to 5
Carbocoat 115	Alkyd – Primer	1 to 2	1.5 to 2.5
Carboguard 1340	Epoxy – Sealer	1	1.5
Carboguard 2011S	Epoxy – Surfacer	1	15-20

Table 5. Composition of Dimetcote 9

Chemical Name	CAS Number*	%	EC Number	Classification
Zinc powder- zinc dust (stabilized)	7440-66-6	75-100	231-175-3	N;R50/53
Zinc oxide	1314-13-2	2.5-10	215-222-5	N;R50/53

*From Chemical Abstract Service.

Table 6. Composition of Phenolic 305

Chemical Name	CAS Number*	%
Aluminum silicate	1332-58-7	25
Methyl iso butyl ketone	108-10-1	10
Glycidyl ether	--	5
Pthalic acid, dibutyl ester, (dibutyl pthalate)	84-74-2	5
Toluene	108-88-3	5
Xylene	1330-20-7	5

*From Chemical Abstract Service.

Table 7. Composition of Amercoat 90HS

Chemical Name	CAS Number*	%
Epoxy resin	25068-38-6	10-25
Xylene	1330-20-7	10-25
1-Methoxy-2-Propanol	107-98-2	2.5-10
Ethyl benzene	100-41-4	2.5-10
2-Butoxyethanol	111-76-2	2.5-10

*From Chemical Abstract Service.

3 Research Studies

3.1 Basic Chemical Process for Release of Coating Constituents

Three chemical mechanisms control the release of contaminants from coatings: the dissolution of a mineral (solubility control), adsorption (sorption control), and contaminant availability (or total content) in the product. An example of solubility control is the dissolution of a metal oxide present in the product, such as zinc oxides in zinc products.

Some contaminants show affinity for adsorption to reactive surfaces. A number of inorganic constituents are not very reactive and show neither solubility control nor sorption control. Examples are the very soluble salts such as NaCl. Upon contact with water they will dissolve instantaneously and quantitatively. Those elements are controlled by availability, as the total available concentration can be released from the product. Table 8 lists chemical, physical, and external factors that can influence the release of various constituents in an aqueous environment.

Table 8. Summary of the main factors influencing release (Sloot and Dijkstra 2004)

Chemical Factors	Physical Factors	External Factors
Dissolution pH Chemical form Total composition/ availability Composition water Temperature Time	Percolation Diffusion Size (particles or monoliths) Porosity Permeability Tortuosity Erosion	Amount of water Contact time pH of environment Temperature

3.2 Coating Evaluation Studies

In the design and operation of a PWR, consideration has been given to a DBA and the subsequent events that might lead to a fractional release or expulsion of fission products. Engineered safety features include use of radiation-resistant coatings or paints in a reactor containment facility. These coatings are designed to withstand a DBA and remain adhered to their substrate. A study on paints, based on recirculating loop tests, blowdown tests, air-gamma irradiation tests, steam-gamma irradiation tests, and autoclave tests, concluded that several coatings, notably epoxy, modified epoxy, modified phenol, inorganic zinc, and polyurethane, were acceptable for containment requirements (Watson et al. 1971).

For PWRs, coatings are applied to the reactor building liner plate, structural steel, steam generator support steel, gallery steel and polar crane, exposed uninsulated carbon steel surfaces of equipment and piping, and all concrete surfaces inside the reactor building (Berger 1977). The DBA test stipulates that coatings remain intact following DBA and shall not be removed by the DBA environments, from the reactor containment facility or equipment, so as to affect the subsequent recirculation system. Coatings have been DBA tested at temperatures up to 340°F and for times up to 26 days to establish the viability and integrity of the coating. It has been reported that the favored coating systems contain epoxy resins that are catalyzed and cross-linked using phenolics, polyamides, or amines.

Recently, Almusaliem et al. (2003) evaluated the effectiveness of surface coatings for improving concrete durability and identifying inherent problems associated with coatings on concrete. They noted that, concrete being alkaline, any coating that is not alkali resistant will eventually break down and be destroyed by the alkali content in the concrete. Concrete contains a permanent amount of free moisture that can evaporate or be absorbed, depending on the relative humidity in which the structure exists. Any coating that lacks excellent adhesion will undergo blistering or failure. Concrete has a relatively low tensile strength and may crack. Any coating that does not have adequate crack-bridging ability will eventually break, losing its barrier properties. Failure of the coating due to calcium carbonate buildup at the concrete/coating interface is also a potential cause for degradation.

