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Stainless Steel Interactions with Salt Containing Plutonium Oxides

By

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Abstract

Salt containing plutonium oxide materials are treated, packaged and stored within nested, stainless steel containers based on requirements established in the DOE 3013 Standard. The moisture limit for the stored materials is less than 0.5 weight %. Surveillance activities which are conducted to assess the condition of the containers and assure continuing 3013 container integrity include the destructive examination of a select number of containers to determine whether corrosion attack has occurred as a result of stainless steel interactions with salt containing plutonium oxides. To date, some corrosion has been observed on the innermost containers, however, no corrosion has been noted on the outer containers and the integrity of the 3013 container systems is not expected to be compromised over a 50 year storage lifetime.

Introduction

The 3013 container system was designed to contain plutonium bearing materials that are >30 wt. % plutonium (Pu) plus uranium (U) and are stabilized to achieve a moisture content <0.5 wt. %. The requirements and assumptions documented in the DOE-STD-3013 [1] were defined to support a 50 year storage lifetime that may be required prior to the final disposition of the plutonium bearing materials. To ensure that the 3013 container system maintains integrity during storage the DOE-STD-3013 Standard specifies that a surveillance program be performed at the storage site. The current surveillance program includes both destructive and non-destructive surveillances. This paper focuses on the destructive surveillances of a statistical sampling of packaged 3013 containers stored at SRS [2, 3, 4] and a number of engineering judgment samples that were chosen for destructive examination [5] because of their package contents and data obtained from laboratory testing and the ongoing storage surveillance program.

The 3013 container system consists of nested welded 300 series stainless steel containers with the outer container credited to stay leak tight throughout a 50 year period of storage. To date containers packaged at Rocky Flats Environmental Test Site (RFETS) and Hanford have been examined destructively, Figure 1. Future examinations will include containers from Lawrence Livermore National Laboratory (LLNL), Savannah River Site (SRS), and Los Alamos National Laboratory (LANL). During destructive examination, the containers are punctured to collect gas samples [6], sectioned to collect Pu oxide samples [7] and the empty containers are metallurgically examined to determine the condition of the various containers, including the welds, lids and other regions in the container system. The results of these metallurgical examinations are provided in this paper.

Destructive Examination Observations

During the destructive examinations (DE), the outer, inner and convenience containers are visually examined with an emphasis on the condition of the welds, other regions of high residual stress, and the Pu-bearing material/container metal interface. These regions are of particular interest because of the possibility of stress corrosion cracking (SCC) [8, 9] in these areas. Other areas of significance include the headspace of the containers because environments generated above the Pu bearing materials have been known to create pits in stainless steel [10] and such pitting may be a precursor to stress corrosion cracking if sufficient chloride containing electrolyte is available at the metal surface.

The outer container is a standard design and is used at all the packaging sites. It is the barrier credited to contain the plutonium-bearing materials while in a storage configuration. One or two other stainless steel containers in the nested system provide separation between the plutonium-bearing materials and the outer container which is neither in contact with the plutonium-bearing materials nor the headspace gas. Because of this lack of contact with the plutonium-bearing materials, little to no degradation of the outer container was expected [11] and a typical outer container visually examined as part of the DE showed no indication of degradation, Figure 2. Additionally, the metallurgical examination of the outer containers corroborates the visual observations and showed little or no storage induced degradation of the container welds, lids or walls.

Conversely, the inner and convenience containers are exposed directly to the Pu-bearing materials and/or the headspace gas over the Pu-bearing materials and are therefore more susceptible to corrosion induced degradation. A number of destructively examined 3013 containers have been evaluated via optical metallography, scanning electron microscopy (SEM), and/or energy dispersive x-ray (EDX) analysis. Table 1 provides a list of containers examined to date and indicates the extent of the analyses performed. In general, extensive analyses were only conducted on a small number of 3013 containers that were packaged with high chlorides because these were the only containers that showed evidence of significant corrosion.

Convenience Container Examinations

Analyses of several convenience containers from the stored 3013 packages showed evidence of corrosion but nothing significant enough to affect the integrity of the container. For example, two RFETS convenience containers showed signs of pitting corrosion on the silver coated threads of the convenience container body, as shown in Figure 3. The silver coated threads, specific to the RFETS convenience containers, were used to ensure galling did not occur during packaging and unpackaging operations. Although discreet particulates of the chloride containing plutonium oxide appear to be associated with the pitting, initial observations of the threaded region did not provide evidence for the pitting. Subsequent evaluation suggests that the pitting happened after the container was opened for surveillance because seasonal high temperatures and humidities were experienced during the surveillance process. These conditions coupled with the high chloride content of the container were the primary contributory factors for this pitting.

One feature specific to the Hanford convenience containers is a metal filter welded into the center of the lid. This filter prevents the possibility of gas buildup in the convenience container because any gases generated are free to flow through the filter to the inner container. However, the filter is designed to prevent the transfer of oxide particulate.

Three filter sections were examined to evaluate unanticipated features observed during the visual examination. Ultimately, it was decided that the observed features were inherent to the welding process used to install the filter into the convenience can lid and did not represent storage induced degradation. Figure 4 shows a typical weld interface for a filter housing and because this feature was shown to be typical of the welding process, no anomalous conditions are attributed to this visual observation.

The most common observation evaluated as part of the DE metallurgical examination was the presence of particulates and coatings on the inside surface of the convenience container walls and lid. In several cases the particulates and coating were easily removed by gentle wiping with a clean cloth and no degradation of the stainless steel was observed. This is illustrated in Figure 5 which shows the steel surface after coating removal. The fact that the coating was so easily removed is consistent with a conclusion that the particles simply deposited on the surface and that there were no interactions with the underlying metal. However, one convenience container had evidence of minimal corrosion beneath the coating.

