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Alternative Liquid DSA Containers for Sludge Slurry Storage in the SRNL Shielded Cells

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EXECUTIVE SUMMARY

A pending revision of the Documented Safety Analysis (DSA) for the Savannah River National Laboratory (SRNL) defines "DSA containers" for liquid sludge slurries as containers not susceptible to a flashing spray release in a fire and requires that a list of DSA containers be maintained. High Level Waste (HLW) samples are typically received from the Savannah River Site (SRS) tank farm after retrieval from the storage tanks. Glass bottles are preferred for long-term storage of radioactive liquid sludge slurry samples but are not on the DSA container list. An evaluation has been conducted to identify vessel lids for the glass bottles that would vent prior to pressurization and liquid superheating in a fire event. Low melting Field's Metal eutectic alloy with a melting point of 62 °C has been identified as a preferred material of construction for vessel lids for this application because the material is resistant to puncture and is expected to have good chemical compatibility and radiation stability in the shielded cells environment. A test vessel was designed to evaluate the alloy and confirm that it would melt before the water in the vessel reaches the boiling point. The tests confirmed: 1) that the reported melting point of the alloy was accurate, 2) that a top fashioned from this material will melt creating an open atmosphere in the vessel headspace prior to sample boiling under moderate and fast heating rates, and 3) that nonuniform heating of the bottle from the bottom also results in melting of the alloy prior to boiling. Based on the results, neither an engulfing fire with standing or toppled bottles or a fire producing localized heat at the vessel bottom would result in flashing spray conditions.

Based on these results, it was recommended in Revision 0 of this document that glass vessels of various volumes ranging from 125 mL to 1 gallon with modified tops containing the specified Field's Metal eutectic alloy which are appropriately designed to avoid flashing spray material releases be added to the DSA container list. These vessels will be utilized in the Shielded Cells for the storage of radioactive liquid samples of sludge slurries. Use of these vessels will also be advantageous for other liquid samples containing accountable amounts of nuclear material throughout other SRNL laboratories. Similarly constructed paraffin vessel lids could also potentially be added to the approved list, though additional testing would be required.

Revision 1 of this report includes results of additional corrosion evaluations of Field's Metal alloy in the following solutions: 0.1 M HNO_3 (pH 1), a mixture of 0.0001 M HNO_3 and ~0.02 M HCOOH (pH 3.5-4.0), a mixture of 0.0001 M HNO_3 and ~0.02 M $HOCH_2COOH$ (pH 3.5-4.0), 0.1 M NaOH (pH 13), and 1.0 M NaOH (pH 14). Significant corrosion of Field's Metal alloy pellets was observed visually and gravimetrically after 3 days of contact with 0.1 M HNO_3 at ambient temperature without agitation. Visual indication of corrosion was observed in 0.1 and 1.0 M NaOH solutions, but no mass loss occurred after 3 contact days. Many accountable sludge slurry samples will be in the basic pH range. In additional tests conducted near pH 4 with mixtures of nitric acid and either formic or glycolic acid neither visual nor gravimetric observations indicated that corrosion had occurred. Tests with mixtures of dilute nitric and organic acids are generally representative of accountable sludge slurry samples produced from SRAT and SME testing in the SRNL Shielded Cells that will require storage. The results indicate that corrosion of Field's Metal Alloy should have minimal impacts on vessel and sample integrity in the Shielded Cells across the pH range from 3.5 to 14.

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ELN	electronic laboratory notebook
SRNL	Savannah River National Laboratory
SRS	Savannah River Site

1.0 Introduction

A pending revision of the Documented Safety Analysis (DSA)[1] for the Savannah River National Laboratory (SRNL) defines "DSA containers" for liquids as containers not susceptible to a flashing spray release in a fire and requires that a list of DSA containers be maintained.[2,3] Liquid containers not included in the list of DSA containers are classified as "Limited Use" containers. Greater than de minimis quantities of radioactive liquid materials in Limited Use containers are controlled below a very low facility limit. Liquids in the DSA include damp sludges, sludge slurries, and solutions.

High Level Waste (HLW) samples are typically received from the Savannah River Site (SRS) tank farm after retrieval from the storage tanks. Liquid SRS tank farm samples containing no or very low levels of sludge solids typically contain below de minimis levels of radioactive materials and are stored in polymer bottles. Dry sludge samples containing <5 wt. % water are considered solids, are not subject to flashing spray release, and are typically stored in glass bottles (due to radiation-induced degradation of polymer bottles). Sludge samples containing >5 wt. % water, such as damp sludge or sludge slurry samples, are classified as liquids and may be subject to the flashing spray risk. Approved containers are required for storage of liquid sludge slurry samples. For short-term studies and applications, these radioactive liquid (sludge slurry) samples are typically stored in approved polymer bottles. Specific types of polymer bottles are included in the list of DSA containers for liquids. Long-term storage of liquid (sludge slurry) samples in polymer bottles frequently results in degradation and failure of the bottles over time due to the radiation field within the Shielded Cells environment. As a result, polymer bottles containing these liquid samples require frequent monitoring, inspection, and replacement. Common practice in the Shielded Cells has been to use glass bottles with plastic caps for long-term storage of liquid (sludge slurry) samples. Glass bottles, regardless of cap type, are not currently on the list of DSA containers for liquids. As a result, an evaluation has been conducted to identify vessel lids that could be utilized on glass bottles that would vent prior to pressurization and liquid superheating in a fire event with the goal of adding glass vessels with modified tops to the list of DSA containers for liquids.

Various design options and materials were considered for the container lids. Strategies considered included metal screens with small screen openings, commercial devices designed to engage and create an open atmosphere in the vessel head space above known temperatures below the boiling point of water, and materials of construction for the tops that are known to melt well below 100 °C. Prototypes of various design options using these materials were prepared and evaluated. Based on the prototypes, the latter approach involving low melting materials was selected as the preferred option to pursue. Two low melting materials were considered: paraffin wax and a eutectic metal alloy of bismuth, indium, and tin known as Field's Metal. The reported melting points of paraffin and the metal alloy were 77 and 62 °C, respectively. Of these two materials, the alloy was selected as the preferred material since the metal was much more resistant to puncture and was expected to have better radiation stability in the Shielded Cells environment. A test vessel was designed to evaluate the alloy and confirm that it would melt before the water in the vessel reaches the boiling point. In addition, corrosion evaluations of Field's Metal alloy were conducted in both acidic and basic solutions.