Apart from these mechanisms for degradation of coatings, the common type of chemically induced deterioration of organic binder is hydrolysis, which involves reaction of the binder with water. It generally occurs at either high or low pH. Attack occurs in polymers containing hetero atoms (O, N, S, etc.) at their bonding with a carbon atom. Ester linkages are particularly vulnerable to hydrolysis, especially under alkaline conditions. Amides, ureas, and urethanes are also susceptible but less so than the esters (Hare, 2000).

Alben et al. (1989) determined the composition of leachate from coatings used to prevent corrosion in potable water distribution systems. Leaching was studied from five organic coatings: three polymeric

(vinyl chloride-acetate, chlorinated rubber, and epoxy) and two hydrocarbons (asphalt and coal tar). Emphasis was given to the rate of leachate production and the leachate composition. Experiments used steel test panels that had been sand blasted, coated, and air-dried for 3 weeks. The test panels were immersed in water at 23°C and pH in a range of 8-9. The volume-to-surface area ratio was 0.164 m³/m² (4 gal/ft²). This volume-to-surface area ratio allows the in-depth analysis of leachate composition because it is a factor of 15 to 70 times smaller than that in field systems. Solvents in leachate samples were analyzed by gas chromatography with photoionization detection. Typically, water samples were collected at intervals of two to three days; monitoring was continued for one month. Results were expressed in terms of a rate of leaching (mg/l-day). To convert the rates of leaching found in laboratory experiments to those expected in the field, and to compare laboratory results with those obtained by monitoring full-scale systems, a dilution factor based on relative volume-to-surface area ratios was applied to the laboratory results. The rate of leaching per unit surface area of a coating was calculated (in mg/m²-day), and this value was assumed to be constant for a given coating, independent of the volume-to-surface area ratio of the system in which leaching was studied.

Organic contaminants were found at the parts-per-billion levels in water compared to the parts-per-thousand levels in the coating. It was concluded that on the first day of immersion, the polymeric coating had a higher rate of leaching than the hydrocarbon coatings. Also, the total organic content of leachate from coatings was largely due to the solvents used as a vehicle for application. The pH of the material and the pH of its environment were reported to be crucial in determining the release of many constituents. This observation was valid for all sorts of coating materials. The pH value of the surrounding fluid determined the maximum concentration in the water at that pH value, and each material had its own pH-dependent release curve. Temperature increase generally led to a higher solubility. In addition, an increase in temperature had increased the chemical reaction rates, and thus also increased transport by diffusion.

Abeyasinghe et al. (1982) studied the various properties of five polyester resins, which includes their adsorption of water and its relation to the temperature and the leaching of unbound substances from the network. Table 9 lists the resins studied by this research group. They found that isophthalic acid was detected in all cases, and large quantities of free propylene glycol leached from resin Nos. 2 and 4. Table 10 gives the total quantity of the leached substances from the resins, and Table 11 gives the results of leachate analysis of various coatings.

Table 9. Resins used for the study (Abeyasinghe et al. 1982)

Resin No.	Molar Proportion					
	PA	MA	IPA	PG	DEG	Styrene
1	-	1	1	1	1	41
2	-	1	1	2	0	38
3	-	1	1	0	3	32
4	-	3	2	4	0	38
5	1	1	1	1	1	31

PA: phthalic anhydride; MA: maleic anhydride; IPA: isophthalic acid; PG: 1,2 propylene glycol; DEG: diethylene glycol.

Table 10. Total quantities of leached substances from resins (Abeyasinghe et al. 1982)

Resin No.	Immersion Time (h)	Immersion Liquid	Temperature (°C)	Leached Amount (wt.%)
1	6,000	2 M NaCl	65	0.5
1	13,000	2 M NaCl	65	2.2
1	10,000	6 M H ₂ SO ₄	65	0.9
1	8,000	0.78 M NaOH	65	32
2	1000	H ₂ O	50	0.6
3	1000	H ₂ O	50	2.7
4	750	H ₂ O	50	2.1

