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Examination of Shipping Package 9975-04194

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Summary

In December 2017, K-Area personnel attempted to open package 9975-04194 to remove its contents. The upper fiberboard assembly could not be initially removed due to an interference fit that had developed against the lead shield. Corrosion of the shield created two specific conditions that caused this interference. First, there was widespread heavy blisters over the shield surface. Corrosion of the lead under the surface (associated with porosity in the as-cast shield which is open to the surface) appears to have caused the blisters to form. Second, corrosion also formed in a gap between the lead shield and the internal stainless steel liner, pushing the top edge of the shield outward into the upper fiberboard assembly. In both cases, portions of the shield are pushed outward since the corrosion product occupies a greater volume than the metallic lead it replaced.

A review of available evidence from 9975 surveillances and other activities shows widespread blistering of the shield surface identified to date is confined to packages within the range of serial numbers from 3982 to 5088. Given the incidence rate observed to date, an estimated 91 additional packages might be expected to have shields with widespread moderate to heavy blistering. The blistering of the lead shield surface appears to be associated with porosity in the as-cast shield which is open to the surface. Radiographs suggest the large majority of pores are open to the surface and of limited depth.

Background

Package 9975-04194 was received in K-Area Complex (KAC) in October 2007. It contained an internal heat load of less than 1 watt. KAC personnel opened package 9975-04194 on December 8, 2017 following a storage period of about 10.2 years, and were unable to remove the upper fiberboard assembly. Three days later, the upper fiberboard assembly was removed using an L-hook tool (as allowed by procedure). On January 11, 2018, this package was re-opened in KAC by Daugherty, Smock (SRNL Materials Science & Technology), Allen, Leduc (SRNL Packaging Technology and Pressurized Systems), McEvoy (9975 Design Authority Engineer), Grimm (NMM Engineering) and Stevens (KAC Operations Support). The upper fiberboard assembly and lead shield were examined at this time, although the shield was not removed from the package. Subsequently, the empty package was transferred to SRNL, where the shield was removed for further examination on February 21, 2018.

This report documents the findings from these examinations of the 9975-04194 lead shield and fiberboard.

Results

Several observations can be made from photographs taken during the initial inspection on December 11, 2017.

- A line of material from the shield is seen embedded in the fiberboard within the 6^{th} fiberboard layer (about 2.5 to 3 inches) from the bearing plate (Figure 1).
- A portion of the bottom edge of the upper fiberboard assembly suffered flaking / peeling damage from dragging against the shield as it was removed (Figure 2).

- The shield contains numerous blisters on the exposed surface, and the diameter of the shield is seen to extend significantly beyond that of the shield lid (Figure 3).

During the January 11, 2018 inspection, measurements of the shield and upper fiberboard assembly were taken. Some features of the shield were measured again on February 21 and March 19, 2018. Additional photographs of the shield were also taken on these dates after the shield was completely removed from the package. When the shield was lifted out of the package, the lower fiberboard assembly initially started to come with it, indicating some degree of interference. However, that interference was easily broken, allowing the two components to separate. The sides and bottom of the shield after removal from the package are seen in Figures 4 and 5.

The initial difficulty in removing the upper fiberboard assembly resulted from a very tight fit between the upper fiberboard assembly and the lead shield. While the upper assembly was easier to remove during subsequent inspections (on January 11 and February 21), it still required greater effort than normal.

The upper fiberboard assembly ID was measured on January 11, 2018. Values of 8.557 and 8.582 inches were obtained ~90 degrees apart, and are consistent with drawing tolerances. The clearance between the upper fiberboard assembly and shield would normally be 0.15 – 0.338 inch (based on drawing tolerances). In this case, the shield measurements taken on January 11 and February 21, 2018 indicate a nominal clearance ranging from 0.004 to 0.08 inch. These shield measurements were taken along the top edge of the shield and of necessity included some degree of bumpiness (although care was taken to avoid the largest blisters).

On March 19, 2018, additional shield OD measurements were made, capturing the dimension using manual swing calipers which was then measured with electronic calipers. Several such measurements were made at varying distances from the top of the shield, as recorded in Table 1. With the small tips on the manual swing calipers, it was generally possible to take measurements where no blisters existed. These results show the shield OD is the largest within 1 inch of the top (8.42 – 8.46 inch), and is less further from the top (8.29 – 8.32 inch). The measured shield dimensions are summarized in Table 1.