2.0 Identification of Liquid DSA Container Lid Alternatives for Sludge Slurries

Various design options and materials were considered for the glass bottle lids. Strategies considered included metal mesh screens with small screen openings, commercial devices designed to engage and create an open atmosphere in the vessel head space above known temperatures below the boiling point of water, and materials of construction for the tops that are known to melt well below 100 °C. Prototype tops of the following basic types were prepared as described in detail in Section 3. Field's Metal used in the last two prototypes is a low-melting eutectic alloy containing 51.0 wt. % indium, 32.5 wt. % bismuth, and 16.5 wt. % tin.

Vessel Lid Alternative Prototypes Evaluated

- Fire Sprinkler Head
- Stainless-Steel Mesh Screen
- Supported Paraffin Sheet
- Cast Paraffin Plate
- Cast Paraffin Plug in Swagelok Bulkhead
- Cast Field's Metal Alloy Plug
- Cast and Machined Field's Metal Alloy Disc

3.0 Experimental

Materials of construction used for the various prototypes were either obtained from on-site supplies or ordered from commercial suppliers. The fire sprinkler head was of a design previously used on site. The paraffin casting wax sheets were ordered from Freeman Manufacturing and Supply Company in Avon, OH. The Field's Metal alloy was ordered from Rotometals, Inc. of San Leandro, CA.

3.1 Preparation of the Fire Sprinkler Head Vessel Top Prototype

A standard brass fire sprinkler head containing an orange, fluid-filled glass ampule was attached to a modified plastic vessel top with an opening diameter selected to fit the sprinkler head. Orange ampules are certified to burst in the temperature range from 135 to 170 °F. A photograph of the prototype is provided in Figure 3-1.

Figure 3-1. Fire sprinkler head attached to the top of a 125 mL glass jar.

3.2 Preparation of the Metal Mesh Screen Vessel Top Prototype

Stainless steel wire mesh screens with 10 µm openings were cut down to the appropriate circular shape and diameter to fit the top of one of the glass jar sizes used for sample storage in the Shielded Cells. A plastic jar top was modified by drilling a 1.5-2.0 inch diameter hole in the center of the top. The mesh screen was placed on top of the glass jar and the modified top was attached such that the screen was fixed in position across the top of the vessel. A second piece of stainless-steel screen with a large diameter opening (>2 mm) was cut to the appropriate circular shape and diameter to fit the top of the glass jar. This second screen was inserted into the plastic top against the stainless-steel wire mesh sheet to serve as a support. The 10 µm screen was observed to provide moderate resistance to air flow but did not allow water to pass through under gravity force over a 15-minute period. Photographs of the prototype are provided in Figure 3-2 and Figure 3-3.

Figure 3-2. 10 µm stainless-steel mesh screen attached to the top of a 1-gallon glass jar.

Figure 3-3. 10 µm stainless-steel mesh screen attached to the top of a 1-gallon glass jar (view from underneath).

3.3 Preparation of the Supported Paraffin Sheet Vessel Top Prototype

Thin paraffin sheets (~1 mm thickness) were ordered and cut to the appropriate circular shape and diameter to fit the top of one of the glass jar sizes used for sample storage in the Shielded Cells. A plastic jar top was modified by drilling a 1.5-2.0 inch diameter hole in the center of the top. The paraffin sheet was inserted into the underside of the modified top. A piece of stainless-steel screen with a large mesh diameter (>2 mm) was cut to the appropriate circular shape and diameter to fit the top of the glass jar. This screen was inserted into the plastic top against the paraffin sheet to serve as a support for the paraffin. The modified top containing the paraffin and support screen were attached to the glass jar. A photograph of the prototype is provided in Figure 3-4.

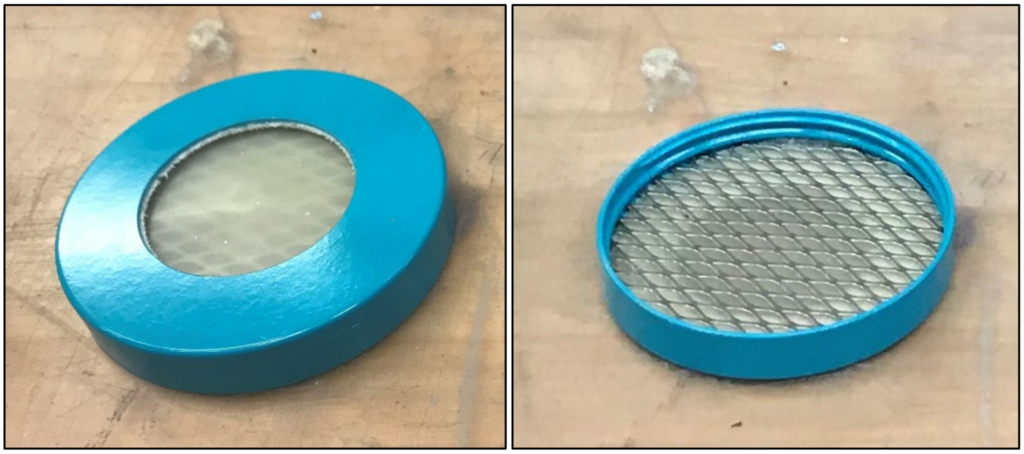

Figure 3-4. Supported paraffin sheet vessel top prototype.

3.4 Preparation of Cast Paraffin Plate Vessel Top Prototype

A plastic jar top was modified by drilling an ~1.5 inch diameter hole in the center of the top. Paraffin wax was melted and cast into the top to form a thick (several millimeters) layer of paraffin on the bottom surface of the top such that the opening in the top was sealed with wax. A photograph of the prototype is provided in Figure 3-5.

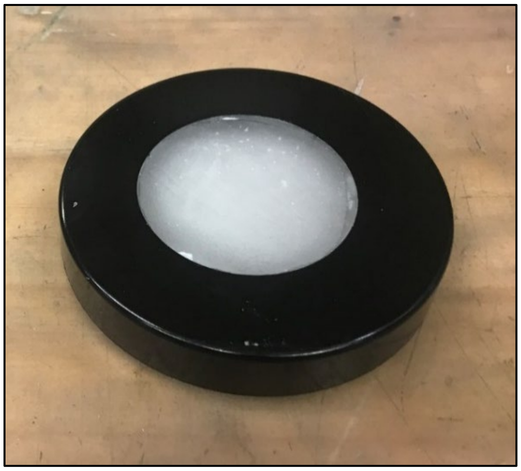

Figure 3-5. Cast paraffin plate vessel top prototype.

