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Failure Analysis: Wastewater Drum Bulging

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Abstract

A 55 gallon wastewater drum lid was found to be bulged during storage in a remote area.. Drum samples were obtained for analysis. The interior surface of these samples revealed blistering and holes in the epoxy phenolic drum liner and corrosion of the carbon steel drum. It is suspected that osmotic pressure drove permeation of the water through the epoxy phenolic coating which was weakened from exposure to low pH water. The coating failed at locations throughout the drum interior. Subsequent corrosion of the carbon steel released hydrogen which pressurized the drum causing deformation of the drum lid. Additional samples from other wastewater drums on the same pallet were also evaluated and limited corrosion was visible on the interior surfaces. It is suspected that, with time, the corrosion would have advanced to cause pressurization of these sealed drums.

Introduction

The Savannah River Site (SRS), operated by the Washington Savannah River Company, a Department of Energy contractor, stores various waste forms, including liquids, prior to consolidation and possible disposal. A couple of years ago, wastewater in a reactor area was consolidated into a Tuff Tank, (vented container). The transportable Tuff Tank is a 330 gallon low density polyethylene square bottle inside a heavy-duty wire mesh cage. A year later, the Tuff Tank was transferred to a Liquid Waste Staging Area. At this time, the Tuff Tank contained approximately 240 gallons of liquid, in three layers (primarily water), with an oil layer at the top, an aqueous layer, and a layer of solids/sludge at the bottom. The liquid contained a collection of water from a crane wash tank, various skid pans, and sample bottles from the reactor area. Analysis of the water was performed, including screening for radionuclides. Approximately a month later, the Tuff Tank was transferred to a second staging area for sampling and liquid transfer to 55 gallon drums for disposal. The Tuff Tank contents were pumped into five new drums. Four of the drums contained aqueous material (No's 1114, 1115, 1116, &1117) and a fifth drum contained oil. Some oil/sludge carryover into the aqueous drums may have occurred. Local work practices call for leaving a 10% head space in all liquid waste containers. The drums were relocated to the Slug Vault Liquid Waste Staging Area for storage. Routine inspection is performed by Operations on a weekly basis in all liquid waste storage areas. During weekly rounds a month later, no unusual drum features were found. Approximately one week later, a bulge on one drum (No. 1117) was found within a four drum pallet assembly and was reported. The drum was punctured at the top for pressure relief with wastewater remaining in the drum for approximately 7 months prior to liquid transfer to a new drum (1117(II)). The pH was adjusted in all the drums at this time to $4.5<pH<8$ (field measurements). The top of the deformed drum and adjacent drums are visible in Figure 1-Figure 4. The National Fire Protection Association (NFPA) hazard label was not visible in Figure 2 and therefore was reproduced in the lower right corner. A number one was indicated in the blue health hazard diamond which designates that a NFPA hazard determination was made for the wastewater in these drums. The 55 gallon drums were manufactured from carbon steel with an epoxy phenolic coating on the interior as shown in Figure 5. The drums are approximately 35 inches tall and 23 inches in diameter. The epoxy phenolic coating has a one mil nominal thickness.

The exterior of the drum was visually inspected and it was determined that the drum was pressurized. The following was performed :

- Depressurization of the drum
- Assay water from the drum • Empty drum and transfer contents into same drum type with vented bung cap
- Vent remaining drums containing Tuff Tank contents by installing vented bung caps
- Raise pH of all drums to ≥ 4.0
- Inspection of the deformed drum interior
- Drum samples were cut and shipped to SRNL for evaluation

This paper documents a detailed characterization and analysis of drum coating/steel samples, and provides the most likely cause for drum pressurization.

Sample Analysis

Five 4 ½ inch diameter disks were cut from the bulged drum in both head and sidewall positions. A typical surface of the drumhead ID is shown in Figure 6. The sidewall ID surface is shown in Figure 7. Corrosion is very evident on the interior surface of the drumhead samples. Corrosion was preceded by blistering which is shown on the sidewall sample shown in Figure 8. Samples were cut from the sample in Figure 7 where the cut lines are indicated. These samples were used for close-up metallography and XRD (X-ray diffraction) analysis. XRD analysis revealed the presence of hematite (Fe_2O_3), magnetite (Fe_3O_4), talc, $Fe(OH)_2$ and the carbon steel base metal. Hematite is visible in Figure 8 with the normal rust color while magnetite is black and is also visible. Talc is probably from the gloves used to handle the samples.