Table 11. Leachate analysis of various coatings from several studies

Type of Coating	Material Leaching	Amount
Epoxy (Alben et al. 1989)	Methyl isobutyl ketone (MIBK) 0,m,p-Xylene Bisphenol A (Howdeshell et al. 2003)	1891 µg/l-day for MIBK at 1 day 396 µg/l-day for MIBK at 30 days 916 µg/l-day for xylenes at 1 day 158 µg/l-day for xylenes at 30 day 45 µg/l-day Increase in the drying time decreases the leachate concentrations
Vinyl (Alben et al. 1989)	Methyl isobutyl ketone (MIBK) Methyl isoamyl ketone (MIAK) Toluene	303 µg/l-day for MIBK at 1 day 89 µg/l-day for MIBK at 30 days 465 µg/l-day for MIAK at 1 day 104 µg/l-day for MIAK at 30 days 43.6 µg/l-day for toluene at 1 day 9.12 µg/l-day for toluene at 30 days Increase in the drying time decreases the leachate concentrations
Chlorinated rubber (Alben et al. 1989)	Xylenes Alkyl acetates (solvents in the original coating or its thinner) Alcohols	239 µg/l-day for xylenes at 1 day 95 µg/l-day for xylenes at 30 days 68 µg/l-day for alkyl acetates at 1 day 20 µg/l-day for alkyl acetates at 30 days 137 µg/l-day for alcohols at 1 day 41 µg/l-day for alcohols at 30 days
Chlorinated rubber (Spires et al. 1991)	Cl ⁻ SO ₄ ⁻²	0.048 µg/cm ² /day 2.04 µg/cm ² /day
Inorganic zinc (Race and Kelly, 1994)	Zinc	6 µg/cm ² /day
Epoxy phenolic	Dibutyl pthalate (Hem 2002) Ethyl benzene (Hem 2002)	150 µg/mg (leached in ethanol) 60-70 µg/l
Moist cure zinc coatings	Chromate (Hem 2002)	23.8 mg/m ² (leached in NaCl, after 60 days)

The coating systems under study are primarily composed of topcoat, primer, and surface treatment. The topcoat provides structural material protection against chemical, moisture, and mechanical degradation. Certain polymers used in the formulation of coating systems are more susceptible to chemical degradation and moisture attack than others. Furthermore, certain regions within the polymer coating film are more susceptible to degradation compared with the rest of the film. The exact nature of the degradation-susceptible regions is unknown. Research conducted in recent years suggests that the small degradation-susceptible regions in cured polymeric film may have low molecular weight and low levels of cross-linking. The size of these regions may range from nanometers to micrometers, and they are postulated to form from partially polymerized molecules that did not completely cross-link. Corrosion

of polymer-coated metal has been found to occur directly underneath these regions (Mills et al. 1981). It is believed that these degradation-susceptible regions are leached during exposure, thereby creating new pathways/channels for corrosive ions to travel through bulk coating film and eventually reach the coating/substrate interface. This condition leads to corrosion of the substrate. Analysis of the leachate can provide information on the degradation-susceptible regions in the film. The leachate from the polymer film degradation studies indicated the presence of organic species, and the amount of organic carbon in the leachate was proportional to the aging time.

The Electric Power Research Institute (EPRI) conducted an industry-wide survey and obtained “unqualified coating lists” from 27 PWR plants (Eckert 2005). The coating materials included alkyd (25 plants), epoxy (10 plants), acrylics (6 plants), high-temperature aluminum (5 plants), inorganic zinc primer and/or epoxy phenolic topcoat (4 plants), and polyester enamel (4 plants). In the Phase 1 program, they obtained 37 samples of original equipment manufacturer (OEM) coatings, analyzed the generic coating type of each sample, and issued a report entitled “Analysis of PWR Unqualified OEM Coatings” (EPRI report 1009750, March 31, 2005). In the Phase 2 program, they performed DBA qualification testing per ANSI N101.2 and ASTM D3911 on 2 x 4 in. coupons from OEM painted components. The test was conducted for 7 days at 307°F and an irradiation level of 2×10^8 rad in borated water spray solution. Radiation exposures were conducted at the University of Massachusetts (Lowell), and autoclave testing was done at Keeler & Long/PPG. Delamination was the dominant failure mode. A Phase 2 report (EPRI report 1011753) entitled “DBA Testing of PWR Unqualified OEM coatings” was issued in June 2005.

The Savannah River Technology Center (SRTC) evaluated an epoxy-polyamide primer and topcoat applied to a steel substrate (Sindelar et al. 2000). The experimental approach involved measurement of critical properties of the coating materials at conditions representative of a post-LOCA period, the development of a predictive model for coating system failure, exposure of coating systems to DBA conditions, and comparison of model and test results to judge predictive capability. Both the degree of failure and characteristics of failed coating debris were documented. Figure 1 shows a schematic of coating defects on a steel substrate and possible ingress of chemical constituents from the exposure environment.

