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SRPPF Aqueous Recovery System Sorbent Testing

W. C. Jolin

K. L. Broadwater

September 2022

SRNL-STI- 2022-00433, Revision 0

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EXECUTIVE SUMMARY

This study details preliminary testing of 7 inorganic sorbents for the solidification of the surrogate SRPPF aqueous recovery system liquid excess material of 4M sodium nitrate. Sorbents were subject to various mixing methods to incorporate sodium nitrate solution including static, rotating, and in situ paddle mixing. Paddle mixing was found to be the most effective mixing technique, while simple static tests were also successful, though only for some of the sorbents. Setting tests were performed to ensure that the sorbent sequestered the liquid without release through a conical paint filter. Recommended set times ranged from near immediate to 7 days. The set mixtures were investigated further using ultra-centrifugal liquid release testing, thermogravimetric analysis, and visual microscopy to understand the mechanism by which the sorbent sequestered the liquid. Most sorbents seem to incorporate liquid by sorbing it onto and into the sorbent particles, while Drierite®, anhydrous calcium sulfate, created a crystal structure that bound the surrogate liquid. Overall, four sorbents are recommended for continued testing: Aquaset II, Aquaset IIG, Drierite®, and Spill-X-A.

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LIST OF ABBREVIATIONS

ARS	Aqueous Recovery System
LLC	Liquid Loading Capacity
rpm	Revolutions per minute
SRNL	Savannah River National Laboratory
SRPPF	Savannah River Plutonium Processing Facility
TGA	Thermogravimetric Analysis
WAC	Waste Acceptance Criteria
WIPP	Waste Isolation Pilot Plant

1.0 Introduction

The current Savannah River Plutonium Processing Facility (SRPPF) Aqueous Recovery System (ARS) flow sheet proposes to solidify the liquid effluent using a grout formula that was developed and tested for the Waste Solidification Building process.[1] The Portland-cement based mixture results in a high pH solidified form which may not be acceptable to the Waste Isolation Pilot Plant (WIPP) in large quantities. As such, the SRPPF project is investigating the use of sorbents to solidify the liquid effluent.

The ARS liquid effluent would be added to one or a mixture of the solidification agents found in Table 4-4 of the Basis of Knowledge for Evaluating Oxidizing Chemicals in TRU Waste for disposal to WIPP.[2] A preliminary assessment has screened out solidification agents that do not meet criteria or are expected to significantly increase excess material volume.[3]

Seven candidates have been identified for small scale testing and evaluation as the solidification agent [3]:

1. Absorb-N-Dry
2. Aquaset II
3. Aquaset II-G
4. Zeolite (10 A pore)
5. Zeolite (4 A pore)
6. Drierite®
7. Spill-X-A

The study details preliminary testing of the ability of these sorbents to solidify the surrogate SRPPF aqueous excess material stream of 4M sodium nitrate.[1,3] Primary analysis of the mixing requirements, set time, and characteristics of the solidification agent and surrogate mixture was performed.

2.0 Methods

2.1 Sorbents and Loadings

Absorb-N-Dry, manufactured by Balcones Minerals, was acquired from HEXA Containment. Aquaset II (powder) and Aquaset IIG (granular) was provided by the manufacturer, Fluid Tech LLC. Zeolite 4A and 10A were obtained in the pellet form (1.6 mm diameter) as molecular sieves 4A and 13X from Sigma Aldrich. A powdered form of zeolite 4A was also from Sigma Aldrich. Drierite® (granular, 20-40 mesh, non-indicating) was from W.A. Hammond Drierite Company. Spill-X-A was from Ansul. Each sorbent was used as received. Pictures of the sorbents are provided in Appendix A.

The Basis of Knowledge for Evaluating Oxidizing Chemicals issued by WIPP defines measured liquid loading capacity (mL liquid/g sorbent) and the weight percentage of oxidizing chemical allowed. This weight percent corresponds to the dry weight of oxidizer, in this case sodium nitrate, that, when mixed with the sorbent, does not exhibit the hazardous characteristic of ignitability due to oxidizing properties and accounts for the desiccating salt environment of the WIPP disposal units.

These allowable weight percent oxidizer and liquid loading were compared regarding 4M sodium nitrate to determine which of these properties was limiting for each of the seven sorbents. To facilitate the comparison, a liquid loading capacity (LLC) was determined for each weight percentage oxidizer.

$$LLC = \frac{fw}{(1-fw)mo}$$

Where *fw* = the allowable weight fraction of oxidizer (weight percentage/100)
mo = mass of oxidizer per volume of liquid (4M sodium nitrate: 0.340 g/mL)
All sorbents were limited by the liquid loading capacity, and, as such, all testing was performed at or near measured loading capacity (97-100%) per the Basis of Knowledge.