3.5 Preparation of Cast Paraffin Plug in Swagelok Bulkhead Vessel Top Prototype

An approximately 1-inch long plug of paraffin wax was cast into a stainless-steel Swagelok bulkhead fitting. A photograph of the prototype is provided in Figure 3-6. A plastic jar top was modified by drilling a hole in the center of the top and the fitting was attached (not shown in the photograph).

Figure 3-6. 3.5 Cast paraffin plug in Swagelok bulkhead vessel top prototype.

3.6 Preparation of Cast Alloy Plug Vessel Top Prototype

A plastic jar top was modified by drilling an ~1 cm diameter hole in the center. A sample of Field's Metal eutectic alloy was melted in warm water and cast into the top to form a plug of alloy in the opening of the top such that the opening was sealed. A photograph of the prototype is provided in Figure 3-7.

Figure 3-7. Cast alloy plug vessel top prototype.

3.7 Preparation of Cast and Machined Alloy Sheet Vessel Top Prototype

A sample of Field's Metal eutectic alloy was heated and melted in warm water in a beaker to form a thin sheet of metal across the bottom of the beaker. After cooling, the metal sheet was removed from the beaker and machined to the appropriate diameter to fit across the top of a glass jar. The sheet was placed on the top of the jar and a modified plastic top with a hole was used to attach the alloy to the jar. Photographs of the prototype are provided in Figure 3-8 and Figure 3-9.

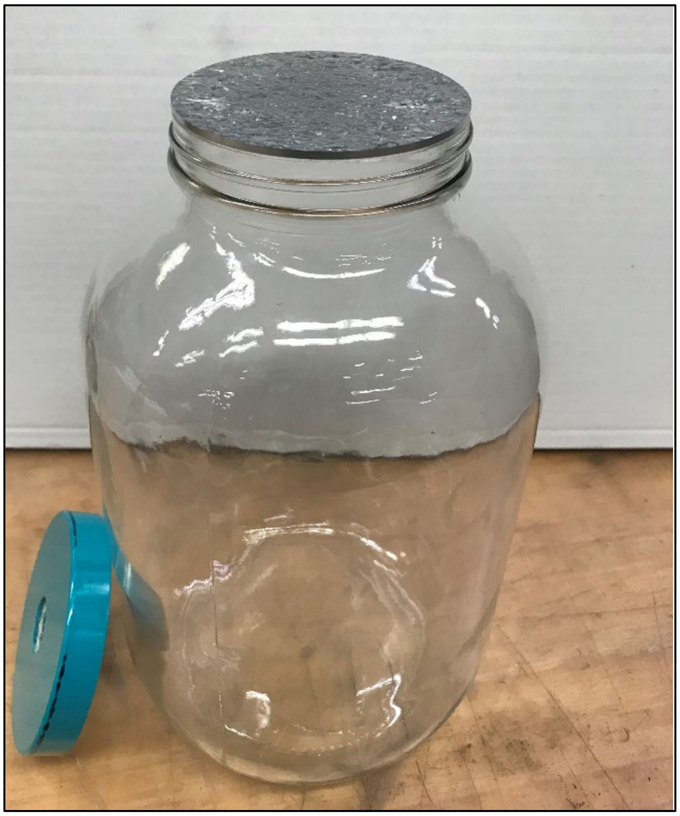

Figure 3-8. Machined alloy sheet vessel top prototype on a 1 gallon jar.

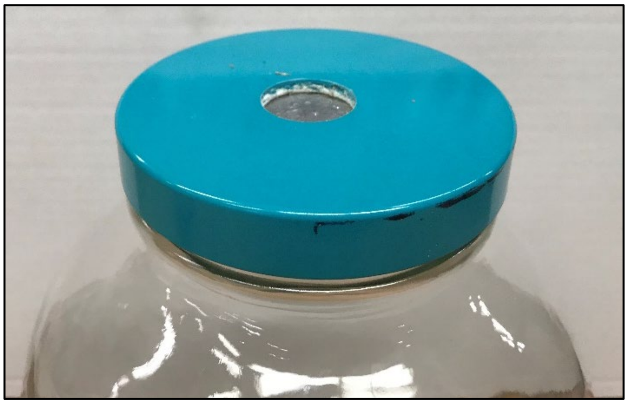

Figure 3-9. Machined alloy sheet vessel top prototype on a 1-gallon jar (second view).

3.8 Laboratory Testing of the Eutectic Alloy

3.8.1 Alloy Melting Evaluations

To confirm that the eutectic alloy (Field's Metal) would melt prior to sample boiling, a glass stand was prepared to hold a disc of alloy in position above a 100 mL beaker containing water. A photograph of the beaker and stand are provided in Figure 3-10. Testing was conducted using a 21.9 g sample of the alloy that was formed into the shape of a flat disc by heating in warm water in the bottom of the test beaker. After cooling and removal of the water, the disc could be removed by inverting the beaker and gently tapping the beaker on a leather work glove laid out on the bench top. A photograph of the alloy disc is provided in Figure 3-11. The goal was to form a flat disc ranging from 1-2 mm in thickness that would fit on the beaker stand. There were typically some gaps in the disc after hardening, but that was not believed to significantly affect the test results.

Two types of tests were performed with the apparatus. 50 mL of water were added to the beaker for all tests. The first test type was intended to represent a fire that engulfs the entire vessel such that similar temperatures occurred across the entire bottle height. This was conducted by preheating an oven with a front view window to temperatures of 115 and 160 °C in two separate tests. The two different preheating temperatures were intended to create different heating rates for the test vessel. After oven preheating, the beaker with water, the stand, and the Field's Metal disc were placed in the oven and thermocouples were placed in the water and in the air near the alloy disc. The beaker was placed on an insulating pad to minimize heat transfer directly to the bottom of the beaker from the lower metal surface of the oven. A photograph of the sample vessel in the oven is provided in Figure 3-12. The oven door was closed and the temperature reading of each thermocouple was recorded periodically while the alloy disc was monitored for signs of melting. During the melting process the alloy typically quickly fell into the bottom of the beaker where it was immersed in the water. Since the water was below the melting point of the alloy for the oven tests, the partially melted metal quickly hardened. The tests were completed by continuing to monitor the water temperature in the oven until the alloy was observed to melt again. This was done to confirm the melting point of the alloy. After the metal melted, the beaker was removed from the oven and refashioned (by manually swirling the beaker) into a disc as the water cooled so that the alloy disc could be used for subsequent tests.