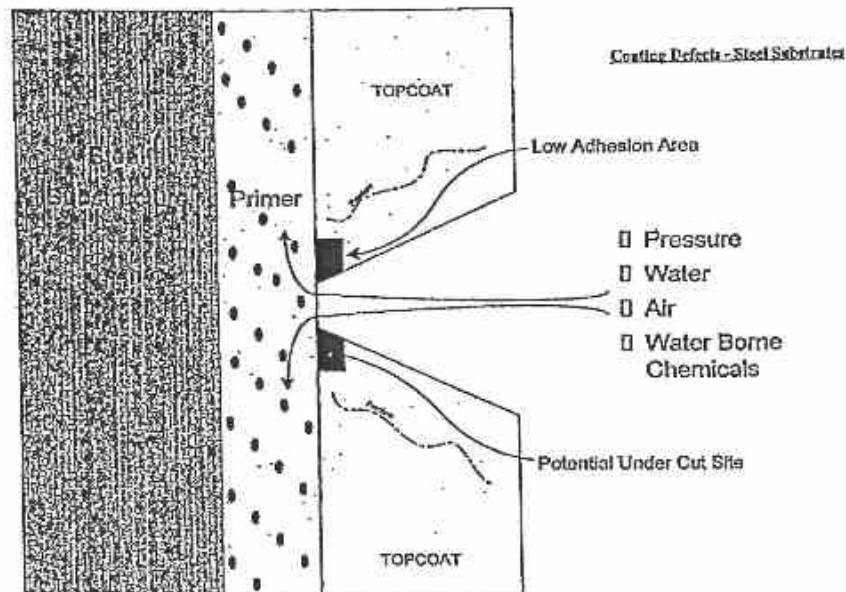


Figure 1. Schematic of coating-environment interactions (Sindelar et al. 2000).

One interesting aspect of the SRTC survey is that information obtained through a phenomena identification and ranking table (PIRT) were integrated into experiments and/or analytical modeling to simulate accident scenarios or conditions of safety concern. Table 12 shows the coating systems investigated in the SRTC project and those evaluated by the PIRT panel for industry coatings (Sindelar et al. 2000).

Table 12. Coating systems investigated by the SRTC project and those evaluated by the PIRT panel for industry coatings (Sindelar et al. 2000)

Component	Coating	Example of Coating Product
Steel	Epoxy- phenolic over inorganic Zn	Phenoline 305 over carbozinc 11 Dimetcote 9 Amercoat 90HS over Amercoat 370 Amercoat 370 over Amercoat 370
	Inorganic Zn	
	Phenolic modified epoxy over inorganic Zn	
	Epoxy polyamide over epoxy polyamide	
Concrete	Epoxy phenolic over surfacer	Phenolic 305 over starglaze 2011s surfacer
	Epoxy over surfacer	
	Epoxy over epoxy	
	Epoxy phenolic over epoxy phenolic	

Table 13 shows a PIRT ranking summary for potential coating defects and phenomena of importance for a steel substrate with epoxy primer and epoxy topcoat. Under the environmental exposure category, the PIRT has been given a high rank for primer and topcoat in Phase 1 (normal service from time of application and through 40 years of reactor operation) and for primer in Phase 5 (beyond 2 hours after a LOCA). Furthermore, oxidation of substrate/primer interface had a high rank in Phases 3 through 5 (40 s to beyond 2 hours after a LOCA). Table 14 presents a coating PIRT summary from the SRTC survey for several coating constituents under normal operating conditions. Phenomena of importance include environmental exposure effects leading to possible chemistry changes in polymer coatings and potential breaking of bonds between the primer and topcoat.

Table 13. Coating defects and phenomena of importance (Sindelar et al. 2000)

Phases -> Process & Phenomena		1	2	3	4	5
Substrate (Steel)		No High or Mediums identified.				
Substrate /Primer Interface	Blistering & De-lamination Oxidation		H	H H	H H	H H
Primer	Environmental Exposure	H	M	M	M	H
	Mechanical Damage	H				
	Minor coating anomalies					H
	Air/water & chemical intrusion Above pool			M	M	H
	Below pool					H
	Air/Water & Chemical Diffusion					M
Primer/Top Coat Interface	Blistering & De-lamination	H	H	H	H	H
Topcoat	Expansion and contraction		M			
	Environmental exposure	H	M	M	M	M
	Mechanical damage	H				
	Minor coating anomalies		M	M	M	M
	Air/water & chemical intrusion Above pool			M	M	M
	Chemical attack					M

Processes/Phenomena ranked HIGH and MEDIUM

Blistering & De-lamination
Oxidation
Environmental exposure
Mechanical damage
Minor coating anomalies
Air/water/chemical intrusion

Phase 1: Normal service from time of application and through 40 years operation.
Phase 2: 0 to 40 seconds into loss-of-coolant accident (LOCA).
Phase 3: 40 seconds to 30 minutes after a LOCA.
Phase 4: 30 minutes to 2 hours after a LOCA.
Phase 5: Beyond 2 hours after a LOCA.