Table 2-1. Material and a comparison weight percentage of oxidizing chemical allowed and liquid loading capacity for the sorbents in this study

Sorbent	**Material**	**Weight % oxidizing chemical allowed***	**Liquid Loading Capacity (ml/g)***	**LLC based on W% for 4 M sodium nitrate**
Absorb-N-Dry	Bentonite or Fullers Earth	28	0.683	1.14
Aquaset-II	Sepiolite	45	1.44	2.41
Aquaset-IIG	Sepiolite	36	1.33	1.65
Zeolite 10A	Zeolite 13X	44	1.12	2.31
Zeolite 4A	Zeolite 4A	35	1.15	1.58
Drierite®	Calcium Sulfate	29	0.843	1.20
Spill-X-A	Magnesium oxide 60-100% Attapulgite 7-13% Sodium carbonate 5-10%	33	0.605	1.45

*From ref [2]

2.2 Mixing Methods

2.2.1 Static Tests

Static tests involved simply combining the sorbent and sodium nitrate solution and determining if, and when, liquid incorporation occurred. Liquid first tests were performed by adding the nominal 4M sodium nitrate solution to a 50 mL centrifuge tube then adding the corresponding mass of sorbent. Time to liquid incorporation, and if homogeneity would be reached, was determined visually. Solid first tests were performed in the same manner with the solids being placed in the tube before the liquid.

2.2.2 Mixer Tests

Mixer tests were performed using a Caframo overhead mixer outfitted with a flat blade. Solid first preparations were performed to simulate a drum preloaded with sorbent brought into the facility. Solid first testing also avoided the mixing blade interfering with solid addition into the vessel. Sorbent solids were placed in a 30 mL digestion vial and the mixing blade was pressed into the solids until it was about a quarter of an inch from the bottom of the vessel (Figure 2-1). The mixer was started and then the corresponding mass of sodium nitrate solution was added to the vial. The mixer was run at 100 revolutions per minute (rpm). Time to liquid incorporation and if homogeneity was reached were both determined visually.

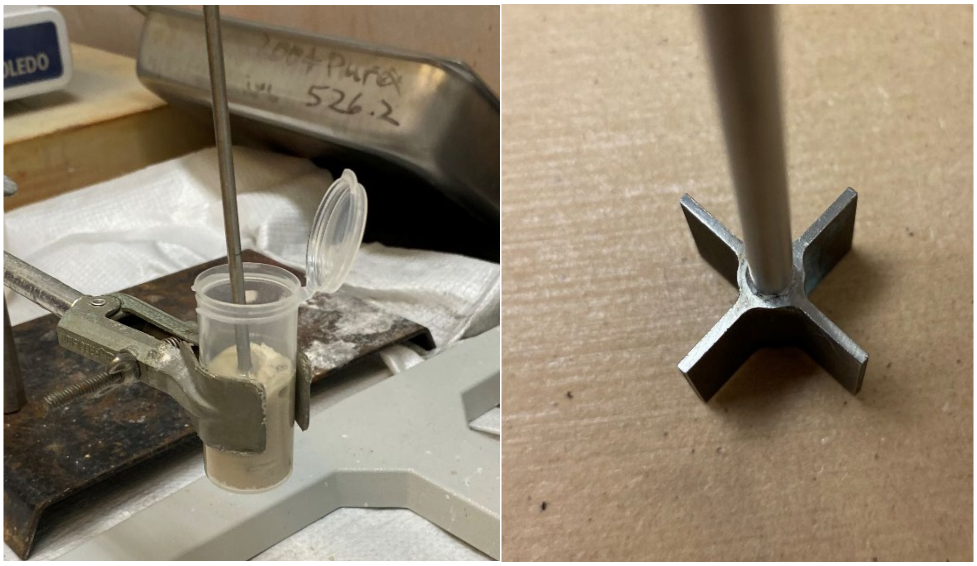

Figure 2-1. Mixer set up and flat blade.

2.2.3 Rotator Tests

Rolling and end over end mixing tests were performed on a Global scientific GTR-HD rotator set to 50 rpm. Solid first tests were performed by adding sorbent solid to a 50 mL centrifuge tube, adding the corresponding mass of sodium nitrate solution, then placing the centrifuge tube on the rotator and starting rotation. The rotator has attachments that vertically (end over end) and horizontally (rolling) rotate the tubes around the axis. Generally, the mixer took 45 sec to reach 50 rpm. Time to liquid incorporation and if homogeneity was reached were both determined visually. Liquid first tests were also performed for roller mixing in the same manner with the liquid being placed in the tube first.

2.3 Setting/Paint Filter Tests

The amount of water that can still flow out the of the solidified surrogate excess material after allowing the sorbent/sorbent sodium nitrate mixture to set for various periods of time was performed using a paint filter test (EPA SW 9095A [4]). A conical paint filter (226 µm nylon mesh) was placed on a funnel over an Erlenmeyer flask and the mixture of sorbent and sodium nitrate solution was placed inside the filter (Figure 2-2). Liquid that flowed, by gravity, through the filter into the Erlenmeyer flask within a 5-minute period was considered to be flowable liquid representative of the observable liquid content in the WIPP Waste Acceptance Criteria (WAC).[5] Further visual inspection determined if liquid wet the paper portions of the paint filter. Mixtures were created for each of the sorbent and sodium nitrate solution pairs per the liquid loading, as detailed in section 2.1. These mixtures were manually mixed until homogeneity was achieved (physical shaking of the bottle) and then either immediately placed on the filter (within 5 minutes of mixing) or allowed to sit for 24 or 48 hours. Mixtures with flowable liquid or those that had observable wetting of the filter after 48 hrs, were further tested at 96 hrs (4 days) and 168 hrs (7 days) as needed. Each time interval was performed in duplicate for each sorbent. Set tests were performed in closed containers to minimize effects from changes in ambient humidity. Laboratory temperature was not monitored, but would be expected to have limited impact on setting in the closed containers. Mixing methods described in section 2.2 were not utilized for mixing to ensure all sorbents reached homogeneity allowing for direct comparison.