Visual examination photographs from the inside walls of the convenience container that showed evidence of corrosion are shown in Figure 6.. The coated surface was in the headspace region of the container and the coating easily flaked off the wall when the can was sectioned for further analysis. This is seen in Figure 6 as the clear edge around the perimeter of the cut sections. This particular 3013 container was an engineering judgment sample chosen for DE because it had one of the highest moisture and chlorides content in the packaged materials. The analyses performed on this container included SEM and EDX of the container surface, Figure 7. The regions of the sample surface where the coating flaked off during sectioning are readily observed in the SEM and, in general, the coating is chloride rich with no evidence of the alkaline salts being present. X-ray diffraction and Fourier Transform Infrared Resonance analysis of the coating identified it as ammonium chloride (NH_4Cl). This coating formed during storage and condensed onto the cool surface of the container above the oxide material [12]. Beneath the NH_4Cl coating the surface of the container is nearly void of machining grooves and irregularly oriented fissures are seen across the surface, Figure 8. These features are artifacts from the flow forming process used to manufacture the container. The bottom of this same convenience container was also sectioned for SEM/EDX examination of the inside surface, as shown in Figure 9. A network of regularly shaped pits across the bottom inside surface of the container was observed. The depth of pitting is superficial at approximately 5 µm and is not severe enough to affect the integrity of the convenience container.

The inside lid from another convenience container showed particulate matter adhering to the surface. Samples of the particulate were collected for SEM/EDX analysis and pits were noted on the underlying surface. No evidence of alkaline earth salts was seen and the particulate was identified by EDX to contain chlorine, Figure 10. Further evaluation of this convenience container is in progress with emphasis on determining the extent of the degradation resulting from chloride rich particulates.

The convenience can observations demonstrate that, under certain conditions, a chloride rich deposit (probably ammonium chloride) can be generated. This deposit provides evidence for chloride transport from the convenience can to the inner can [12]. Additionally, the development of chloride rich particles on surfaces exposed to the headspace region of the containers may induce pitting on the container surfaces, particularly the lids [12].

Inner Container Examinations

One RFETS inner container showed the presence soot from the closure welding operation, Figure 11. This observation was consistent with RFETS reports that there were times when excessive soot developed during welding of the inner containers. No corrosion and/or corrosion product was observed in the sooted region. This observation was therefore considered a pre-storage condition and no evidence of container degradation was attributed to the soot.

Detailed analyses were conducted on several Hanford inner containers which showed evidence for corrosion and/or corrosion products during the DE visual examination. In the majority of examinations, SEM/EDX identified a heavy coating on the container walls and/or chloride rich particulates adhering to the inside lid surface, as shown in Figure 12. The SEM examination of these lids showed no significant depth to the observed corrosion.

Additionally, several of the inner containers examined by DE had a thin powdery coating adhering to the surface. This observation of coating development was similar to what was seen in the convenience containers, but the coating developed to a lesser extent. The coating and particulates were easily removed by wiping the surface and no pitting or surface corrosion was seen. Figure 13 shows the container surface beneath a layer of particulates that was removed during the DE inspections.

One inner container was analyzed because of the unusual features observed on the inner surfaces of the convenience container, Figure 6. These features suggested the presence of chloride on the inner container surfaces. To evaluate the possibility of chloride transport to the inner container, sections were obtained from the closure weld region, as shown in Figure 14, where a gap exists between the can sidewall and the lid, Figure 15. This gap and associated weld region are of interest because these areas are more susceptible to corrosion, including SCC, than other regions of the container [8, 9]. In order to better examine this region of the inner container, each section was cut to remove the weld ligament thereby creating two samples, one of the lid and one of the sidewall. The examination emphasized the gap and weld region but no evidence of corrosion or surface coatings was seen except on the lid region adjacent to the gap. However, examination of the surface of the inner container lid including the lid region adjacent to the gap showed the presence of small, closely spaced, and coalesced pits which formed along the machining grooves, Figure 16. The maximum pit depth observed was approximately 23 μm which is more conservative than the depth predicted by laboratory studies of pit growth in stainless steel exposed to the headspace gas of plutonium bearing oxides [10].

Sidewall sections of the inner container, particularly near the gap region, also showed the presence of particulate matter, some which is expected to be associated with the Pu bearing materials and some which is considered miscellaneous debris. The inner container evaluation showed that, even under conditions where chloride transport to the inner container has occurred, its integrity was not compromised.

Discussion and Conclusions

The presence of pitting corrosion in the headspace region of certain 3013 containers has been observed during destructive examination. The postulated headspace pitting mechanism requires the presence of a radiation source, alpha from the plutonium material, to dissociate and ionize the gases present and form a more volatile vapor or gas containing chlorine. The chloride rich vapor or gas provided a mechanism to transport chloride to stainless steel surfaces exposed only to the headspace region and make that region susceptible to corrosion [12].

The degradation, if any, observed during destructive examination of convenience and inner containers could be correlated with the chemistry of the plutonium bearing materials stored in the convenience containers. The surveillance observations showed that none of the containers from the pressure bin displayed any evidence of corrosion on any of the surfaces. The majority of indications of incipient corrosion occurred in the headspace gas region of containers that stored plutonium bearing materials with high chloride and moisture contents. Little to no damage was observed in the plutonium oxide contact region of the convenience container. All of these observations are consistent with observations in laboratory testing of small containers [10]. Additionally, no evidence of stress corrosion cracking has been observed in any of the containers examined to date.