Table 14. PIRT summary of coating constituents used in SRTC study (Sindelar et al. 2000)

COATING DESCRIPTION: Steel Substrate, Epoxy Primer, Epoxy Topcoat (SRTC System 5)				
Phase I Normal Operation	Component	Processes & Phenomena	Rank	Definition
	Substrate (steel)	Expansion and contraction	Low	Liner plate response to changes in containment pressure and temperature due to normal operation and ILRT's. Neutron fluence generated due to operations.
		Increased radiation exposure	Low	
	Substrate/Primer Interface	Differential expansion and contraction	Low	Different coefficients of thermal expansion between substrate and primer. Condensation of water from warmer, humid atmosphere to surfaces of cooler steel structures. Chemical interaction of moisture and air at the surface of the substrate (substrate/primer interface).
		Cold wall effect	Low	
		Oxidation	Low	
	Primer (epoxy)	Expansion and contraction	Low	Primer response to changes in containment pressure and temperature due to normal operation and ILRT's. Chemical interaction of moisture, air and the primer coat. Exposure to ambient conditions (heat) during operations. Results from normal application process. Damage due to dropped equipment. Neutron fluence generated due to operations.
Oxidation		Low		
Environmental exposure		High		
Minor coating anomalies		Low		
Mechanical damage		High		
Primer/Topcoat Interface	Increased radiation exposure	Low		
	Differential expansion and contraction	Low	Differing rates between primer and topcoat Changes in concentration of air/water Breaking of bonds between primer and topcoat.	
	Air, water and chemical intrusion	Low		
Blistering and delamination	High			
Topcoat (epoxy)	Expansion and contraction	Low	Topcoat response to changes in containment pressure and temperature due to normal operation and ILRT's. Chemical interaction of moisture, air and the primer coat. Exposure to ambient conditions (heat) during operations. Polymer chemical changes. Results from normal application process. Damage due to dropped equipment. Neutron fluence generated due to operations.	
	Oxidation	Low		
	Environmental exposure	High		
	Discoloration	Low		
	Minor coating anomalies	Low		
	Mechanical damage	High		
Increased radiation exposure	Low			

The Ameron International Protective Coatings & Finishes Group surveyed the performance of aged coatings in nuclear power plants. Table 15 gives typical information obtained for four operating nuclear power plants.

Table 15. Survey results on coating performance from Ameron International

Plant and location	Kepeco, Mihama No. 2, Fukui Pref. Japan (source: Amercoat Japan)	Electrobel, Doel NPP, Antwerp, Belgium	OPPD, Fort Calhoun, NE	SCE, San Onofre NGS, Units 1&2 San Clemente, CA
Reactor type/ service level	PWR/Level 1	PWR/Level 1	PWR/Level 1	PWR/Level 1
Coating system	90/90	NuKlad 114A/2200/2202/300A	NuKlad 110AA/66	Amerlock 400NT (maintenance system applied over original Valspar or Keeler & Long coating systems)
Qualification testing	ANSI, 310°F	ANSI N101.2, ASTM D5144	ANSI, 300°F	ANSI, 340°F
Where applied	Tanks	Walls	Floors	Floors, liner plate
Substrate	Steel	Concrete	Concrete	Concrete, carbon steel
Surface Preparation	Abrasive blast	Abrasive blast	Abrasive blast	Abrasive blast and SP-11
Years in service	34	30	34	>20
Existing condition	Excellent	Performing with no problems	No report	All coatings adhered and in good condition

4 Summary

This letter report presents the results from a survey of open-literature information on the leaching characteristics of coatings applicable to nuclear power plants. Coating supply companies such as Keeler & Long/PPG, Ameron International, and Carboline, and the Electric Power Research Institute were contacted for the available information on the leaching characteristics of coatings and test results, if any, under various anticipated aqueous environments pertinent to PWRs. The survey, in general, indicated a complete lack of information on leachability, leaching rate, and potential leaching constituents of such coatings. Furthermore, there seemed to be no concerted test program to evaluate the role of coating parameters and environmental factors (such as temperature, pH, and pressure) on the long-term chemical performance of the coatings. Most of the testing emphasized evaluation for DBA conditions and resistance to irradiation.