The second melting test type was intended to represent the (perhaps unlikely) scenario in which the bottle is heated non-uniformly from the bottom in a fire. In these tests, the vessel was heating from the bottom with a hot plate. The first test was conducted with no cover to decrease heat losses to the atmosphere through the open vessel top. A photograph of this test configuration is provided in Figure 3-13. The second test was conducted with a loose aluminum foil cap to decrease heat losses from the vessel top. The water temperature was monitored in these tests until the water boiled or until the alloy melted, whichever occurred first.

3.8.2 Alloy Corrosion Evaluations

Pellets of Field's Metal were prepared by melting a sample of alloy in water in a beaker on a stir plate and then pouring the alloy into a second beaker filled with cool water in such a manner that small semi-spherical pellets formed. 2-3 pellets weighed approximately 1 g. For initial tests, ~1 g samples of alloy were placed in polymer bottles along with 10 mL of either 0.1 M HNO_3, 0.1 M NaOH, or 1.0 M NaOH. The solution

Figure 3-10. 100 mL glass test vessel with alloy disc stand.

Figure 3-11. Flattened disc of Field's Metal formed in the bottom of the test vessel.

Figure 3-12. Alloy test vessel in the oven.

Figure 3-13. Alloy test vessel on a stir plate.

pH values were determined using pH paper prior to testing. The alloy samples were weighed, transferred to the bottles containing the solutions, and allowed to stand at ambient temperature for 2.9 days without agitation. A photograph of the alloy samples and bottles prior to solution contact is shown in Figure 3-14 below. Note the shiny appearance of the alloy surface in each pellet.

After completion of the first set of contact tests, additional tests were conducted in the same manner using mixtures of nitric and formic or nitric and glycolic acids. The acid concentrations used for testing were based on SRAT and SME products from SRNL simulant testing provided in **Table 3-1**. The target nitric acid concentration was 0.0001 M which should produce a solution pH near 4. The target formic acid concentration was 2.7E-04 M and the target glycolic acid concentration was 7.4E-05 M. These concentrations were expected to produce solutions with a pH near 4 and nitric:organic acid mole ratios similar to the SRAT/SME products. However, since these tests were scoping in nature and these acids were prepared on the 100 mL scale, a single drop of each organic acid was added to the vessel during preparation. This resulted in elevated concentrations of the organic acids relative to the targets and higher nitric:organic acid mole ratios than the targets. The pellets were contacted with the acids for 3.01 days.

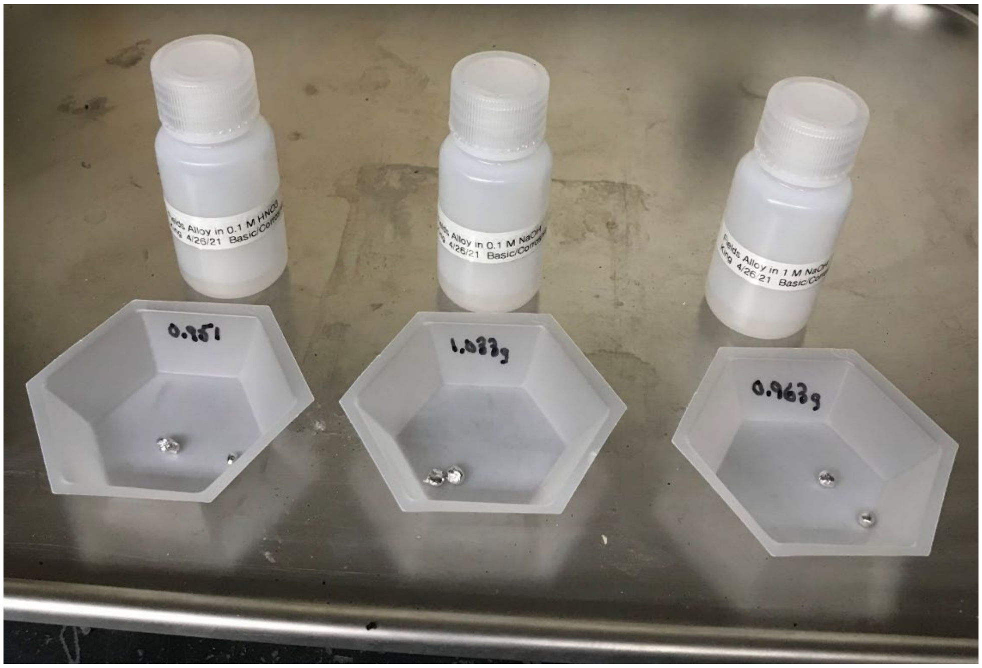

Figure 3-14. Corrosion test samples prior to contact with 0.1 M HNO_3 (left), 0.1 M NaOH (middle), and 1.0 M NaOH (right).

Table 3-1. Nitric/Formic and Nitric/Glycolic Acid Ratios for SRAT/SME Products From SRNL Simulant Testing.

Reference	Flowsheet	HNO_3:HCOOH or $HNO_3/HOCH_2COOH$ mole ratio		pH	
		SRAT	SME	SRAT	SME
SRNL-STI-2016-00281[4]	Nitric-Formic	0.37	0.35	4.0	---
SRNL-STI-2016-00319[5]	Nitric-Glycolic	1.3	1.6	4.7	4.4

4.0 Results

4.1 Fabrication and Evaluation of Vessel Lid Prototypes

Various Vessel Lid Prototypes were prepared as described in Section 3.0. A photograph of the various prototypes is provided in Figure 4-1. Based on the prototypes, it was decided to conduct testing using Field's Metal alloy to determine whether the alloy would melt before water in the same test vessel would boil.

Figure 4-1. Vessel Lid Prototypes.