Chemical analysis of the wastewater in the drums and the Tuff Tank (water sample left over from previous radiolysis analysis) was performed. The analytical results from inductively coupled plasma analysis (ICP-MS) are shown in Table 1. The highest elemental concentrations are sodium and phosphorus with levels from 3000 to 5000 ppm in the Tuff Tank, bulged and non-bulged drums. The only element in the bulging drum that is higher than that in the Tuff Tank or adjacent drum is Fe which indicates corrosion of the steel drum (1117). Fe levels in drum 1114 are low at 29.1 ppm which is even lower than that in the Tuff Tank. Low level contamination in the wastewater is listed in Table 2. Tritium, Co-60, and Cs-137 were detected at low levels. Material was scraped from the sidewall sample of the bulged drum and analyzed by gas chromatography-mass spectrometry (GC/MS). The results, shown in Table 3, reveal significant surface deposits from oil with smaller amounts from branched alkyl benzenes and tributyl phosphate. Oil in the original Tuff Tank was known to exist, the alkyl benzenes are probably from a scintillation cocktail, and the TBP (tributylphosphate) may be from the oil or from other contaminants from sampling of the water during analytical procedures. TBP is used to enhance oil film strength in lubricants.

Measurements of pH in the Tuff Tank and two drums reveal an acidic wastewater, shown in Table 4 with very little differences between the Tuff Tank, non-bulging and bulging drums. In fact, the pH in the Tuff Tank wastewater and the non-bulging drum (1114) is slightly more acidic than the bulging drum. Selected organic acids and their concentrations in Table 5 show that it does not take much acid to lower the pH to less than three.[1]

Samples were cut from a clean spare drum (same design and manufacturer as the bulged drum) to measure coating thicknesses. A dry film thickness gauge (Elcometer model No. 246F) was used on the drum exterior and interior. Exterior coating thicknesses on three areas averaged 0.4 mil while the interior coating thickness averaged 1.2 mils. The drum manufacturer's interior coating process calls for a one mil nominal coating thickness. Coating vendors such as Carboline, Heresite Protective Coatings, International Protective Coatings, and Sherwin Williams prescribe a minimum of a 2 mil primer coat with a 2- 4 mil final coat for two coat coverage or 5 mils for single coat coverage per an internet search for epoxy phenolic type coatings. Based on vendor guidelines, the original drum manufacturer's interior drum coating nominal thickness of one mil may be insufficient for corrosion protection of carbon steel immersed in an acidic wastewater. This thin coating may contain too many holidays (coating defects) to be protective in immersion service.

The contents of each of the three original drums from the pallet and the new drum (1117(II)) were neutralized to ≥ 6, prior to draining and then filling a new set of drums. This draining operation was performed to allow sample cutting of the original drums. The content in the new drums was further neutralized to higher pH, ≥ 7. Samples were cut from the three original drums to characterize the effects of wastewater on the ID coating of the drums. In addition, samples were also removed from the second drum (1117 (II)), which held the original contents of the bulged drum, The location of drum sidewall samples was chosen by SRNL to reveal typical surfaces within the drum. Figure 9 reveals blistering or shrinkage in the sidewall coating from drum 1115. Drum 1117(II) was only exposed to wastewater with a pH of 3.76 for approximately 7 months and still revealed blistering.

Discussion

Blistering is caused in paint coatings by water permeating through the coating and locating at the coating metal interface. Osmotic pressure drives water molecules to permeate through the coating. [2-5] The presence of micro-voids in the coating can also cause water molecules and acidic and/or caustic ions to penetrate through the coating. When the coating is penetrated, pressure builds up until pressure is equalized with that in the liquid. The result is a blister. At the same time, corrosion occurs in the base metal upon reaction with the unprotected carbon steel. The metal dissolution reaction, or anodic reaction, results in the loss of electrons, while the coupled cathodic reaction results in a species gaining electrons. The reaction occurs electrochemically in an acidic and limited oxygen environment where iron is being oxidized to a ferrous species while hydrogen ions are being reduced so that hydrogen is released per the following reactions [6-8] :

$$Fe \rightarrow Fe{+}2 + 2e- \quad (1)$$

$$2H{+} + 2e- \rightarrow H_2\uparrow \quad (2)$$

The failure of the coating can advance as delamination progresses from ruptured blisters. Corrosion of the steel would continue until the acid water is spent or pH increases. Continued hydrogen evolution from corroding steel would cause pressurization of the drum which was probably the case for this bulging drum. Radiolysis of the wastewater by the radioactive elements to cause H_2O_2 (which produces a more aggressive solution) is possible, but is not likely due to the low levels displayed in Table 2.