References

Abeyasinghe, H. P., Edwards, W., Pritchard, G., and Swamipillai, P.G., 1982, "Degradation of crosslinked resins in water and electrolyte solutions," *Polymer*, 23, 1785-1790.

Alben, K., Bruchet, A., and Shpirt, E., 1989, "Leachate from organic coating materials used in potable water distribution systems," American Water Works Association Research Foundation, Denver, CO.

Almusallam, A. A., Khan, F. M., Dulaijan, S. U., and Al-Amoudi, O. S. B., 2003, "Effectiveness of surface coatings in improving concrete durability," *Cement & Concrete Composites* 25, 473-481.

American Society for Testing and Materials, "Manual of coating work for light water nuclear power plant primary containment and other safety related facilities," ASTM D 01.43.

Berger, D. M., 1977, "Coatings for Nuclear Power Plants, *Power Engineering*," p.93

Dallman, J., Letellier, B., Garcia, J., Madrid, J., Roesch, W., Chen, D., Howe, K., Archuleta, L., and Sciacca, F., 2006, "Integrated Chemical Effects Test Project: Consolidated Data Report", NUREG/CR-6914, Volume 1, U.S. Nuclear Regulatory Commission, Washington, D.C.

Eckert, T., 2005, "OEM Unqualified Coatings Testing," EPRI report.

Hare, C. H., 2000, "Chemically Induced Degradation of Coatings: Part 2," JPCL, Vol. 17, p. 63.

Hem, L. J., 2002, "Potential water quality deterioration of drinking water caused by leakage of organic compounds from materials in contact with water," Presented in Plastics Key Proceedings, 20th No Dig Conference, Copenhagen, May 28-31.

Howdeshell, K. L., P. H. Peterman, B. M. Judy, J. A. Taylor, C. E. Orazio, R. L. Ruhlen, F. S. Vomasaal, and W. V. Welshons, 2003, "Bisphenol A is released from polycarbonate animal cages into water at room temperature," Environment Health Perspectives, 111, 1180.

Kline, H. H., 1996, "Inorganic zinc- rich," JPCL, 73-104.

Mills D. J., and Mayne J. E. O., 1981, in *Corrosion Control by Organic Coatings*, Ed. H. Leidheiser, NACE, Houston, TX, p. 12.

Park, J. H., K. Kasza, B. Fisher, J. Oras, K. Natesan, and W. J. Shack, 2006, "Chemical Effects Head-Loss research in Support of Generic Safety Issue 191," NUREG/CR-6913, to be published.

Pinney, S. G., 1998, "Correctly select tank linings for immersion service," Chemical Engineering Process, pp. 65-68.

Race, T. D., and Kelly, M. A., 1994, "A comparison of metal leachate rate and zebra mussel control efficacy for coating and materials," U.S. Army Construction Engineering Research Laboratories, Champaign, IL, Proc. Fourth International Zebra Mussel Conference, Madison, WI, p. 319.

Sindelar, R. L., Dupont, M. E., Lyer, N. C., Lam, P. S., Siddmore, T. E., Utsch, P. R., and Zapp, P. E., 2000, "Degradation and failure characteristics of NPP containment protective coating systems – Interim report," Westinghouse Savannah River Company Report, WSRC-TR-2000-00079.

Sloot, H. A., and van der Dijkstra, J. J., 2004, "Development of horizontally standardized leaching tests for construction materials: a material based or release based approach? Identical leaching mechanisms for different materials," Energy Research Center, Netherlands, ECN-C-04-060.

Spires, G. V., Tombaugh, R. S., and Doebler, R. F., 1991, "Rubber linings in nuclear power plant water treatment systems," Journal of Protective Coatings & Linings, p.50.

USNRC Generic Letter 98-04, 1998, "Potential for degradation of the emergency core cooling system and the containment spray system after a loss-of-coolant accident because of construction and protective coating deficiencies and foreign material in containment," July 14.

USNRC website, <<http://www.nrc.gov/reactors/operating/ops-experience/pwr-sump-performance/tech-references.html>>

Watson, C. D., Griess, J. C., Row, T. H., and West, G. A., 1971, "Protective coatings (paints) for PWR and BWR reactor containment facilities," Nuclear Technology, 10, 538.