4.2 Testing and Evaluation of Field's Metal Eutectic Alloy for Use as a DSA Compliant Vessel Lid

4.2.1 Alloy Melting Evaluations

Four tests were conducted under different conditions to evaluate Field's Metal as a material for DSA Compliant vessel lid construction to determine the time required for melting relative to the time required for water boiling in the same vessel. All tests were conducted using the same test vessel, stand, and alloy disc shown in Figure 3-10.

Two tests were conducted in an enclosed oven with a sight window. In Test #1, the oven was preheated to ~115 °C and the beaker test vessel was placed on an insulating pad on the oven floor. The temperature of the water in the beaker and the air in the oven was monitored as the temperature increased and the alloy disc was monitored for signs of melting. The data for Test #1 is provided in Table 4-1. The alloy was observed to melt rapidly after 6 minutes in the oven at an air temperature of 110 °C and a water temperature of 47.8 °C. At this time the entire disc fell into the water at once as shown in Figure 4-2, indicating that a top fashioned out of this material would catastrophically fail under these conditions. At the time that the alloy melted, the temperature of the water in the beaker was 52.2 °C below the boiling point of water. A second test (Test #2) was conducted at a higher heating rate by preheating the oven to a higher temperature of ~160 °C. The test data is provided in Table 4-1. In this case, the metal was also observed to melt and quickly fall into the beaker, but the melting occurred after only 3 minutes when the water temperature was 49.3 °C (50.7 °C below the boiling point of water). The air temperature in the oven at the time of alloy melting in Test #2 was 163 °C. Tests 1 and 2 which were conducted in the oven on an insulating pad are representative of an engulfing fire where the entire sample bottle is exposed to the same elevated temperature. Given the heating characteristics demonstrated for the Field's Metal and the glass beaker in this test, it is expected that even more rapid heating of the container in a fire would produce the same failure of the metal alloy long before boiling of the water occurs in the glass container. (Note: Reactions between the melted alloy and waste sludge slurries in the bottom of storage vessels during a fire have not been studied, but such reactions are not expected to contribute greatly to risk presented by the fire itself.)

Table 4-1. Data Collected During Field's Metal Testing in the Oven.

Test #	Oven Preheat Temp. (°C)	Heating Time (min.)	Water Temp. (°C)	Air Temp. (°C)	Observations/Comments
1	115	1	29.6	85	---
		2	33.4	98	
		3	37.0	104	
		4	40.3	107	
		5	43.7	104	
		6	47.8	110	alloy melted and fell into beaker
Alloy remelting water temperature following Test #1			62-64	---	initial melting on edges at 62 °C; then complete melting at 64 °C confirmed by removing the vessel from the oven (see Figure 4-2)
2	160	1	38.9	137	---
		2	45.7	159	
		3	49.3	163	alloy melted and fell into beaker
Alloy remelting water temperature following Test #2			60.7	---	initial indication of melting
			64.0		almost completely melted; upon mixing all material melted

Figure 4-2. Oven Test #1: Left photo - melted alloy disc collapsing into beaker at a water temperature of 47.8 °C; Right photo - remelted alloy after heating water to 64 °C.

After Tests 1 and 2, the alloy disc melted and fell into the beaker of water which, in each case, was at a temperature below the alloy melting point. As a result, the alloy resolidified. The vessel was left in the oven after each test to determine the melting point of the alloy as the temperature increased while immersed in water. This condition was expected to represent the actual alloy melting point. As shown in Table 4-1, initial indication of melting was observed from 61 to 62 °C in the two tests with confirmation of complete melting at 64 °C. Confirmation of melting was accomplished by removing the beaker from the oven and observing the physical form (liquid versus solid) of the alloy sample as shown in Figure 4-2. Melting of the alloy immersed in water is representative of a scenario where the storage bottle is toppled over and laying on the side.

Additional tests were subsequently conducted on a hot plate to represent the (perhaps unlikely) situation where the bottom of the container is heated faster than the top. Non-uniform vessel heating is not discussed as part of the DSA revision, but it was evaluated during testing to determine the alloy performance under this condition. For Test #3, the vessel was placed on the hot plate and the temperature was monitored as the water warmed and approached the boiling point. The data from this test is provided in Table 4-2. As indicated in the table, the alloy disc was observed to melt in Test #3 after 9 minutes just as the water was about to boil at a temperature range from 96 to 110 °C. Photographs of the alloy during initial and after complete melting in Test #3 are provided in Figure 4-3 and Figure 4-4, respectively. It was difficult to determine the exact temperature when melting occurred in this test. This test is conservative relative to a sealed sample bottle of a similar size since heat is lost from the top of the vessel because it is an open vessel and heated water vapor escapes. As a result, the alloy disc is expected to heat up and fail faster for a tighter sealed container.

Table 4-2. Data Collected During Field's Metal Testing on the Hot Plate.

Test #	Heating Time (min.)	Water Temp. (°C)	Observations/Comments
3*	2.0	40.5	---
	4.0	49.7	
	6.0	66.5	
	7.0	78.8	
	8.5	96.0	
	9.0	96-100	portion of alloy melted and fell into beaker just as water began to boil
4*	3.0	72.3	---
	4.5	92.8	first drop of melted alloy observed in beaker bottom
	4.5-5.0	95.4	more alloy melting
		98.0	almost all alloy on bottom of beaker
	5.0	99.0	all metal melted in beaker bottom

* Test #3 included no covering to reduce heat loss; Test #4 included an aluminum foil cap over the vessel top and the alloy disc (see Figure 4-5)

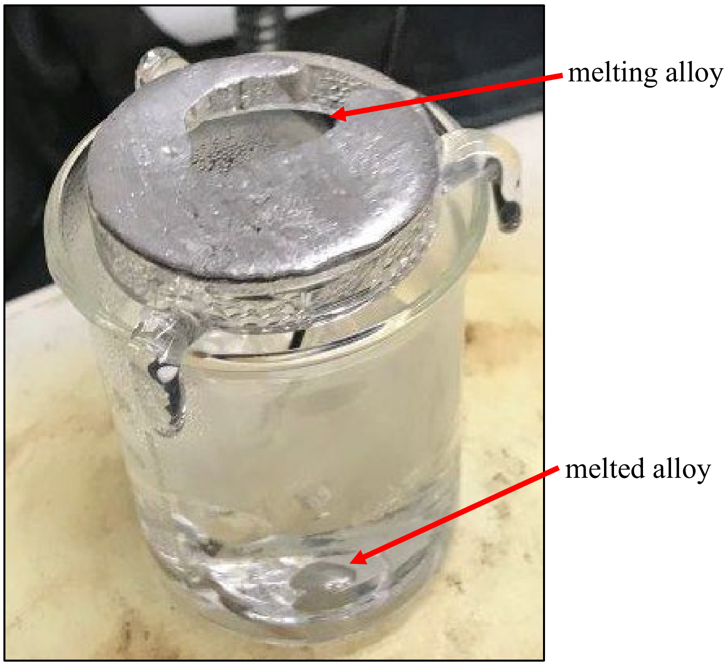

Figure 4-3. Alloy disc melting at 96 °C during uncovered hot plate Test #3 (no top foil covering).