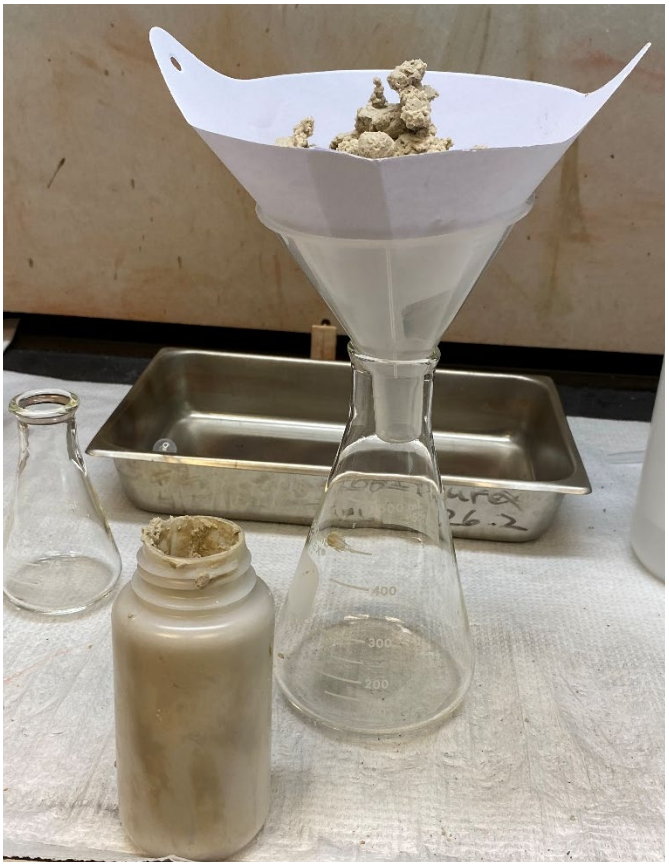

Figure 2-2. Paint filter/setting test setup with Aquaset II.

2.4 Bulk Density

Once the set time was determined with the paint filter testing, dry and mixture bulk density was determined for each sorbent. Dry bulk density was determined for the sorbents before contact with sodium nitrate in duplicate by filling a 100 mL graduated cylinder with the sorbent and weighing the cylinder before and after sorbent addition.

For Aquaset II, Aquaset IIG, and Spill-X-A, mixture bulk density was determined by adding sodium nitrate solution to sorbent at the defined liquid loading capacity and physically mixing until homogeneity was reached. The mixture was then allowed to set for the recommended set time determined with the paint filter testing (see section 3.2) The mixture was then used to fill 30 mL digestion vials. Volume of the 30 mL vials was verified with > 18.2 MΩ deionized water in quintuplicate. Bulk density was determined by net weight of the sorbent sodium nitrate mixture and volume of the vials in quintuplicate.

For Drierite®, the approach was modified to account for the solid nature of the surrogate solidified excess material form. Immediately after mixing the liquidous (pre-set) mixture of Drierite® and sodium nitrate, it was poured into three graduated cylinders and allowed to sit for the 7-day set time recommended in section 3.2. Mixture bulk density was determined before and after the allotted set time. Bulk density was determined by net weight of the sorbent/sodium nitrate mixture and the volume marking of the graduated cylinder, which were confirmed with > 18.2 MΩ deionized water.

Absorb-N-Dry mixture bulk density was not determined as the mixture did not set within 7 days (section 3.2), and observable liquid would leach from the bottom of the surrogate solidified excess material (section 2.2.1).

2.5 Ultra-Centrifugal Liquid Release Testing

Ultracentrifugation was performed to understand how strongly liquid was bound in the set surrogate solidified excess material. Sorbent/sodium nitrate solution mixtures were allowed to set for the recommended set time per determined with the paint filter testing (see section 3.2). An aliquot of the mixture (15- 20g) was placed on Whatman 42 fast filter paper in a sample holder of an UFA centrifuge apparatus which consists of the sample holder and a liquid collection cup. The apparatus is set up so that as centrifugal force is applied, the pore water from within the sample can flow through the filter and a hole in the sample holder into the collection cup. The sample was centrifuged at 2700 rpm for 5 minutes which corresponded to a full body force of 50 psi, the same pressure used in the liquid release testing for hazardous waste under overburden pressure.[6] The full body force is not analogous to the surface pressure used in liquid release testing, but it does provide insight in to how strongly the liquid is retained in the matrix. The weight of the liquid released from the material was determined by mass difference in the collection cup. Liquid mass loss percentage was calculated from the liquid loading in the mixture and the liquid released following ultracentrifugation. Mixture mass loss was calculated from the liquid release and original mass of the mixture added to the sample vessel.

2.6 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) on a Netzsch TG 209 F1 Iris was used to determine adsorbed water content. Specimen mass loss was monitored upon heating to 300 °C at 10 °C/min. Initial mass loss curves under 150 °C corresponded to evaporation of free and adsorbed water. Subsequent mass loss was attributed to the evolution of bound water.