The height of several individual blisters was measured, and ranged from ~0.05 to 0.09 inch. In addition, the surface layer over two blisters was pried back, and the corrosion product underneath was scraped away (Figure 6). The cavity under one of these blisters extended about 1/8 inch below the surrounding shield surface, while the other had minimal depth below the surrounding shield surface.

The lead had separated from the inner stainless steel liner and bolting lugs in two regions along the top edge of the shield. Figure 7 shows one of these regions. Some corrosion product is visible in the gap this created. The width of the gap between the lead and inner stainless steel liner appears consistent with the increased OD along the top edge of the shield. Measurements at several locations on the top edge show the lead ranging from 0.463 to 0.523 inch thick, with an adjacent gap of 0.073 to 0.087 inch thick and the inner stainless steel liner about 0.033 inch thick. The average measured radial gap of 0.082 inch corresponds closely to the observed diameter increase in the top 1 inch of the shield of ~0.14 inches.

The thickness of the lead carbonate (lead corrosion product) remaining on the shield was measured on January 11, 2018 with an Elcometer 345 FN coating thickness gage, which uses an eddy current technique. The probe was zeroed on a non-ferrous base material, and then verified with a non-metallic shim set. The gage was then used to measure the lead carbonate thickness at several locations on the side and top edge, including blistered and non-blistered locations. In the non-blistered areas, the lead carbonate thickness ranged from 4 to 17 mils (11 mils average) on the top edge of the shield, and from 0.9 to 1.4 mils (1.2 mils average) on the side of the shield. The lead carbonate thickness on the blistered areas ranged from 14 to 27 mils (20 mils average) on the top edge of the shield, and from 17 to 32 mils (25 mils average) on the side of the shield.

After the shield was removed from the package, it was taken to PMCS QA (K. Alexander) for X-ray examination. The specific goal of this examination was to identify whether the shield contained either internal or surface porosity that might explain the observed corrosion behavior. Two approaches were used, and the following results were reported. Images from the two approaches are shown in Figures 8 and 9.

“The first image was made using Ir192 and is a shot of one wall of the shield. It appears the pitting goes from just forming and then to fairly advanced with apparently some depth. The second image was made using Co60 with a technique to demonstrate the sidewall (side profile) view of the shield to determine if any porosity was below the surface. No evidence of porosity throughout the side wall thickness was evident. Appears all pitting started on the surface and not from within.“ [1]

Three samples of the corrosion product from the 9975-04194 shield were removed for examination in a scanning electron microscope using energy dispersive X-ray spectroscopy (EDX). These samples included the outer gray surface of a blister, the white corrosion product from inside a blister, and corrosion product from the gap between the lead and inner stainless steel liner. The goal was to identify if any impurities were present that might influence the observed corrosion process. No impurities were identified in any of the samples. Note, however, that the practical sensitivity of EDX is typically a few tenths of a percent, so any impurities less than this concentration would not be detected.

Discussion

The height of several blisters was measured to be 0.05 – 0.09 inch high. Given a number of larger blisters all around the shield, one might assume they add ~0.07 – 0.08 inch to the effective outer radius, or ~0.15 inch to the effective OD of the shield. With this amount added to the measured OD (not including blisters), the effective shield OD was ~8.59 inches at the top, and 8.47 inches further down. This increase in the effective OD of the lead shield would create interference between the measured fiberboard ID and the top edge of the shield, but would not create significant interference away from the top edge. It should be recognized that the highest blisters may have been knocked off during the initial package opening. In fact, Figure 1 shows such material that likely transferred from the shield to the fiberboard assembly.

Most of the blisters on the shield surface were covered with the same gray corrosion product as the rest of the shield. In the few spots examined, the skin of the blisters was a thin layer of metallic lead covered by gray corrosion product. White corrosion product was built up under this skin. With a uniform gray surface layer of corrosion over the entire surface, it appears that relatively little lead was lost from any of the blister locations.

None of the blisters imaged in the radiograph (Figure 8) show as much contrast as the stainless steel bolting lug, indicating X-ray attenuation at the blisters (the net shielding created by the lead and lead corrosion product) is greater than that of the bolting lug. Since the density of stainless steel is 70% that of lead (8.0 g/cc vs 11.3 g/cc [2]), and the shield curvature increases the effective thickness at the lug location (~1.5 inches from radiograph center) by about 9%, significantly more than 77% of the nominal lead thickness remains at the blister locations. However, since the radiographs show dark spots at the blister locations (indicating less material), it is concluded that these locations were initially pores in the lead casting. Any pores, cracks or gaps open to the surface would become filled with corrosion product, but the added carbon and oxygen would not significantly change the X-ray density.