Calculations were performed to show that estimated pressures can be produced from corrosion generated hydrogen based on Equation A.

$$\mathbf{G_r = 3.8 \times 10^{-5} (K) (S_A) (F) \quad (A)}$$

where G_r = H_2 generation rate (moles H_2/hr); K = Corrosion Rate (mpy); S_A = Surface Area (ft^2); and F = fraction of total corrosion generating H_2 (assumed to be 1).[8] The calculated pressures, based on an assumed corrosion rate of 0.5 mil/yr. (0.0005 in./yr.) over a period of 8 weeks, 6 months and one year, range from 7.9 to 51 psi. Pressure calculations were also performed based on the Fe contents of two drums, the bulged drum (1117) and an adjacent drum (1114). Using the Fe content in these drums, per Table 1, pressure was calculated using the Fe corrosion reaction stoichiometry (one mole of Fe creates one mole of H_2) in acidic water and the ideal gas law. The calculated pressure, using 196 ppm Fe (in 1117-1), was 12.5 psi, versus 1.8 psi for the 29.1 ppm Fe in the 1114 drum. This calculation may be high since there was existing Fe in the Tuff Tank. If one assumes that the actual Fe from corrosion were that value obtained by subtracting the Fe amount in the Tuff Tank (54 ppm) from the maximum 1117 value (196 ppm), the calculated pressure is 8.9 psi. This pressure value is close to that calculated from steel corrosion rates based on 8 weeks exposure at a corrosion rate of 0.5 mpy but varies from 0.2 to 15.7 psi depending on corrosion rate. Based on Department of Energy experience, open head 55 gallon mild steel drums can begin to exhibit bulging at approximately 6 psi internal pressure.[9] Bulging in tight head (also known as closed head) drums should occur at similar pressure values. Vertical movement of the top head of the bulged drum was estimated at 2 cm based on Figure 3. When compared to pressure testing data generated on both closed and open head drums (Figure 10), a vertical deformation of 2 cm results from drum pressures ranging from 10 to 15 psi for a closed head drum. These results are very similar to the calculated values from corrosion. Thus, bulging in drum 1117 likely resulted from pressures generated by hydrogen released from corrosion.

The coating supplier stated that their epoxy phenolic coating would degrade in an acidic environment with pH $\leq$ 4. Thus, in addition to blistering from water diffusion into the coating, the epoxy phenolic coating would be degrading from the acidic environment. The epoxy phenolic coating (70 % epoxy/30 % phenolic) is only recommended in an environment with pH $\geq$7. A 100% phenolic coating is recommended in a pH $\leq$ 4 and a phenolic epoxy coating (70% phenolic/30 % epoxy) is recommended in pH range between 4 and 7 per the coating supplier. This recommendation is only for this supplier's coatings. Each supplier develops their own coating materials and no general guide was found to provide corrosion resistance of various coating materials. Each supplier would have to be contacted separately for their specific recommendations.

The blistering and softening noted in the three additional drums sampled in this report and the bulged drum confirms that this epoxy phenolic coating was not compatible with the wastewater from the Tuff Tank. A second drum (1117(II)), containing pH adjusted wastewater, also revealed blistering, an indication of coating incompatibility. A baked epoxy phenolic coating (EP-6308) from another supplier, Heresite Protective Coatings Inc., was rated only good in acid immersion service but excellent in alkaline immersion. The supplier's recommendations for this coating include a total dry film thickness of 5-7 mils for a 3-4 coat system. This thickness recommendation and those mentioned earlier are approximately twice the one mil nominal thickness of the drum manufacturer's internal coating and the measurements made on an actual drum. Insufficient coating thickness for immersion service may have also contributed to this coating failure.

Conclusions

Drum pressurization is due to a coating material (epoxy phenolic) which did not prevent osmotic blistering, coating degradation, and subsequent corrosion of the carbon steel drum in the acidic wastewater. Early coating degradation may also be the result of insufficient coating thickness. It is recommended that future drum choices be made after chemical analysis and pH measurement of intended contents are performed. Other specific drum coatings could be used but would have to be special ordered. A stainless steel drum is the preferred choice for acidic wastewater, especially when specific contents are not known prior to use. The second choice is a high density polyethylene drum. Adjustment of pH to levels >7 is also possible. Caution is advised since neutralization of acidic liquids causes heat generation and high temperatures if neutralized too quickly. Coating supplier recommendations for the proper coating and its thickness should be closely followed to achieve the desired corrosion resistance for future storage of waste materials in new drums.