2.7 Visual Microscopy

Low magnification images were taken using a Keyence® Laser Confocal Microscope (LCM, VK-X3000)

2.8 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.

3.0 Results and Discussion

3.1 Mixing Method Testing

3.1.1 Static Tests

Static testing revealed that most sorbents require some sort of mixing to reach homogeneity, though some to all of the liquid can be incorporated without mixing.

Absorb-N-Dry quickly incorporates the sodium nitrate solution (less than a minute, Table 3-1) reaching a homogeneous state. However, following the original incorporation, the liquid seems to leach out of the bottom on the surrogate solidified excess material, wetting the sides of the container. This leaching was further tested/quantified with the set/paint filter testing (see section 3.2). No further mixing method test was performed for Absorb-N-Dry as the liquid incorporation occurred too rapidly to warrant further testing. There was no difference between liquid first and solid first testing for Absorb-N-Dry.

Aquaset II incorporated the sodium nitrate solution rather slowly. Liquid incorporation occurred more quickly with liquid first tests compared to solid first (Table 3-1). Neither method reached homogeneity, as dry portions of the sorbent were still visible. A higher liquid loading may be feasible. Mixing would be required for the use of Aquaset II based on the slow time to incorporate the solution and lack of homogeneity.

Aquaset IIG incorporated the sodium nitrate solution much more quickly compared to Aquaset II. The sodium nitrate solution was incorporated into the sorbent in under 1 minute for liquid first testing and just over 4 minutes for solid first static testing (Table 3-1). Homogeneity was reached without mixing.

Drierite®, when first incorporating the sodium nitrate solution, becomes liquidous, producing a small amount of heat, likely due to the hydration of the anhydrous calcium sulfate. Liquid incorporation and homogeneity are reached quickly (within one minute, Table 3-1).

Spill-X-A was the only sorbent that did not incorporate all liquid under the liquid first testing as a film of liquid was present at the top of the mixture. Solid first static testing did incorporate all liquid after almost an hour of contact (Table 3-1). The difference between solid first and liquid first tests may have arisen from differences in wetting curves: the liquid first sample partially wets more of the solid decreasing the affinity of liquid for the sorbent while solid first tests provided layers of dry material wicking the sodium nitrate further into the solid. Homogeneity was not achieved with either method, and dry areas were visible. Mixing was deemed necessary for Spill-X-A

Zeolite pellets were originally chosen for this study as powders are difficult to work with, pour, and handle. The zeolite pellets reacted violently with the sodium nitrate solution producing heat and gas. The pellets may have been pressed using an organic binder that reacted with the oxidizing sodium nitrate. These samples did not incorporate all of the liquid. A powder form of zeolite 4A was then tested and heat was still produced and the tube was hot to the touch. No gas was formed with contact with the powder. Zeolites can produce heat when becoming hydrated [7] which may have been the case for the zeolite powder and may have contributed to the reaction observed for the pellets. This preliminary test with zeolite powder did not set for over three weeks with the mixture easily flowing inside the centrifuge tube. As such, between the large amount of heat produced and lack of setting, zeolites were not tested further.

Table 3-1. Visually determined time to liquid incorporation and if homogeneity was achieved for mixing methods. Values are average of the triplicate tests and error the standard deviation.

	Static: Liquid First		**Static: Solid First**		**Mixer**		**End Over End**		**Roller: Solid First**		**Roller: Liquid First**	
Sorbent	Time to Liquid Incorporation (min)	Homogeneity Achieved	Time to Liquid Incorporation (min)	Homogeneity Achieved	Time to Liquid Incorporation (min)	Homogeneity Achieved	Time to Liquid Incorporation	Homogeneity Achieved	Time to Liquid Incorporation (min)	Homogeneity Achieved	Time to Liquid Incorporation + (min)	Homogeneity Achieved
Absorb-N-Dry	0.10 ± 0.06	no[1]	0.06 ± 0.01	no[1]								
Aquaset II	26.5 ± 4.7	no[2]	125 ± 3.4	no[2]	1.51 ± 0.21	no[2]	14.7 ± 6.35	no[2]	50.82 ± 9.19	no[2]	19.0 ± 17.6	no[2]
Aquaset IIG	0.86 + ± 0.07	yes	4.21 ± 1.50	yes	0.16 ± 0.02	yes	4.13 ± 1.31	yes	ND	no	1.1 ± 0.0	yes
Drierite®	0.62 ± 0.46	yes	0.93 ± 0.51	yes	0.13 ± 0.02	yes	34.3+ ± 1.69	yes	ND	no	3.9 + ± 2.0	no[2]
Spill-X-A	ND	no[2]	57.12 ± 13.03	no[2]	0.20 ± 0.08	yes	41.9 ± 7.14	no[2]	52.50 ± 4.20	no[2]	31.3 ± 4.8	no[2]

ND: Not determined/Did not incorporate all liquid
1: Visible wetness on bottom of vessel
2: Dry/unreacted areas of sorbent present

3.1.2 Mixer Tests

Paddle/blade mixing of the sorbent as the liquid is added provides a marked improvement in time to liquid incorporation for all sorbents tested. Aquaset II incorporated the sodium nitrate solution in under 2 minutes (Table 3-1). Aquaset II did not reach homogeneity likely due to the mixer blade sitting just above the bottom of the vessel. All liquid in the mixed portion of the sorbent was incorporated resulting in a dry area of sorbent near the bottom of the vial. When removing the mixer blade, the paste-like Aquaset II would adhere to the metal, making the reuse of the mixer difficult in a production setting, lending to a lost paddle design. Aquaset IIG, Drierite®, and Spill-X-A incorporated all liquid quickly and reached homogeneity (Table 3-1). Overall, in situ mixing with a blade/paddle was the quickest and most effective mixing technique investigated in this study.