The region of the shield shown in the Figure 8 radiograph was examined visually and photographed. Figure 10 compares some of the more prominent features imaged in the radiograph with those on the photograph. Most of the features in the radiograph correspond to blisters in the photograph, and vice versa, but a few do not. Two radiographic features that do not correspond to visible surface features are highlighted in red in Figure 10. These features could represent subsurface porosity.

Two possible causes for the gray color of the lead corrosion product were identified, although neither has been confirmed to date. Heavy discoloration of the normally white lead corrosion product has been described for a test package in Reference 3. In this case, the corrosion product was dark brown and black. EDX examination of that corrosion product identified the presence of chlorine, which likely came from the fiberboard. On the 9975-04194 shield, the contrast between the gray exterior corrosion product and the white corrosion product under the blisters suggests that the corrosion product under the blisters was isolated from whatever caused the discoloration on the surface. It is plausible that the much lighter graying of the corrosion product on the 9975-04194 shield results from a lower concentration of chlorine (below the EDX detection level). The second possible cause is identified from the literature. Reference 4 describes the corrosion product that can form on lead with varying concentrations of acetic acid and moisture. In one case, black clusters of corrosion were observed and identified to be lead oxide carbonate hydroxide, rather than the more common lead carbonate hydroxide. Reference 5 describes several corrosion products forming on lead in the presence of specific concentrations of acetic acid and high humidity. These include lead oxide carbonate hydroxide, lead acetate oxide hydrate, and lead oxide. The color of these compounds includes yellow and red. Insufficient data are available to compare the conditions in these references with the environment in a 9975 package, but it is plausible that small concentrations of some of these other lead compounds can alter the appearance of the corrosion product.

Implications for Other Packages

Data from other 9975 packages were reviewed in order to estimate the possible extent of similar behavior in other packages. This review consisted of a qualitative assessment of lead shield photographs taken during field surveillance (from FY2007 through FY2016), and review of notes on a few packages that were previously examined in response to similar anomalous corrosion behavior. The following packages were identified:

- Eight packages with widespread moderate to heavy blistering: 9975-03982, -04142, -04189, -04194, -04389, -04397, -04985, -05088
- Five packages with widespread light blistering (and maybe additional surface roughness): 9975-04016, -04190, -04353, -04697, -04900
- Four packages with very localized blistering or other forms of surface roughness: 9975-01154, -01903, -02028, -04135

The packages that appear to have widespread blistering range from serial number 3982 to 5088. There are 1107 packages within this range of serial numbers, but a few packages would likely have been rejected initially or used elsewhere. Therefore, it is assumed that up to 1100 packages from this range have been stored in KAC. From FY2007 through FY2016, 218 packages were surveilled, including 60 with serial numbers between 3982 and 5088. The number of additional packages opened for reasons other than surveillance was not tabulated, but will be assumed to be on the order of 100, with a similar proportion (28%) between serial numbers 3982 and 5088. Therefore, it is estimated that a total of ~88 packages between serial numbers 3982 and 5088 have been opened in KAC.

Based on these numbers, 13 packages were identified with widespread blistering on the shield out of about 88 packages examined from the 3982 to 5088 range, for an incidence rate of 15%. Of these, the blistering was moderate to heavy on 8 shields, for an incidence rate of 9%. These rates suggest that an additional 152 shields might be expected to have widespread blistering within the total population of serial numbers between 3982 and 5088, of which 91 would have moderate to heavy blistering.

In package 9975-04194, there is a gap between the lead and the internal stainless liner around much of the circumference, with the lead flaring outward over the top ~1 inch or so. This increased the shield OD by about 0.14 inch at the top, creating the limiting location that would have hindered removal of the fiberboard assembly the most. Most of the packages with surveillance photos that appeared to show blistering also showed some degree of gap between the lead and liner, although most were much less extreme. Based on a cursory look, many of the shields without blistering also show some degree of gap between the lead shield and stainless steel liner, but it seems less frequent and less severe than in the blistered shields. It is suspected that if such a gap is present, then the degree of flaring is proportional to the overall amount of corrosion around the top of the shield, whether there is blistering or not.

Conclusions

The difficulty in removing the upper fiberboard assembly from package 9975-04194 resulted from the combination of separation between the lead and inner stainless steel liner (~0.08 inch gap), and the heavy blistering. This led to an interference fit between the top edge of the shield and upper fiberboard assembly.