Acknowledgments

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Table 1. Inductively Coupled Plasma analysis of wastewater chemistry from original wastewater Tuff Tank, bulging drum, and adjacent non-bulging drum.

Analyte	Original Tuff Tank (ppm)	Bulging Drum		Non-Bulging Drum
		1117-1 (ppm)	1117-2 (ppm)	1114 (ppm)
Al	37.1	21.8	20.4	32.4
B	64.8	66	66.1	66.4
Ba		0.952	0.824	1.21
Ca	31.1	31.5	32	30.8
Cu				0.56
Fe	54.4	196	152	29.1
Gd	3.73			0.929
K	405	369	369	398
Mg	5.66	5.9	5.88	5.88
Mn	7.32	8.31	8.23	5.11
Na	3430	3420	3340	3090
P	5150	5230	5130	5280
S	301	335	332	319
Si	48.5	50.7	50.3	49.9
Sr	5.85	6.54	6.62	6.42
V	6.4	6.64	5.52	7.35
Zn	96.9	100	98.7	103

Table 2. Radioactive contamination in original wastewater Tuff Tank, bulging drum, and adjacent non-bulging drum.

Analyte	Unit	Original Tuff Tank	Bulging Drum		Non-Bulging Drum
			1117-1	1117-2	1114
Alpha	dpm/ml	2.02	0.152	0.275	0.702
Non-Vol. Beta	dpm/ml	156	67.1	69.4	76.5
H-3	µCi/ml	209	224	230	240
Co-60	dpm/ml	181	166	162	180
Cs-137	dpm/ml	38.6	42.6	43	40.8
Am-241	dpm/ml	<7.11	<3.17	<3.2	<3.39

Table 3. GC/MS Analysis of Scrapings, mg/kg

Description	Result
Hydrogen Oil	40,000
Branched Alkyl Benzenes	6,700
Tributyl Phosphate	230

Table 4. pH in Tuff Tank and drums.

Tuff Tank	Bulging Drum		Non-Bulging Drum
	1117-1	1117-2	1114
2.89	2.97	2.99	2.86

Table 5. Selected Acid Concentrations and pH [1]

Acid	Concentration	pH
Acetic	0.2 M	2.4
$(CH_3CO_2H_2)$	0.02 M	2.9
"	0.002 M	3.4
Carbonic (H_2CO_3)	Saturated	3.8
Oxalic $(H_2C_2O_4)$	1.0 M	0.8
"	0.5 M	1.6
"	0.1 M	2.1
Nitric (HNO_3)	0.4 M	0.4
"	0.05 M	1.3
"	0.005 M	2.1
"	0.003 M	2.5
"	0.001 M	3.0
"	0.0003 M	3.3

Figure 1. Bulged lid of stored 55 gallon wastewater.

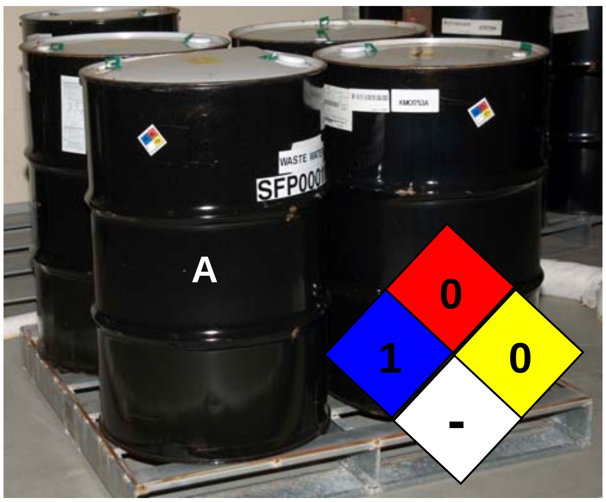

Figure 2. Bulged drum (A) on pallet along with three additional drums containing wastewater. The NFPA hazard label is reproduced in lower right corner.

Figure 3. Close-up view of normal depressed lids on two adjacent drums compared with bulged drum lid to the left. Bulged drum number is 1117.