3.1.3 Rolling and End-Over-End Tests

Overall rolling and end over end mixing provided little benefit compared to static tests. Roller tests with both solid and liquid first demonstrated little ability to create a homogenous mixture with only Aquaset IIG achieving homogeneity. Liquid first roller testing performed better than solid first as Aquaset IIG and Drierite® did not incorporate all liquid for the solid first tests. The liquid and sorbent would become separated with no contact between the solid and liquid as rolling continued. Aquaset II formed a barrier between the liquid which morphed into a ring as mixing progressed. Liquid incorporation was dependent upon the collapse of this barrier/ring and was not consistent across replicates. Rolling is not recommended as means to mix the sorbent and excess material solution.

End-over-end testing performed better than the rolling method. Small increases in time to liquid incorporation compared to static testing were seen for Aquaset II, Aquaset IIG, and Spill-X-A (Table 3-1). Drierite® did not incorporate liquid as quickly as static tests. The wet solids set and created a solid layer between the dry sorbent and liquid, making mixing more difficult, though homogeneity eventually was reached. Homogeneity was also reached for Aquaset IIG.

3.2 Set Time

The WIPP WAC states observable liquid shall be less than 1 percent by volume. As a conservative measure, the volume percent of flowable water of the liquid added to the mixture, neglecting the additional volume from the sorbent, was determined. The percentage of flowable liquid from the paint filter tests varied greatly across sorbents with most eventually being able to sequester all liquid (Table 3-2). Aquaset II immediately sequestered all liquid where no flowable water was observed at any set time. Interestingly, Aquaset IIG, the granular version of Aquaset II, does not have flowable liquid after 24 hrs. but seemingly settles, releasing some liquid from the surrogate solidified excess material at 48 hrs. This liquid was observed at the top of the surrogate solidified excess material. This liquid is no longer present at 96 hrs and a 96 hr set time is recommended. For Drierite®, which, after being mixed with the sodium nitrate solution, becomes liquidous, immediately set and could not be tested. At 24 hrs., Drierite® became a solid mass and breaking up of the material into chunks with a spatula was required. This breakage tended to release liquid from the surrogate solidified excess material and whether this liquid would be present without the breakage could not be determined. At 48 hrs., liquid flowed from only one of the duplicate paint filter tests for Drierite®. At 96 hrs., a small amount of water (not quantifiable) was on top of both duplicates of the Drierite® and, as such, a 7-day set time is recommend at this time. Further testing (radiography, or other in situ liquid determination) may be able to reduce this amount of time. Spill-X-A mixture visibly wetted the paint filter after 24 hrs. and a 48 hrs. set time is recommended. A high percentage of liquid, relative to the other tested sorbents flows from the Absorb-N-Dry mixture even after setting for 7 days and, as such, Absorb-N-Dry is not recommended as a primary sorbent.

Table 3-2. Flowable/observable liquid percentage at various set time intervals and recommended set time for each sorbent. Values are average of the duplicate tests and error is the standard deviation.

Sorbent	Initial	24 hrs.	48 hrs.	96 hrs. (4 days)	168 hrs. (7 days)	Recommended Set Time
Absorb-N-Dry	25.5% ± 0.4%	21.4% ± 0.8	14.5% ± 1.7%	15.3% ± 4.3%	10.0% ± 0.1%	N/A
Aquaset II	None	None	None	NP	NP	Immediate
Aquaset IIG	5.5% ± 1.8%	None	0.8% ± 0.4%	None	NP	4 day
Drierite®	NP	3.3% ± 0.1%	2.0%[1]	None[2]	None	7 day
Spill-X-A	0.9% ± 1.0%	None[3]	None	NP	NP	2 day

1 – Only one duplicate released water
2 – Small, unquantifiable, amount of liquid on top of solidified excess material
3 – Visible wetness on the paint filter

3.3 Mixture Characterization

3.3.1 Visual Observation

Aquaset II begins as fine powder and, once set, forms a paste that adheres to both the vessel, utensils, and the mixer blade. No visible wetness is seen in the surrogate solidified excess material. (Figure 3-1) Once in place, the Aquaset maintains its form unless physically manipulated.

Figure 3-1. Aquaset II Mixture

Aquaset IIG, the granular form of Aquaset II also forms a paste, though it is more visibly wet compared to the powder form of the sorbent (Figure 3-2). The surrogate solidified excess material does not adhere to the sides of vessel. Some movement is observed when maneuvered and the solidified excess material does not fully maintain its shape.