Figure 4-4. Melted alloy in beaker at 100 °C during uncovered hot plate Test #3 (no top foil covering).

An additional test (#4) was conducted on the hot plate, but in this case an aluminum foil cap was placed over the top of the vessel and the alloy disc, as shown in Figure 4-5. Data collected during this test is provided in Table 4-2. In this test, the temperature increased more rapidly as expected due to the addition of the aluminum foil. Initial alloy melting was observed after 4.5 minutes of heating when the water temperature was 92.8 °C and melting was complete before the water began to boil.

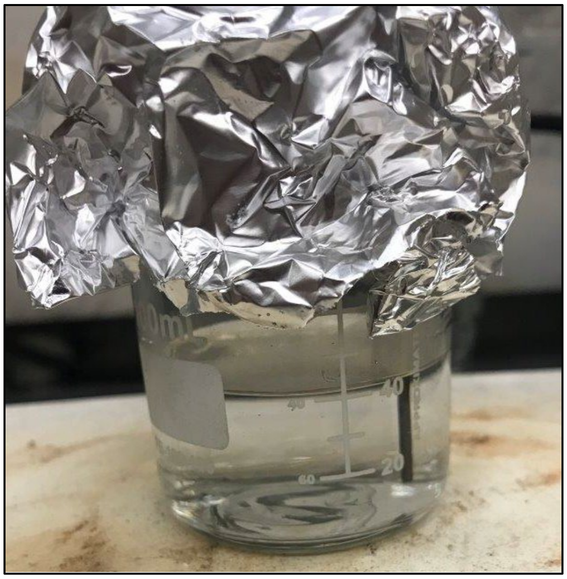

Figure 4-5. Alloy disc vessel during covered hot plate Test #4 (Al foil covering).

4.2.2 Alloy Corrosion Evaluations

Due to the fact that some metal components of Field's Metal Alloy are known to dissolve in acids and bases, initial scoping contact tests were conducted using ~1 g samples of Field's Alloy and 10 mL of either 0.1 M HNO_3, 0.1 M NaOH, or 1.0 M NaOH. Visual observations of the samples at the end of the 3-day contact period indicated that some alloy corrosion and possibly some dissolution had occurred. However, all of the pellets were similar in shape to the original pellets, indicating that catastrophic physical failure of the alloy would not be expected on a short time scale (days). The surfaces of all alloy beads were discolored to some degree with a coating of gray or black oxide. Some surfaces (presumably those adjacent to the bottoms of the bottles during contact) were still shiny. The pellets that had been placed in nitric acid were the most discolored. A photograph of the bottles containing the test solutions immediately following contact and following removal of the pellets is provided in Figure 4-6. The nitric acid solution appeared to be slightly yellow or brown in color. Note how some surfaces of the pellets are still shiny in appearance while others are not. An additional photograph of the alloy pellets following acid contact is provided in Figure 4-7. Close inspection of the photograph appears to indicate that pitting of the surface had occurred. Masses and volumes of the solutions and alloy pellets before and after contact are provided in

Table **4-3**. No mass loss was observed for the pellets immersed in NaOH solutions, but significant mass loss was observed for the pellets immersed in nitric acid at pH 1.

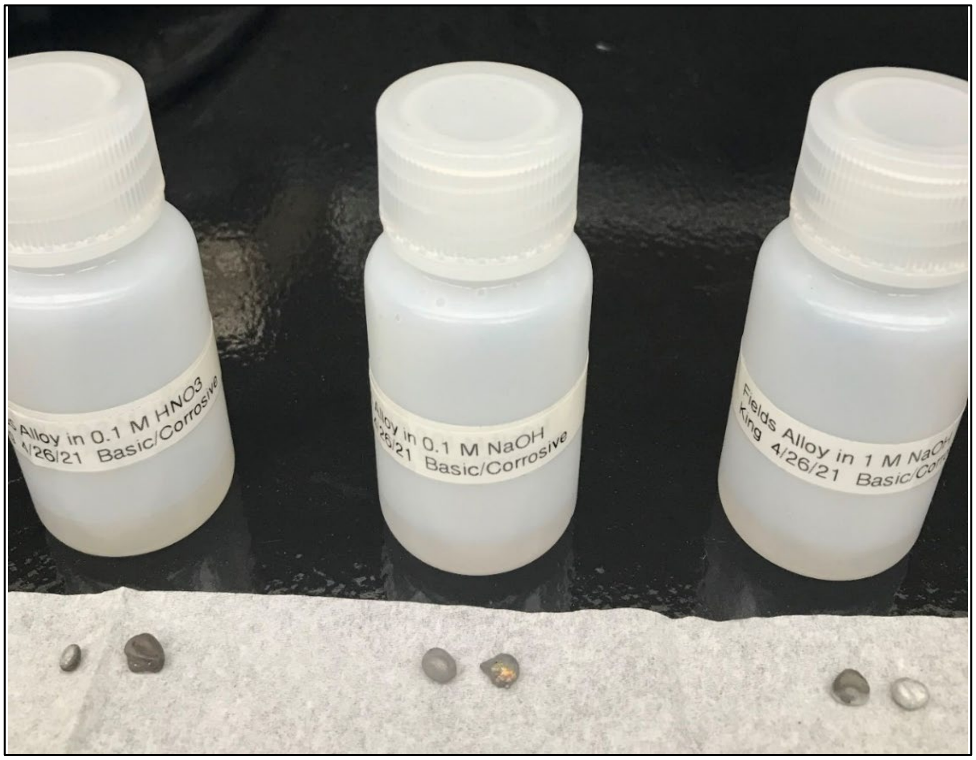

Figure 4-6. Contact solutions and alloy corrosion test samples following contact with 0.1 M HNO_3, 0.1 M NaOH (middle), and 1.0 M NaOH (right).