A review of available evidence from 9975 surveillances and other activities shows widespread blistering of the shield surface identified to date is confined to packages within the range of serial numbers from 3982 to 5088. Given the incidence rate observed to date, an estimated 91 additional packages might be expected to have shields with widespread moderate to heavy blistering. The blistering of the lead shield surface appears to be associated with porosity. The radiographs suggest the large majority of pores are open to the surface and of limited depth.

The development of corrosion product in a gap between the lead and the inner stainless steel liner likely caused the additional separation at the top of the shield. Similar (but smaller) gaps are seen on a number of shields, both within and beyond the 3982 to 5088 range.

References

[1] Electronic mail message "RE: contact for results" from K Alexander to W Daugherty et al., February 28, 2018

[2] web site "theengineeringmindset.com/density-of-metals/", P. Evans, May 18, 2015

[3] SRNL-STI-2010-00185, "Model 9975 Life Extension Package 2 – Final Report", W. L. Daugherty, April 2010

[4] J. Tetreault, J. Sirois and E. Stamatopoulou, "Studies of Lead Corrosion in Acetic Acid Environments", Studies in Conservation, Vol 43, pp17-32, 1998

[5] A. Niklasson, L. Johansson and J. Svensson, "Influence of Acetic Acid Vapor on the Atmospheric Corrosion of Lead", Journal of the Electrical Chemical Society, vol 152 (12), pp B519 – B525, 2005

Table 1. Dimensional check of shield / fiberboard interference

Location	Shield OD (inch)
Shield OD near top 1/11/2018 *	8.53 8.50
Shield OD near top 2/21/2018 *	8.517 8.553
Shield OD ~0.25" from top 3/19/2018 **	8.46
Shield OD ~1" from top 3/19/2018 **	8.42
Shield OD ~2.5" from top 3/19/2018 **	8.32
Shield OD ~6" from top 3/19/2018 **	8.29
Shield OD ~13.5" from top 3/19/2018 **	8.32
Drawing requirement	8.262 - 8.35 maximum

* The measurements made on 1/11 and 2/21 likely included some of the blisters, but did not include the largest blisters.
** The measurements made on 3/19 were captured with a manual swing calipers and did not include any blisters.