Perhaps the most significant observation was that a chloride rich gas was created under certain conditions and provided a mechanism for chloride transport and deposition to regions of the container system that were only exposed to headspace gases. This observation emphasizes the importance of continued surveillances of the stored containers. The surveillance program will continue to evaluate containers to gain sufficient data to validate the 50 year container integrity criteria, as specified in the DOE-STD-3013. Gaseous transport of chloride and the potential for stress corrosion cracking will still be a strong focus of the evaluations as will particle induced pitting corrosion. The integrity of the containers has not been compromised at this time and there is no evidence that the potential for a 50 year storage lifetime will be compromised. However, the observation of incipient, storage induced corrosion in some containers demonstrates the necessity for continuing surveillance evaluations during storage of plutonium bearing materials in 3013 container systems.

Acknowledgements

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Table 1. Summary of additional container analyses performed during destructive examination of 3013 containers

Material Type and Surv. Reason**	**Description**	**Moisture (At packaging / DE)**	**% Actinide**	**Inner Container Analyzed**	**Convenience Container Analyzed**
P / R	No chlorides	0.11 / 0.05	86.6	N/A	N/A
P / R	No chlorides	0.18 / 0.04	84.4	N/A	N/A
P&C / R		0.03 / 0.04	87.6	N/A	N/A
P&C / R		0.10 / 0.19	86.4	N/A	N/A
P&C / EJ	Chloride bearing, Like C06032A	0.36 (FTIR) / 0.19	53.5	N/A	Threads, outside lid
P&C / EJ	Chloride bearing, Like ARF-223	0.28 (FTIR) / 0.06	69.9	N/A	Threads
P&C / R		0.15 / 0.10	86.0	N/A	N/A
P&C / R		0.07 / 0.03	97.4	N/A	N/A
P / R	>3 yrs old	0.17 / 0.02	83.6	N/A	N/A
P&C / R		0.14 / 0.04	77.7	N/A	N/A
P&C / R		0.39 / 0.04	80.8	N/A	N/A
P&C / R		0.16 / 0.14	64.8	N/A	N/A
P&C / R		0.07 / 0.10	71.6	N/A	N/A
P&C / R		0.37 / 0.03	52.3	N/A	N/A
P&C / R		0.19 / 0.10	85.0	N/A	N/A
P&C / R		0.14 / 0.07	71.4	N/A	N/A
P&C / R		0.04 / 0.07	64.7	Radius below weld, inside lid	N/A
P / R	No chlorides	0.06 / 0.06	34.3	N/A	N/A
P / R	No chlorides	0.22 / 0.23	86.7	N/A	N/A
P&C / R		0.29 / 0.29	74.0	N/A	Filter housing
P&C / J	Like ARF-223, high TGA	0.37 / 0.33	74.3	Closure weld, container bottom	Filter housing, container bottom
P&C / J	ARF with weight gain	0.35 / 0.19	70.5	Closure weld, container body inside	Filter housing, lid, container body

Material Type and Surv. Reason**	Description	Moisture (At packaging / DE)	% Actinide	Inner Container Analyzed	Convenience Container Analyzed
P&C / R		0.26 / 0.03	70.4	N/A	N/A
P&C / R		0.07 / 0.07	69.8	N/A	N/A
P&C / J		0.23 / 0.03	78.9		
P&C / J	Visually able to see oxide/ gas interface	0.40 / 0.26	71.8	Inside container wall and inside lid adjacent to weld	Inside lid, inside wall sections
P&C / J		0.32 / 0.22	70.6	N/A	N/A
P&C / R		0.06 / 0.02	60.1	N/A	N/A
P&C / J		0.26 / 0.13	81.6	N/A	N/A
P&C / J	Coating on CC – wiped clean	0.39 / 0.26	70.7	N/A	N/A
P&C / J	Coating on CC and IC – wiped clean	0.39 / 0.25	70.1	N/A	N/A
P&C / J	Coating on CC – wiped clean	0.23 / 0.22	77.4	N/A	N/A
P&C / J		0.29 / 0.02	70.8	N/A	N/A
P&C / R		0.24 / 0.03	71.1	N/A	N/A
P&C / R	Coating on CC & IC – wiped clean	0.23 / 0.19	72.4	N/A	N/A
P&C / R	Coating on CC – Collected on SEM stub for analysis	0.38 / 0.28	70.3	N/A	Coating analyzed by SEM and corresponding sections cut for SEM
P&C / R		0.23 / 0.03	65.4	N/A	N/A
P&C / R		0.06 / 0.05	62.6	N/A	N/A
P&C / R		0.25 / 0.22	63.5	N/A	N/A
P&C / R		0.04 / 0.01	87.9	N/A	N/A
P&C / R		0.28 / 0.27	76.7	N/A	N/A
P&C / R	No corrosion seen	0.18 / 0.09	70.8	N/A	Section cut for SEM to compare to DE12
P&C / R		0.11 / 0.01	84.1	N/A	N/A

**P=Pressure, P&C=Pressure & Corrosion, R=Random, J=Engineering Judgment

Figure 1. 3013 container configurations (a) RFETS 3013 container. Note silver coated threads on convenience container body (circled). (b) Hanford 3013 container. Difference between the two include convenience container design and lid material. Additionally, the inner container body design varied toward bottom of container.

Outside **Inside** **Inside Lid** **Outside Lid**

Figure 2. Typical outer container examination.

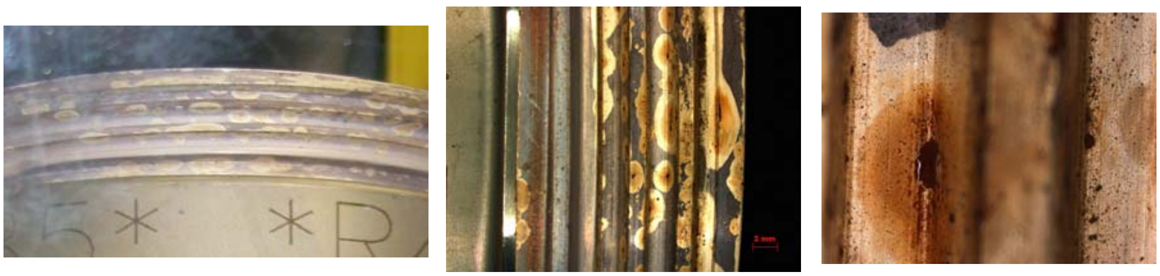


Figure 3 Examination of silver coated threads from RFETS convenience container body. Superficial corrosion pitting observed at threads.