Figure 3-2. Aquaset IIG Mixture

Drierite® forms a hard monolithic solid once set. Liquid is released from the monolith when broken apart to remove it from the vessel. The set material breaks into rigid pieces (Figure 3-3). No observable water is seen on the side or top of the vessel once the monolith is formed and set.

.

Figure 3-3. Drierite® Set Solid Piece.

Spill-X-A forms a mixture with the consistency of wet sand once set. Little to no wetness is visible and the surrogate solidified excess material is mailable but maintains its shape (Figure 3-4).

Figure 3-4. Spill-X-A Mixture.

3.3.2 Bulk Density

Dry and mixture bulk density of the sorbents are reported in Table 3-3. For Drierite, which required modification to determine the bulk density, there was some liquid above the surrogate solidified excess material after allowing it to set in a graduated cylinder. The meniscus of this liquid touched the top of the sorbent/liquid mixture and was concluded to be the result of surface tension in the small surface area of the cylinder. This liquid (1.5 to 2 % of total liquid in solidified form) was discarded before the bulk density was determined. The pre-set and set density were nearly identical for Drierite.

Table 3-3. Dry and mixture bulk density of the sorbents. Values are average replicate tests and error is the standard deviation.

Sorbent	Dry Bulk Density (g/mL)	Set Mixture Bulk Density (g/mL)
Absorb-N-Dry	0.81 ± 0.02	N/A
Aquaset II	0.98 ± 0.004	1.45 ± 0.02
Aquaset IIG	0.85 ± 0.01	1.47 ± 0.02
Drierite®	0.96 ± 0.01	1.66 ± 0.01 (1.64 ± 0.01)[1]
Spill-X-A	1.24 ± 0.02	1.84 ± 0.02

1: Value in parenthesis is the pre-set (wet) density of the liquidous mixture

3.3.3 Ultra-centrifugal Liquid Release & TGA

The mechanism by which liquid is sequestered by the sorbent provides important insight into the release of liquid from the solidified excess material. Liquid will likely be incorporated into the sorbent by three different mechanisms: 1) sorbed onto the surface of the particle or into particle pore structure, 2) chemically incorporated into the crystal structure of the sorbent and 3) free water bound within the bulk solidified material by adhesive forces (note: free water is only a description of the sequestration mechanism and does not constitute observable liquid).

Microscopy, ultra-centrifugal release, and TGA were performed on the sorbent mixtures to begin to understand these mechanisms. For TGA, initial mass loss curves under 150 °C corresponded to evaporation of free and adsorbed water. All sorbent displayed primary mass loss under 150 °C indicating that liquid is either adsorbed onto the material surface or adhesively held in the solidified material. Aquaset II, Aquaset IIG, and Spill-X-A only had single inflection in the TGA curve with one water incorporation mechanism identified. Aquaset II and Aquaset IIG are both sepiolite, a fibrous magnesium silicate mineral, which have high surface areas and narrow channels facilitating the sorption of the liquids. The mass losses of 42% and 43% for Aquaset II and Aquaset IIG respectively (Figure 3-5) are similar to the 52% and 53% water expected within the surrogate solidified excess material after accounting for the mass of sodium nitrate. Some mass is lost above 150°C though the loss mechanism is unknown. Spill-X-A is primarily magnesium oxide and attapulgite (Table 2-1) Attapulgite, another magnesium silicate mineral, sorbs liquid by similar mechanisms to sepiolite while magnesium oxide may provide further surface area to absorb the liquid. The 27% mass (Figure 3-5) loss is close to the water content 38% of the solidified form.

For Drierite®, 31% of mass is lost below 150°C with a second inflection evident corresponding to another almost 4% mass loss (Figure 3-5). Drierite®, anhydrous calcium sulfate, incorporates water into the crystal structure producing gypsum (calcium sulfate dihydrate). The removal of water from gypsum likely produced this second inflection. This incorporation into the crystal structure likely causes the initial liquidous state and reformation of the surrogate solidified excess material.