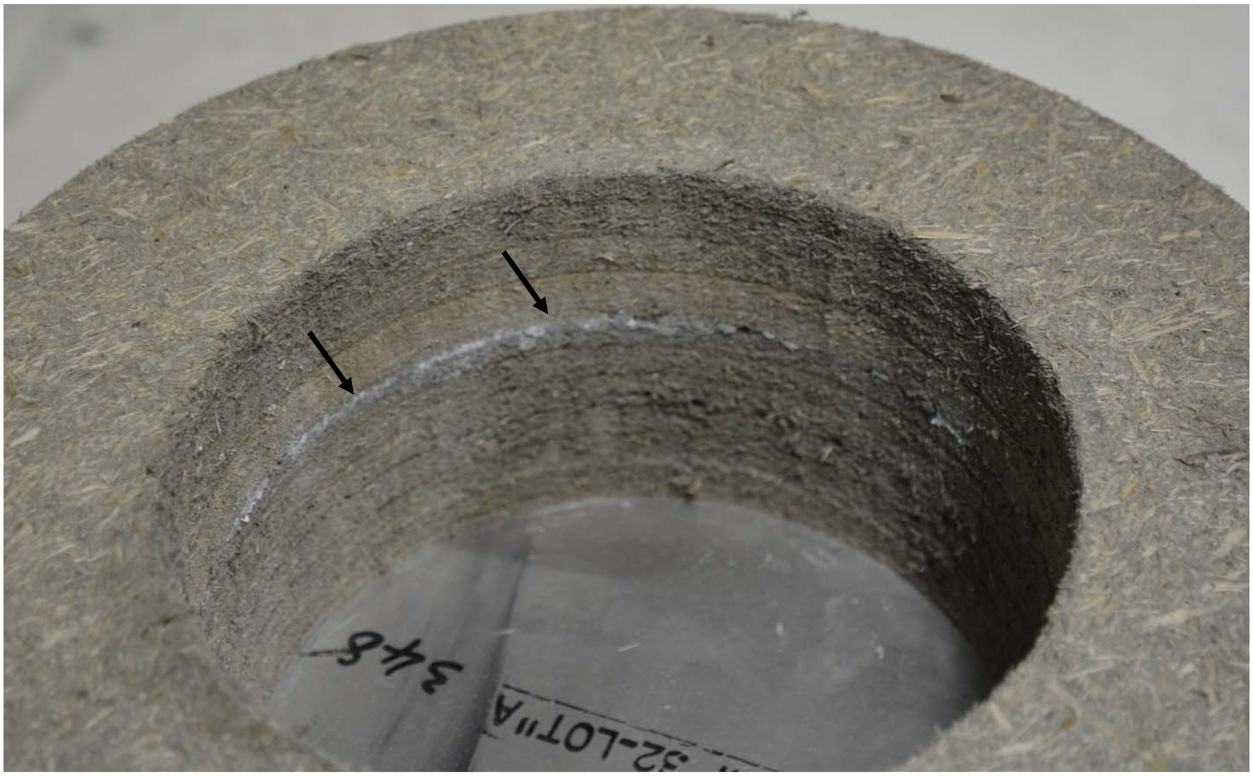


Figure 1. 9975-04194 upper fiberboard assembly after removal on December 11, 2017. Note the line of shield corrosion material that remained embedded in the fiberboard (arrows). Photo taken by KAC personnel.

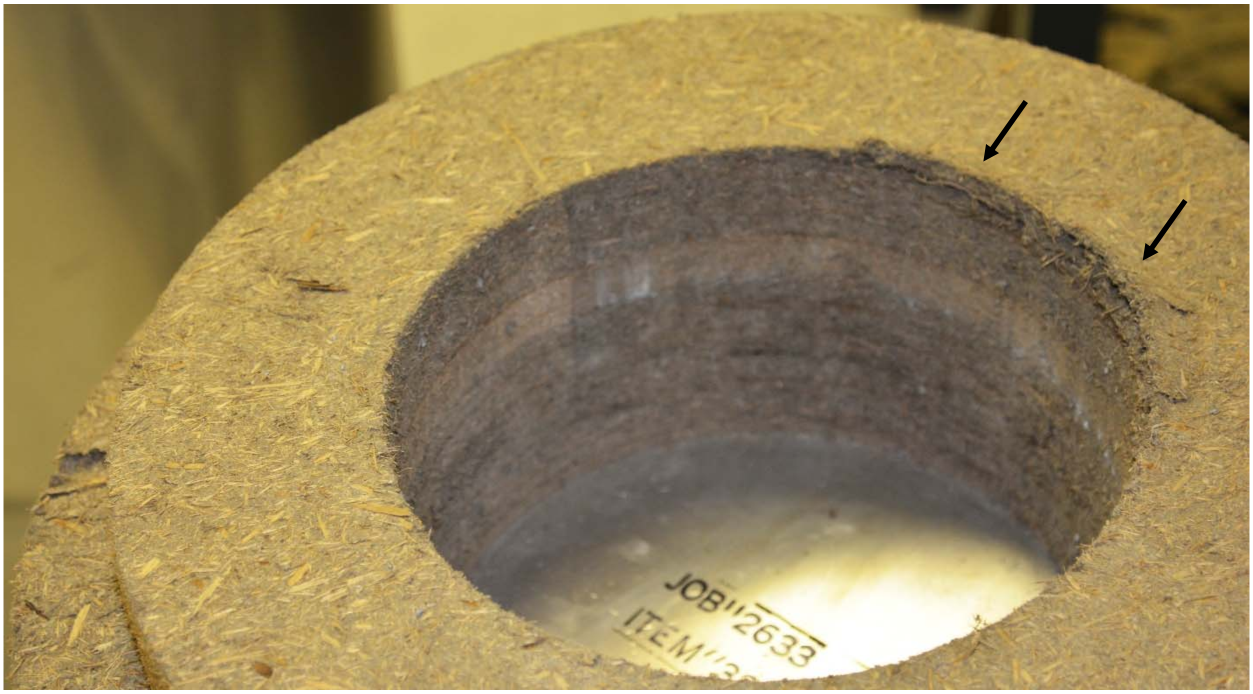


Figure 2. 9975-04194 upper fiberboard assembly showing region of flaking/peeling damage (arrows). Photo taken December 11, 2017 by KAC personnel.

Figure 3. 9975-04194 shield when the package was first opened. Note the surface roughness and the extent to which the shield extends out past the shield lid. Photo taken December 11, 2017 by KAC personnel.

(a)


(b)


(c)


(d)

Figure 4. 9975-04194 shield after removal from the package on February 21, 2018.

Figure 5. Bottom of the 9975-04194 shield.