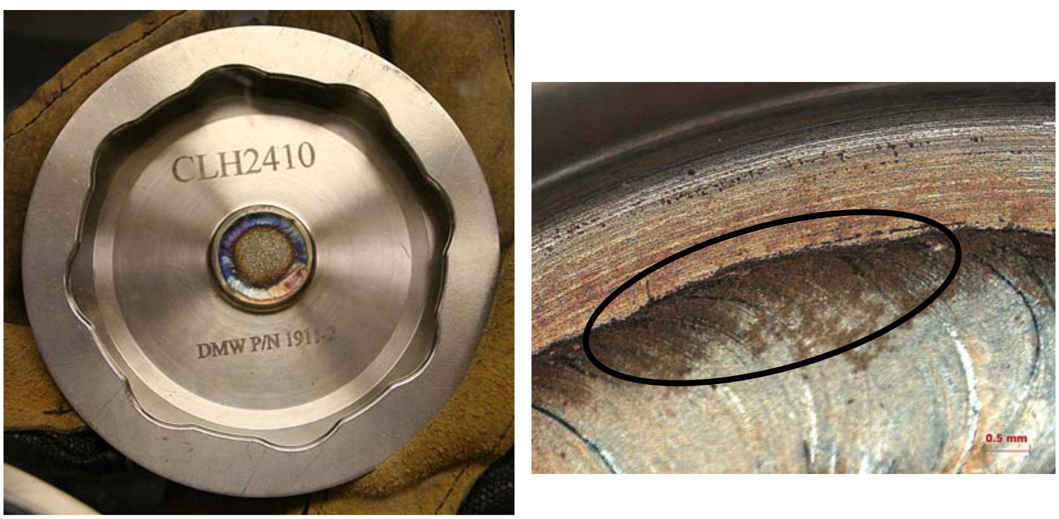


Figure 4 Typical examination of filter area from Hanford convenience container lid. Discoloration (circled) caused by oxidation from weld process. No degradation observed.

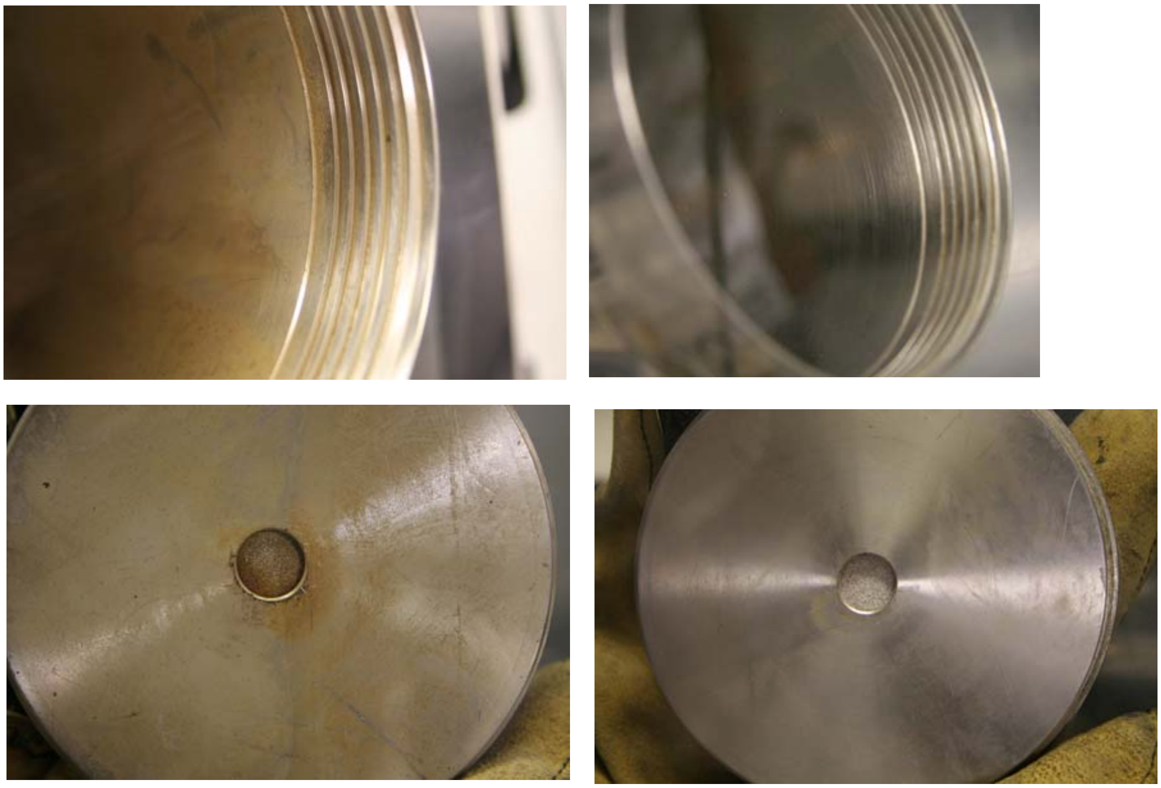


Figure 5. Typical examination of particulate and coating on interior of convenience container.