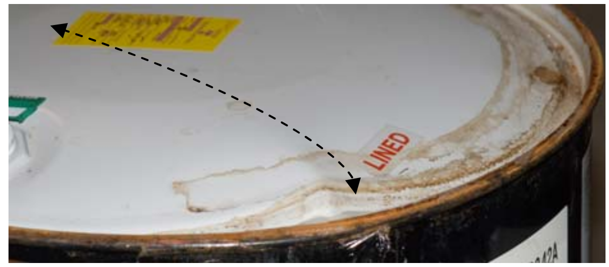

Figure 4. The drum lid crease is shown below dotted line. Drum Label reveals the United Nations uniform drum designation, 1A1/X1.8/300/05/USA.

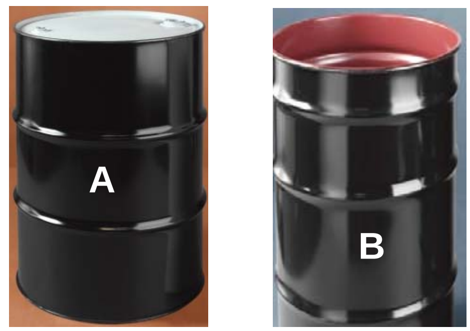

Figure 5. Exterior view of new 55 gallon carbon steel tight head drum (A) in left photo with red epoxy phenolic lined drum (B) shown in right photo (Vendor photographs). Note that the B drum has an extra rolled hoop near the top. SRS drums have two roll hoops as shown in A.

Figure 6. ID surface cut from bulged drum head revealing visible corrosion.

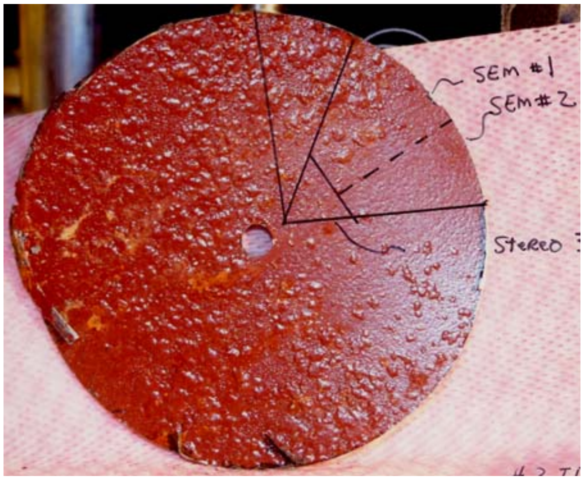

Figure 7. ID surface of sample cut from bulged drum sidewall showing areas cut from disk for SEM evaluation.

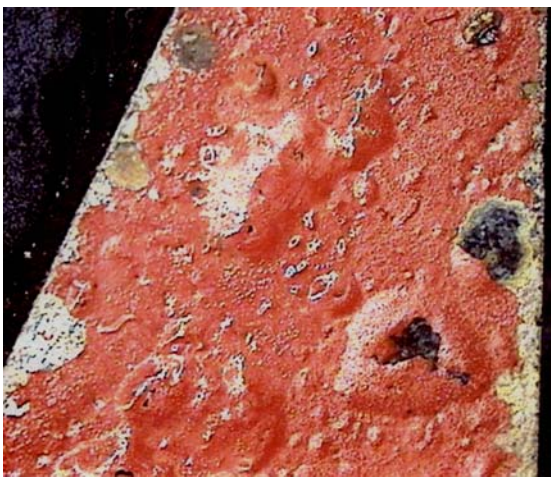

Figure 8. Close-up of surface cut from Figure 7 revealing blisters that burst with black oxide in the middle.

Figure 9. ID surface from non-bulged 1115 drum side-wall.

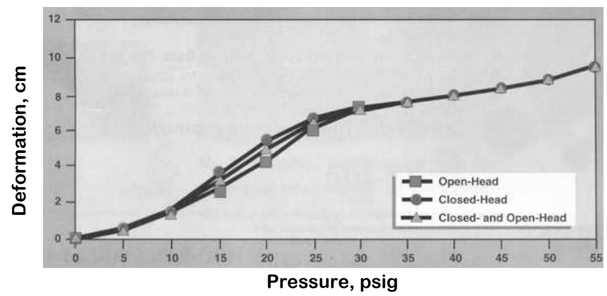

Figure 10. Open-head vs. closed-head drum top deformation averages versus pressure curve (upper graph) for 55 gallon steel drums.[10] The curves overlap each other at low and high pressures, except between 10 and 30 psig.