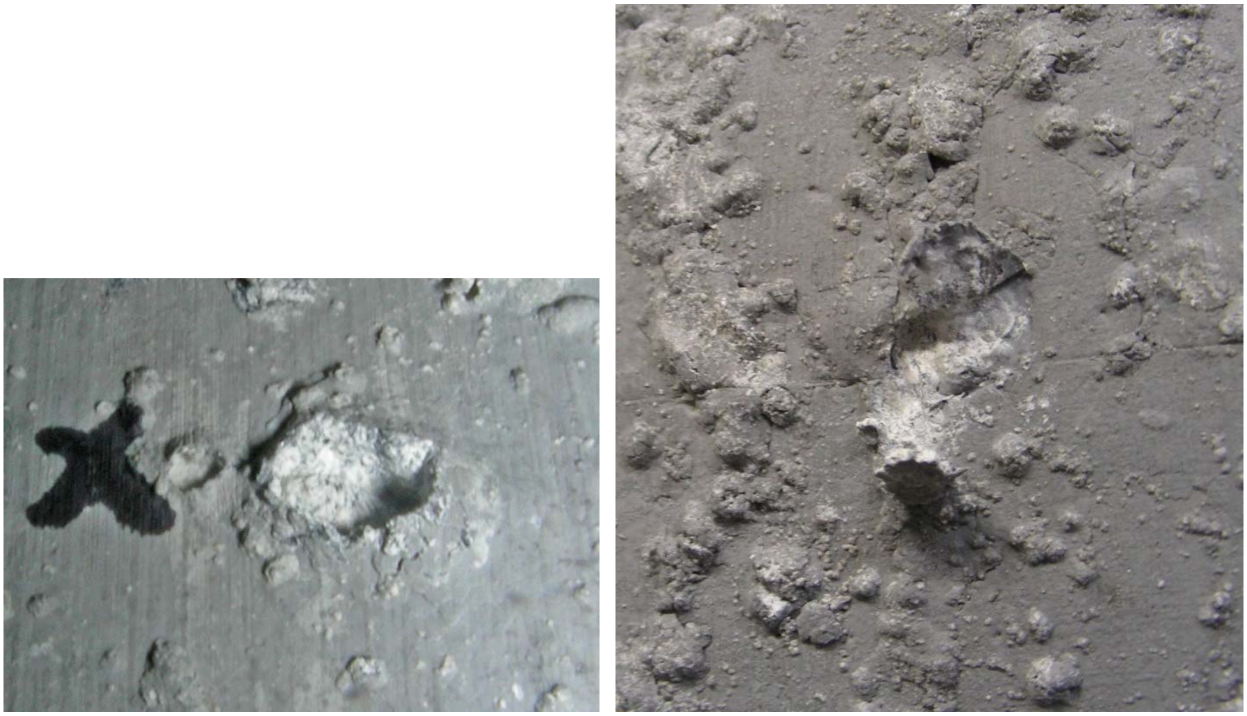


Figure 6. The surface layer over two blisters was peeled back, and the corrosion product underneath was scraped away.

Figure 7. Top edge of the 9975-04194 shield showing a gap between the lead and the internal stainless steel liner.