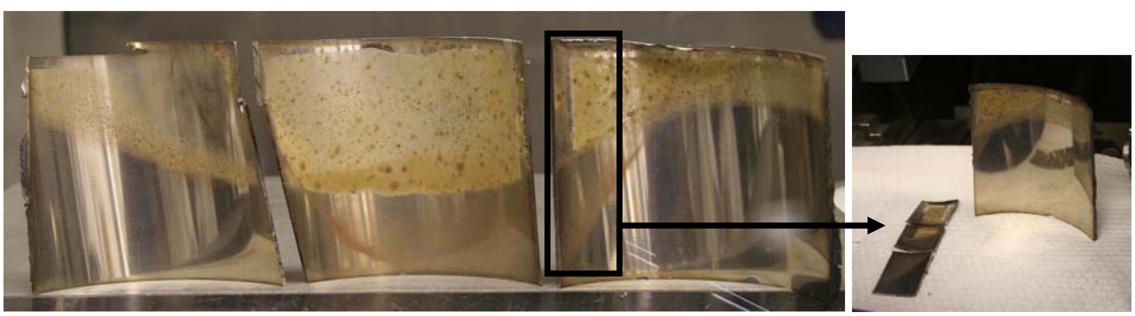
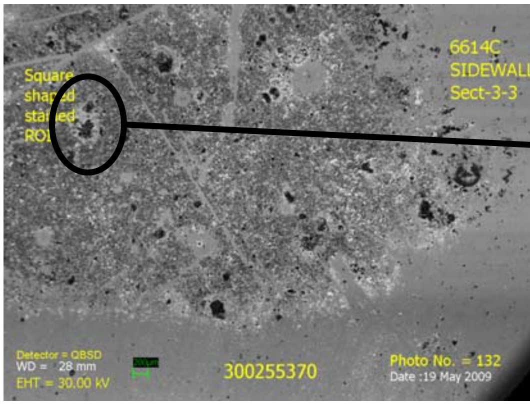
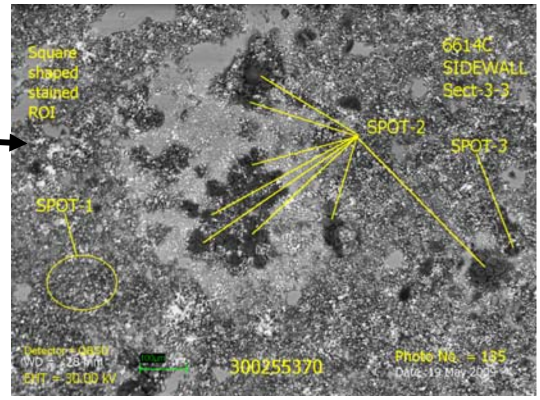


Figure 6. Visual examination photographs from the inside walls of the convenience container. Coated looking surface of convenience container is the headspace region. Sections cut for SEM and EDX examination were taken from region in the box. Portion of coating flaked off during cutting of sample for SEM, as seen in box on left.



(a)



(b)

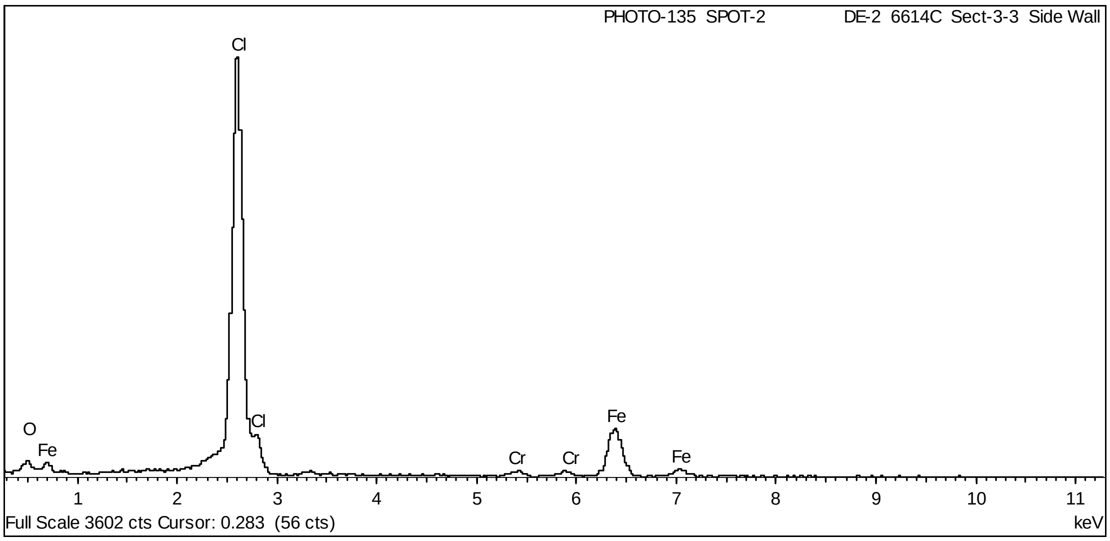


Figure 7. SEM examination and EDX spectrum from convenience container section seen in Figure 6 (a) Shows coating flaked off of sample around perimeter (b) Shows higher magnification of coating still adhered to surface. EDX spectrum shows chlorine rich peak typical of coating on surface.