Figure 4-7. Corroded Field's Metal alloy pellets Following 0.1 M HNO_3 contact.

Table 4-3. Field's Metal Alloy Nitric Acid/Sodium Hydroxide Contact Test Data.

Reagent	0.1 M HNO_3	0.1 M NaOH	1.0 M NaOH
Calculated/Measured pH	1	13	14
mL	10		
g alloy initial	0.951	1.033	0.963
Contact Time (days)	2.86		
g alloy final	0.916	1.033	0.963
% mass loss	3.7	0.0	0.0
Visual Observations	surface corrosion and pitting, yellow/brown liquid	surface corrosion, clear liquid	surface corrosion, clear liquid

Nitric acid solutions with a pH of 1 are more acidic and corrosive that most samples requiring storage. Typical acidic samples in the SRNL shielded cells are the final products from DWPF Slurry Receipt Adjustment Tank (SRAT) and Slurry Mix Evaporator (SME) testing. Nitric and formic acids are currently used to process waste in DWPF. Typical products from this testing have a pH near 4 and contain both nitric and formic acid. The DWPF process will change to glycolic acid reductant in the near future. The final product of SRAT and SME processing using this flowsheet is typically also near pH 4 and the solutions are typically a mixture of nitric and glycolic acids.

As a result, additional contact tests were conducted with nitric/formic and nitric/glycolic acid mixtures in a manner similar to the previous corrosion tests. A photograph of the samples following the 3-day contact is provided in **Figure 4-8**. Data for these tests is provided in **Table 4-4**. In contrast to first contact tests with higher concentrations of nitric acid and with basic solutions, the pellets from these tests were very shiny in appearance and appeared to be cleaner than they were at the start of the test. No mass loss was observed for either sample indicating that no corrosion had occurred in these solutions.

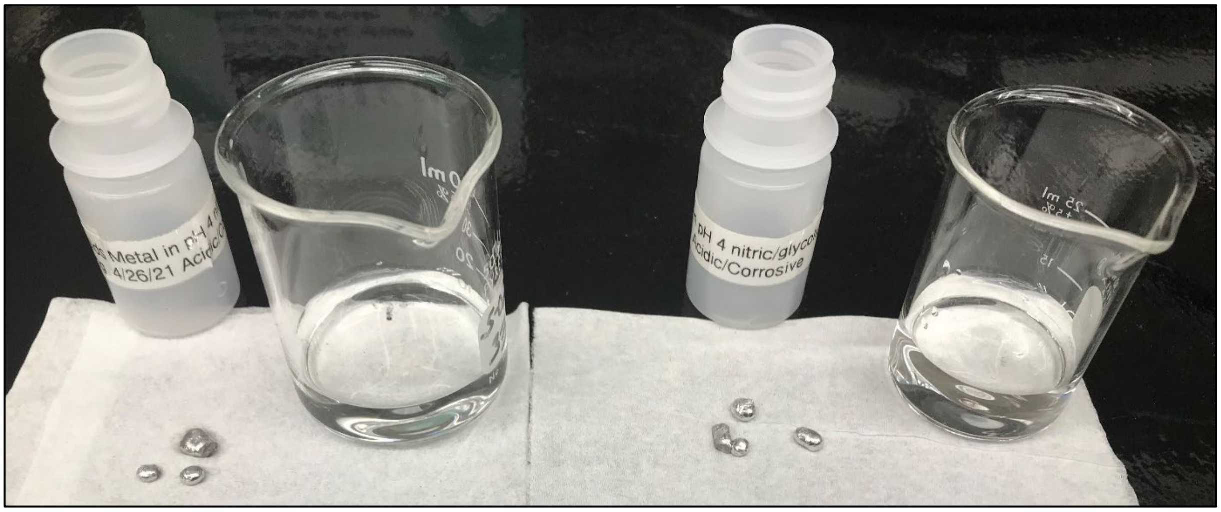

Figure 4-8. Corrosion test samples following contact with pH 4 nitric/formic acid solution (left) and pH 4 nitric/glycolic acid solution (right).

Table 4-4. Data from Nitric/Formic and Nitric/Glycolic Acid Field's Metal Alloy Corrosion Tests.

Contact Solution	$HNO_3/HCOOH$	$HNO_3/HOCH_2COOH$
HNO_3 (M)	~0.00011	~0.00014
$HCOOH/HOCH_2COOH$ (M)	~0.0042	~0.0044
HNO_3:HCOOH or $HNO_3:HOCH_2COOH$ mole ratio	2.2	2.7
Calculated/Measured pH	3.5-4.0	
mL	10	10
g alloy initial	0.8372	0.9768
Contact Time (days)	3.01	
g alloy final	0.8375	0.9768
% mass loss	0.0	0.0
Visual Observations	clear solution, no visible alloy corrosion, shiny pellet surfaces	

4.3 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in Manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. This report and calculations within received a technical review by design verification (Manual E7 2.60, Section 5.3). Data are recorded in the electronic laboratory notebook (ELN) system as notebook/experiment number A2341-00117-17.

5.0 Discussion

5.1 Discussion of Field's Alloy Test Results

The melting tests confirmed: 1) the reported melting point of the alloy, 2) that a top fashioned from this material should melt creating an open atmosphere in the vessel headspace prior to sample boiling under moderate and fast heating rates, and 3) that nonuniform heating of the bottle from the bottom also results in melting of the alloy and production of an open atmosphere prior to boiling. Based on the results, neither an engulfing fire with standing or toppled bottles or a fire producing localized heat at the vessel bottom would result in flashing spray conditions.