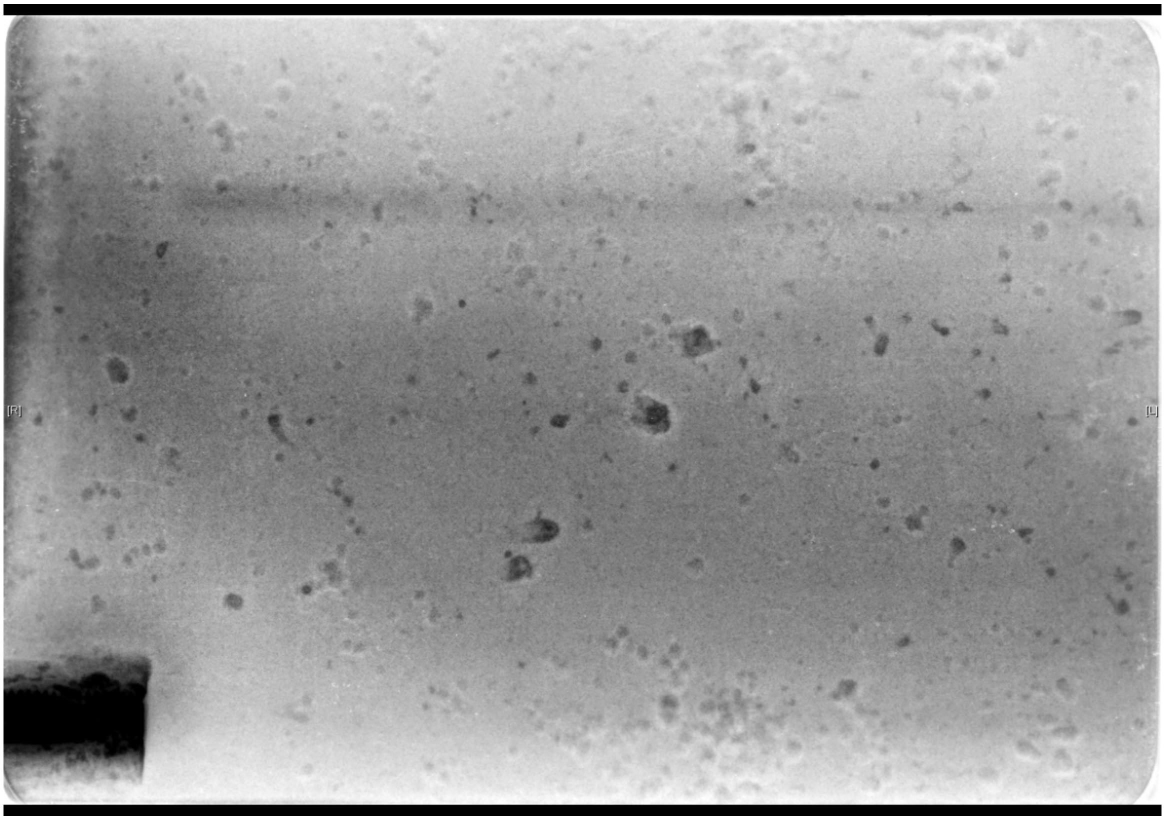


Figure 8. X-ray image taken through a single side wall with Ir192 source.