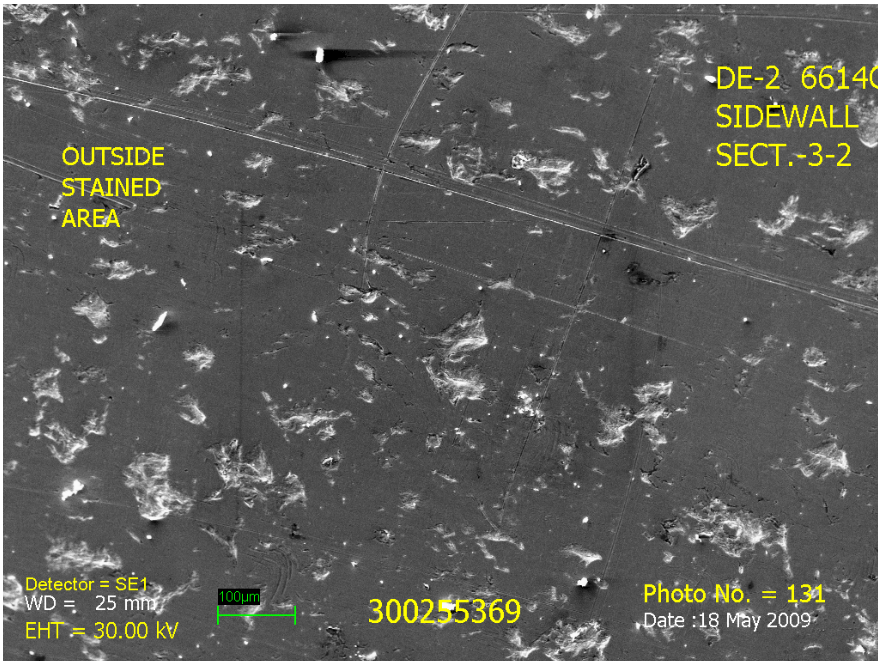


Figure 8. Shows irregularly oriented fissures at location where coating flaked off as seen on SEM.

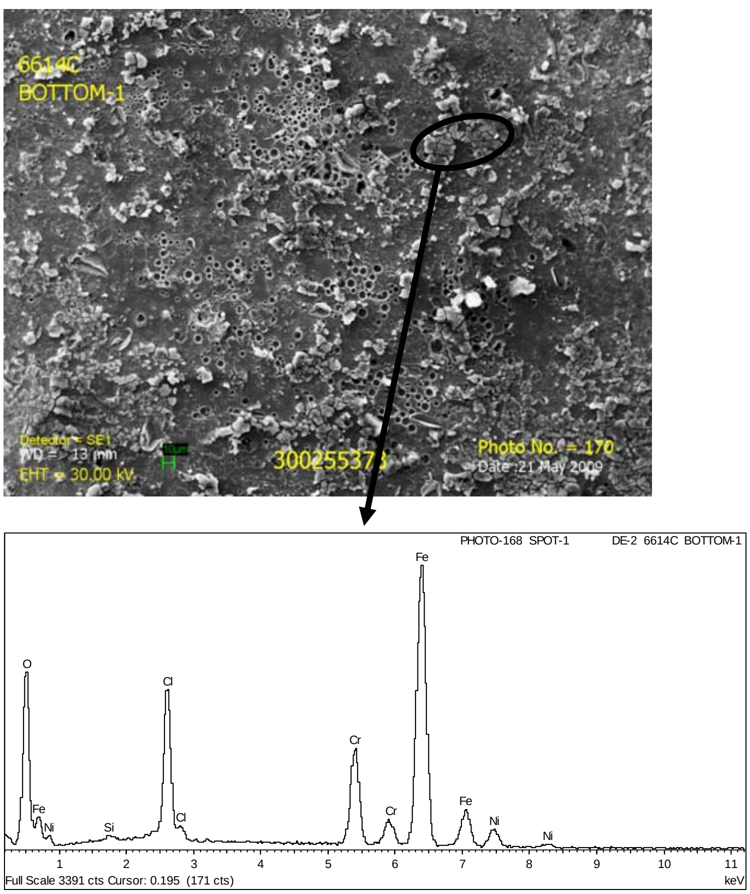
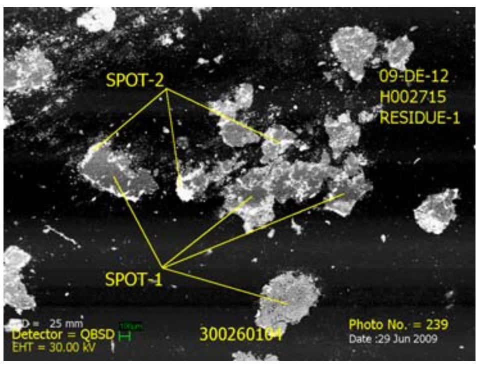


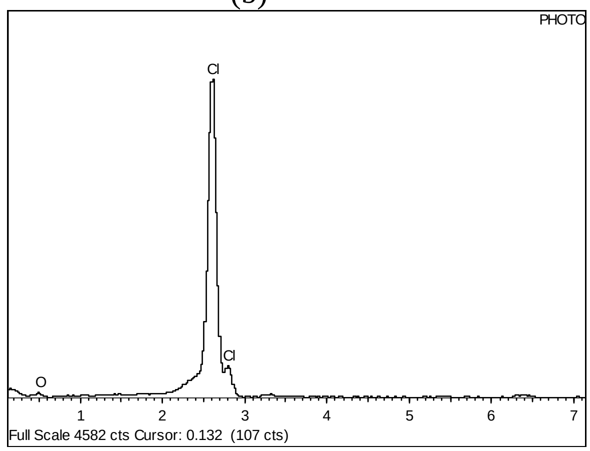
Figure 9. Bottom of convenience container (a) shows regular network of small pits (b) shows EDX spectrum of cracked looking debris rich in chlorine.