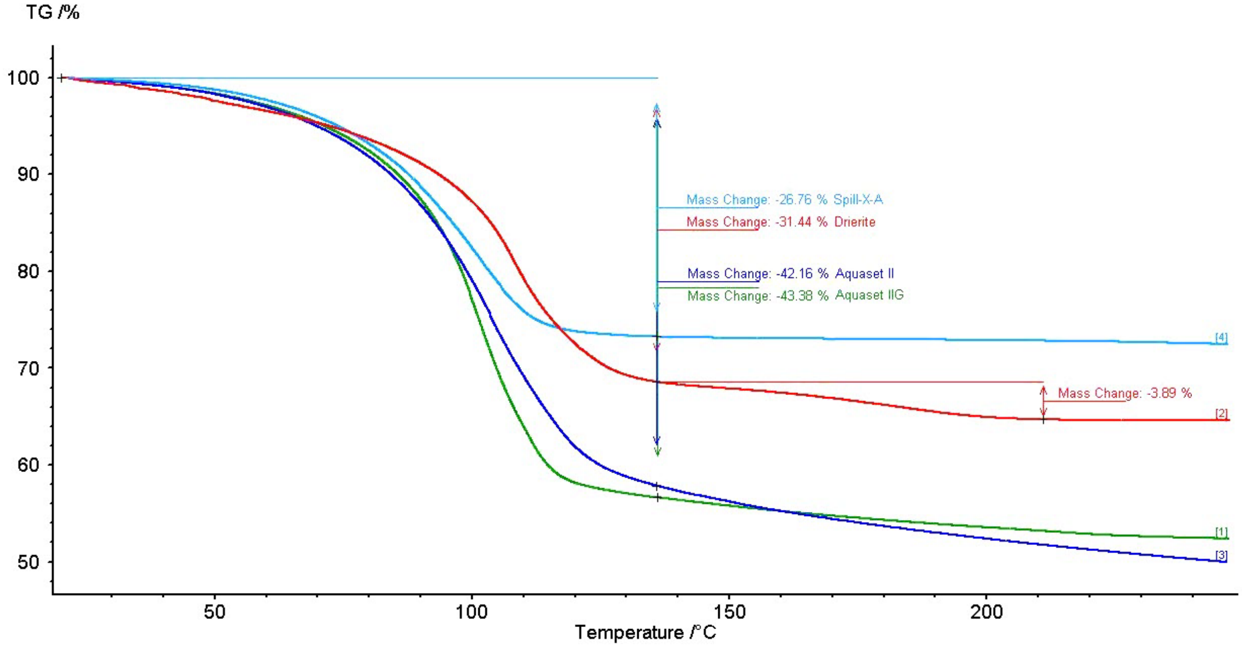

Figure 3-5. Sample weight percentage with increasing temperature during TGA analysis.

Ultra-centrifugal release analyses were performed to understand how strongly the liquid was bound within the surrogate solidified form. Comparison of centrifuged and non-centrifuged portions of the surrogate solidified excess material via visual microscopy provided further insight into liquid incorporation in the mixture. For Aquaset, over 90% of the sodium nitrate solution remained in the solidified form after centrifuging at 2700 rpm or a full body force of 50 psi (Table 3-4). Increasing the rotor speed to 4000 rpm did not increase the amount of liquid released. Visually, little change was seen for Aquaset II before and after centrifugation. Both observations support that liquid is adsorbed onto the particle, incorporated into the pore structure of the mineral, and/or the fine powder of Aquaset II increases the adhesive forces holding liquid in the surrogate solidified material. Slightly more liquid is released from Aquaset IIG with 83% of the bound liquid remaining in the surrogate solidified excess material (Table 3-4). A notable decrease in visual liquid is seen between non centrifuged and centrifuged samples suggesting that the liquid released may be less strongly bound as the particle size of the granular sepiolite increases. Powdered Spill-X-A retained 88% of the liquid (Table 3-4) with some loss of water from the surrogate solidified excess material observed through microscopy (Figure 3-9). The least amount of liquid is retained in Drierite® (31%, Table 3-4) which corresponded mass loss of 35% for the entire mixture, similar to the amount of mass loss during TGA. Microscopy revealed that after centrifugation, crystals consistent with gypsum are left behind. One hypothesis is that liquid is weakly bound between the gypsum crystals and can be pulled from the surrogate solidified material during ultracentrifugation. Such an encapsulation is consistent with the release of liquid as the solidified monolith is broken apart during the paint filter tests. Overall, Aquaset II most strongly binds the liquid in the surrogate solidified material followed by Spill-X-A, Aquaset IIG and Drierite®.

Table 3-4. Percent liquid retained in the surrogate solidified material and mixture mass loss after ultra-centrifugation. Values are average duplicate tests and error is the standard deviation.

Sorbent	Percent Liquid Retained	Mixture Mass Loss
Aquaset II	92.2% ± 0.4%	4.9% ± 0.2%
Aquaset IIG	83.0% ± 0.6%	10.5% ± 0.4%
Drierite®	30.9% ± 1.5%	34.8% ± 0.8%
Spill-X-A	88.3% ± 0.6%	1.2% ± 0.05%

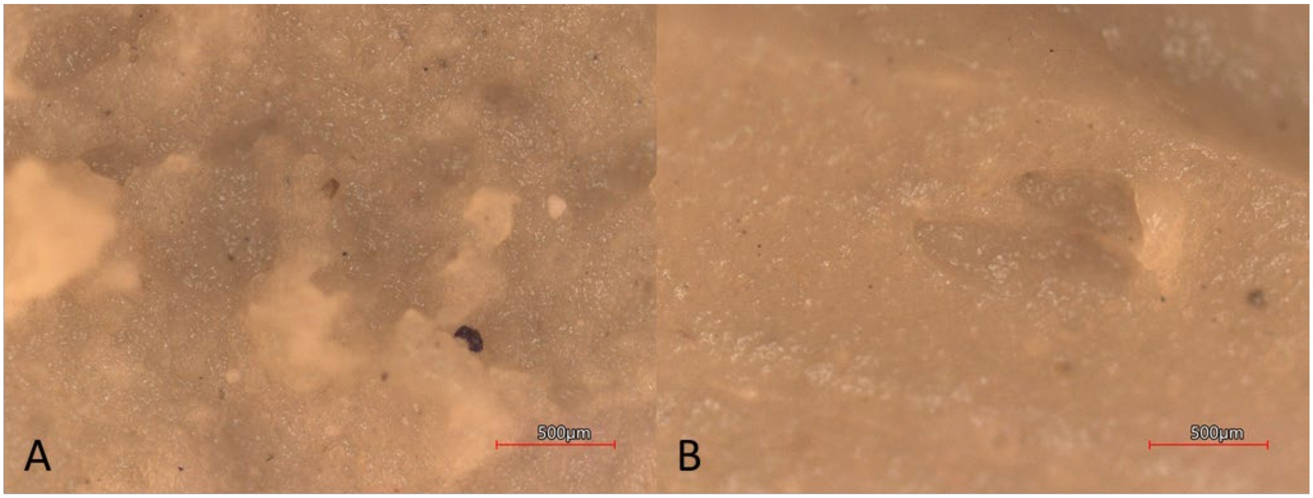

Figure 3-6. Visual microscopy Aquaset II solidified material before (A) and after centrifugation (B)