These tests are conservative for several reasons. The alloy passed the tests using water as the boiling liquid for comparison to the alloy, although the liquid phase in most radioactive samples will contain dissolved salts. The boiling points of salt solutions are elevated relative to water and therefore would boil later than the water. The test vessel was open to the atmosphere such that heat transfer to the bottle top from the heated liquid below was less effective than would be expected for a closed system. Because an open system was used and the sample was heated in an oven for some tests, the liquid inside the vessel was less thermally isolated than would be the case for a closed system with an insulating vessel medium and therefore was easier to heat. For the tests conducted using a hot plate, where heat was applied directly to the glass vessel bottom, the test configuration represents an extreme localized application of heat which is not likely, though it may be possible, in a fire incident.

5.2 Other Considerations Regarding Field's Metal Alloy Use as a DSA Container Lid

Field's Metal contains indium, bismuth, and tin with indium being the primary metal and bismuth being a secondary metal component. These are not RCRA metals and therefore can be disposed as routine contaminated solid waste from the Shielded Cells. All three of these metals can be activated by radiation sources. The primary naturally occurring isotope of indium is ^{115}In (95.6% abundance) and ^{113}In is the remaining natural isotope. Both isotopes can be activated by fast neutron sources forming metastable states.[6] ^{115}In reacts with a neutron to form ^{116m}In which decays by beta emission to excited states of ^{116}Sn with a half-life of 54 minutes. Bismuth has one primary natural isotope, ^{209}Bi, that is unstable with a very long half-life (2×10^{19} years). Polonium (as ^{210}Po) can be manufactured by bombarding ^{209}Bi with neutrons in a nuclear reactor. This produces ^{210}Bi which then decays by beta decay to ^{210}Po with a five-day half-life. ^{210}Po undergoes alpha decay to stable ^{206}Pb with a half-life of 138 days. Astatine (as ^{213}At) can also be produced by bombarding ^{209}Bi with alpha particles. ^{213}At decays back to ^{209}Bi by alpha decay in 125 nanoseconds. Tin has multiple (10) stable natural isotopes and one trace unstable isotope (^{126}Sn with a half-life of $2.3\text{x}10^{5}$ years). Various tin isotopes can be activated in a radiation field.[7] Depending upon the location and duration of vessel storage in the Shielded Cells, the alloy could become activated. Since the cells are shielded, activation primarily impacts personnel dose during lid disposal which is minimized by radiological surveys and procedures implemented during handling. It is possible that lead, a RCRA metal, could be formed from the alloy due to bismuth activation. However, these activations and conversions are expected to occur at trace levels in the Shielded Cells environment and are expected to have small influence on vessel disposal and personnel dose. However, the possibility of alloy activation should be taken into consideration when disposing of the vessel lids. It is assumed that the vessel lids will be reused for various samples and frequent disposal will not be required.

It is also possible that the radiation field in the Shielded Cells could promote chemical oxidation of the metals. This effect can be evaluated by periodic observation of the tops after initial entry to determine the condition.

Given the low melting point of the alloy, it is possible that storage of the vessels near the halogen cell lights could result in melting, failure, and sample contamination. This should also be evaluated upon initial use in the Shielded Cells to determine appropriate storage locations for the vessels which are not directly adjacent to the lights.

Bismuth metal will dissolve in dilute nitric acid and indium metal will dissolve in acids and concentrated base. There was concern that incidental sample contact with the alloy lids could lead to sample contamination with In, Bi, or Sn due to partial dissolution of the alloy. The initial issued version of this document (Revision 0) recommended that chemical evaluations be conducted to confirm that contact with typical acidic and basic supernates does not result in catastrophic failure of the alloy lid or in sample contamination. As a result, simple corrosion evaluations were conducted with a range of acidic and basic solutions.

Based on the corrosion test results, Field’s Metal Alloy is subject to surface corrosion in basic solutions ranging from pH 13 to 14 based on visual observations, but no measurable mass loss was observed over a three day contact period using a liquid:solid phase ratio of 10 mL/g. In contrast, dilute (0.1 M) nitric acid contact promotes both corrosion and slow dissolution of Field’s Metal Alloy pellets under these conditions at a rate of approximately 1 wt. % per day. This corrosion rate indicates that sample contamination with In, Bi, and Sn could occur for bottles that are inadvertently knocked over in the shielded cells and left in this condition for several days. No indication of catastrophic failure of the alloy was observed in this time period that would lead to loss of sample containment. The degree to which nitric acid vapors will corrode the Field’s Metal over extended time periods during storage of upright acidic samples has not been tested. Corrosion would likely occur to some degree but might not result in sample contamination since direct liquid/solid contact has not occurred in this case. Acidic samples with a pH ≤1 may require an alternative lid design. This solution pH is lower than typical samples requiring storage in the shielded cells. One possible design that might be used for samples such as this after appropriate testing and approvals is a vessel containing a Field’s Metal alloy disc protected and sealed by a layer of paraffin sheet positioned between the alloy and the bottle top. Additional corrosion tests conducted with more prototypic solutions containing mixtures of nitric acid with either formic or glycolic acid revealed that these solutions are not corrosive to the alloy.

6.0 Conclusions, Recommendation, and Path Forward

Based on the testing conducted, it is recommended that glass jars with tops constructed out of low-melting Field’s Metal eutectic alloy (such as the ones prepared from discs in this work) be added to the list of liquid DSA containers for use in the SRNL Shielded Cells facility for the storage of radioactive liquid sludge slurry samples. These vessels have been shown not to be susceptible to flashing spray release of radionuclides during a fire event resulting from pressurization of the bottles and superheating of the liquid contents. Field’s Metal melts near 62 °C and can be cast and machined into desired shapes. Vessel lids have been prepared from this material that were shown to melt forming of an open vessel prior to water boiling. To avoid sample losses from evaporation it may be necessary to include a rubber o-ring gasket (probably around the edges of the disc) to seal against the plastic vessel top. Glass bottles with tops similar to those described in this report will be proposed for addition to the list of DSA containers for liquids (sludge slurries). Paraffin wax may be considered as a vessel top material of construction as well, but additional evaluations of this material would be needed including radiation stability.

Field’s Metal Alloy is subject to mild surface corrosion in caustic solutions, but no mass loss occurred after 3 days of contact. Field’s Metal Alloy also does not corrode significantly in nitric/formic and nitric/glycolic acid mixtures at pH 4 which are typical of SRAT/SME test products requiring storage. As a result, there are no corrosion or structural stability concerns for the alloy lids while storing typical samples in the SRNL Shielded Cells.

7.0 References

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