(a)

(b)



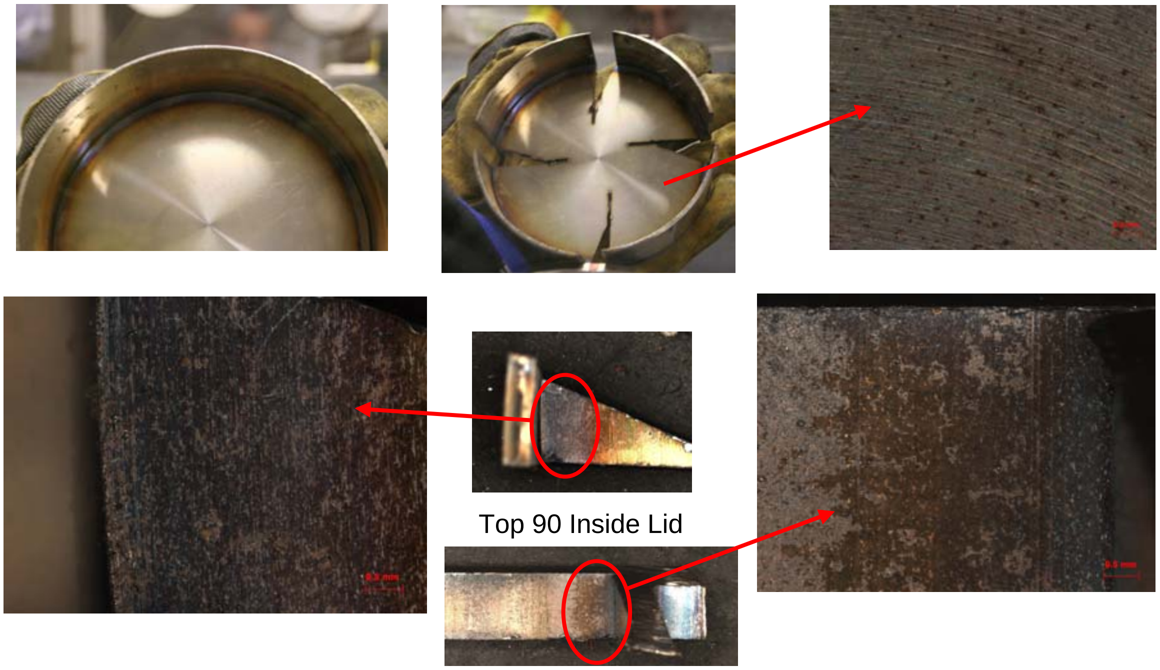
(c)



(d)

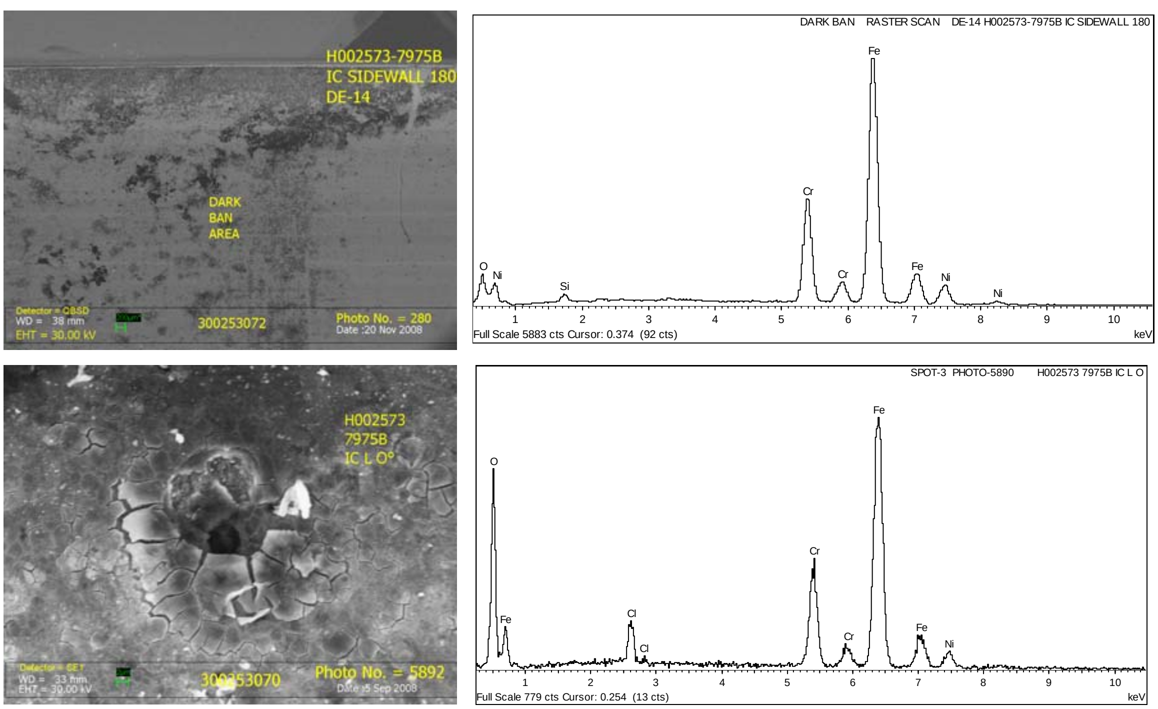
Figure 10. Chlorine rich particulate analyzed from inside lid of convenience can. (a) inside convenience can lid (b) Area where particulate was obtained for analysis (circled) (c) Particulate analyzed (d) EDX spectrum of particulate

Figure 11. Examination of RFETS inner container. The presence of soot from the welding operation was observed. No contact with salt containing Pu oxide.