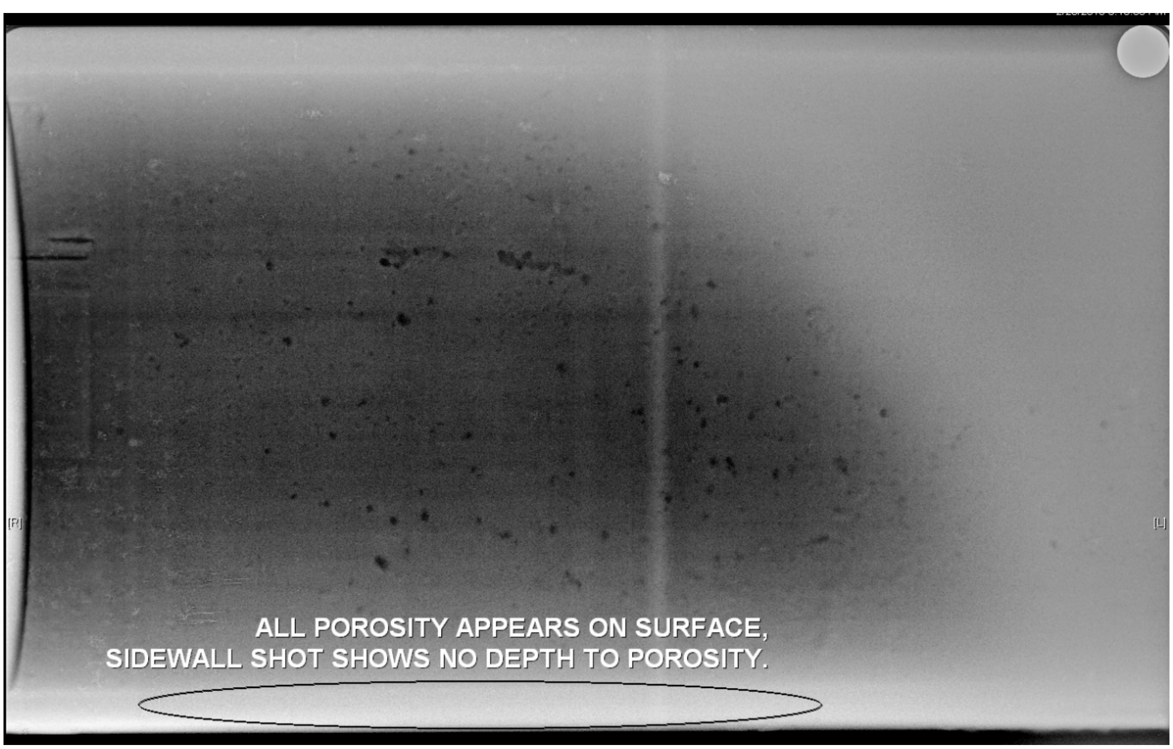
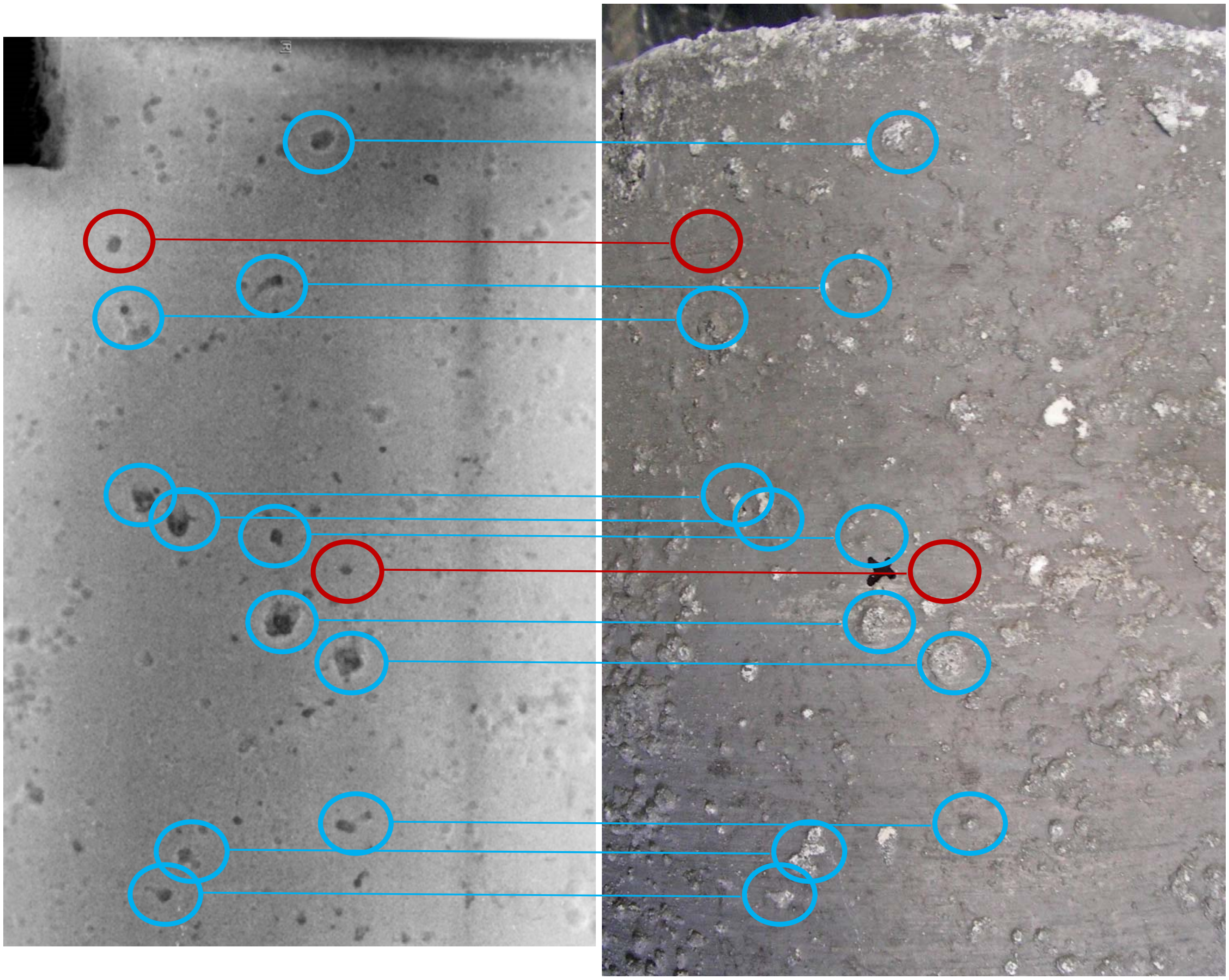


Figure 9. X-ray image taken through entire shield (double side wall) with Co60 source. Note – this is not the same region of the shield shown in Figure 8.



(a) (b)

Figure 10. Comparison of features from radiography (a) and photography (b). Most of the features seen by radiograph correlate to visible features (blisters) on the surface, indicated in blue. The radiograph features indicated in red do not correlate to visible features on the surface.

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