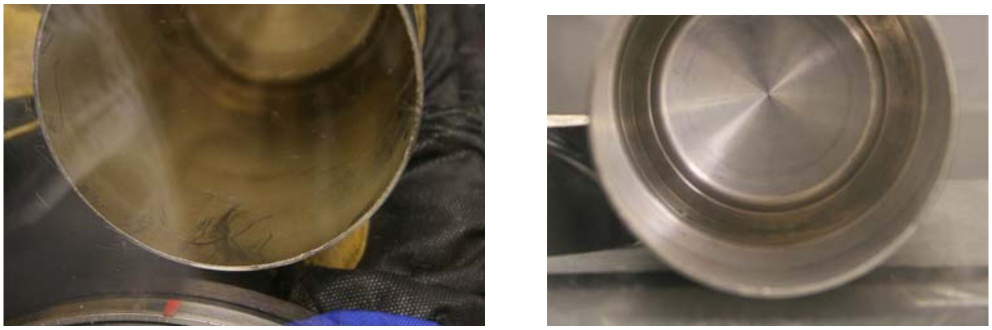
Top 90 Sidewall

(a)



(b)

Figure 12. Additional sections from inner container for further analysis during DE. (a) Appearance of corrosion particulates and “coating” adhering to surface of lid and side wall. No corrosion depth was seen by SEM (b) Coating product on sidewall likely an iron oxide product with the oxide peak shown in the EDX Spectrum at top right. Bottom photo and corresponding spectrum at bottom right shows a chloride peak from corrosion product within incipient pit.



(a) (b)

Figure 13. (a) Presence of adherent layer on inside inner container surface and (b) layer removed through light wiping with clean cloth.

Inside Lid Sections for SEM/EDX

Figure 14. Sections cut from inner container for SEM and EDX analysis.

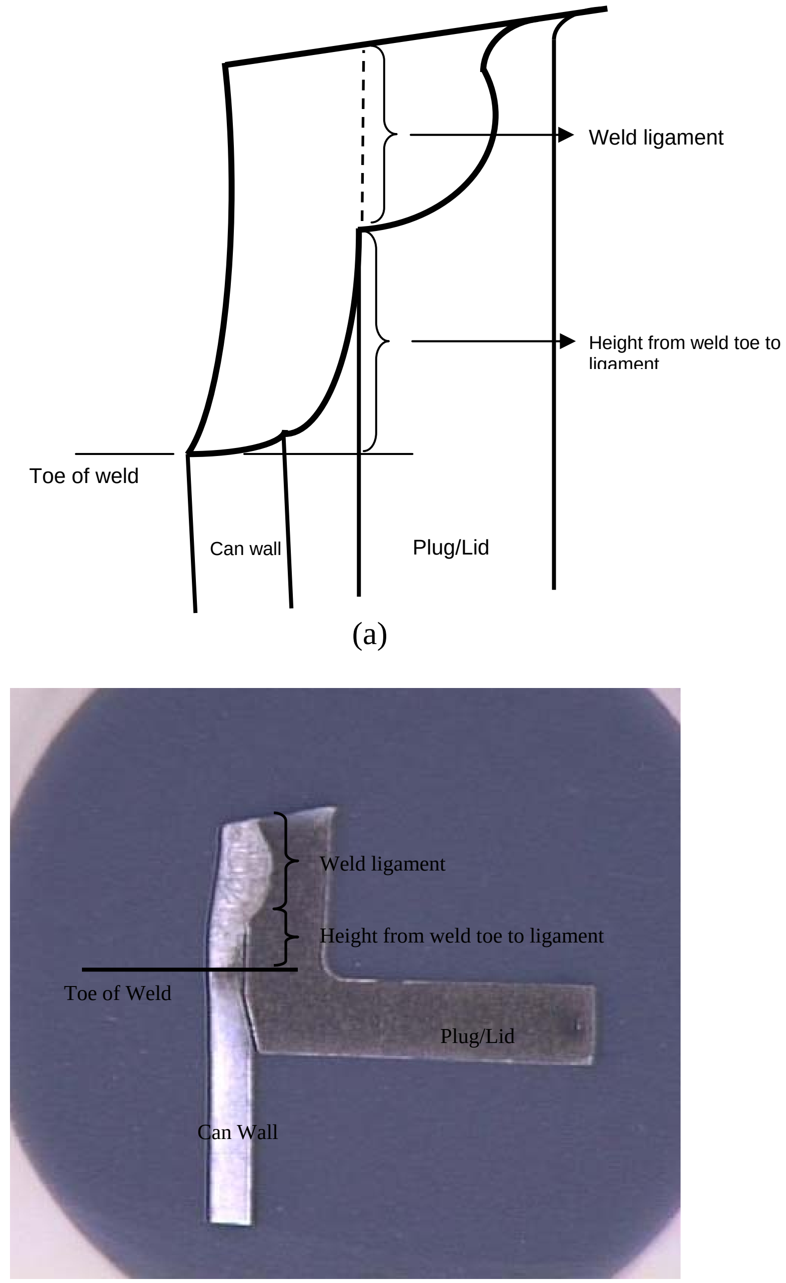


Figure 15. Inner container weld cross section (a) Schematic (b) Metallographically prepared section

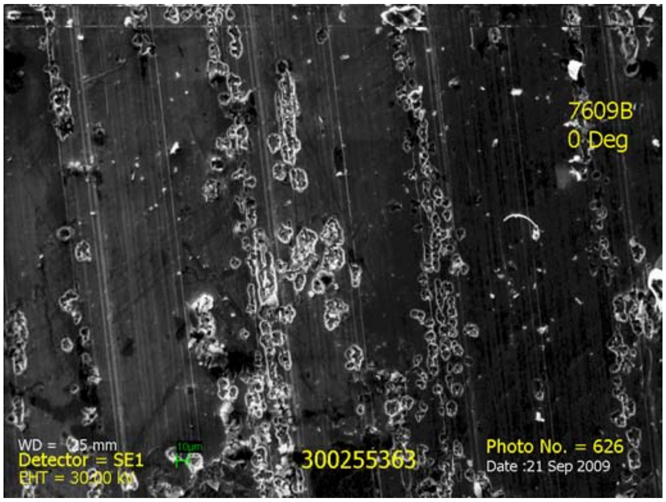


Figure 16. Small coalesced pits on the machining grooves of inner container lid.