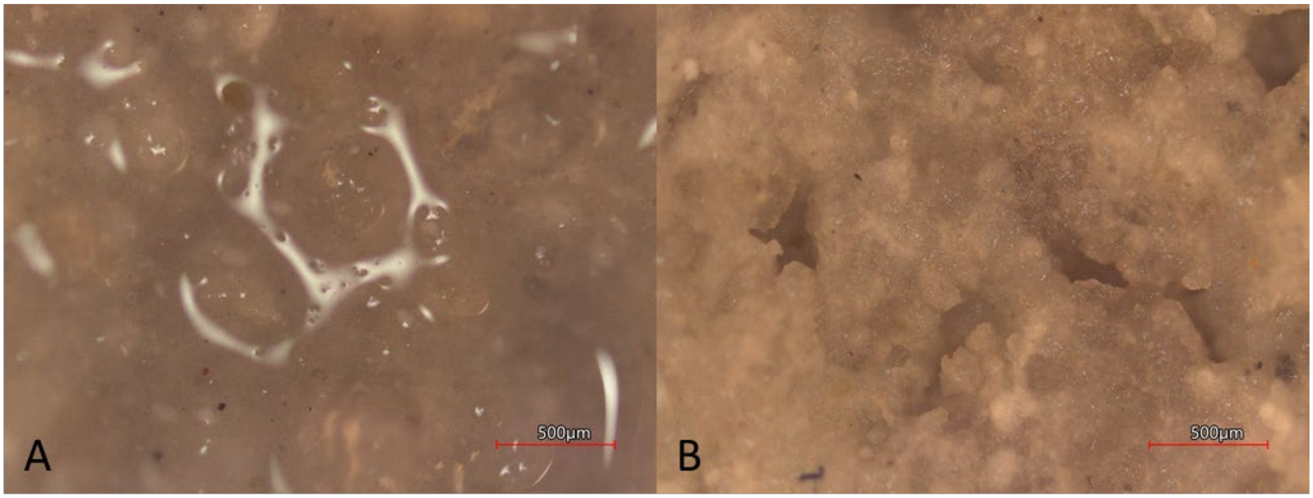

Figure 3-7. Visual microscopy Aquaset IIG solidified material before (A) and after centrifugation (B)

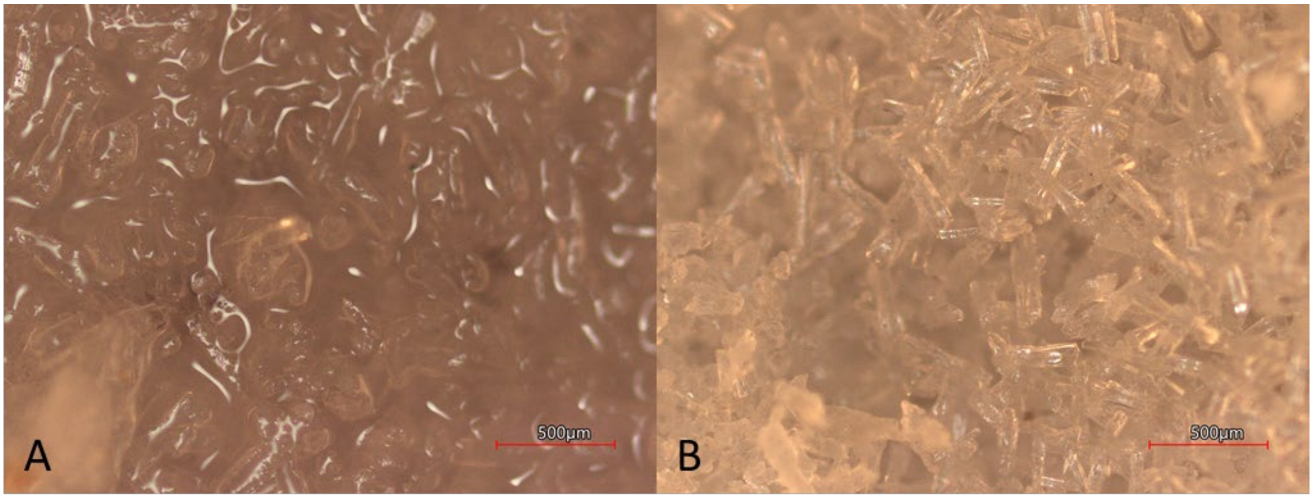

Figure 3-8. Visual microscopy surrogate Drierite® material form before (A) and after centrifugation (B)

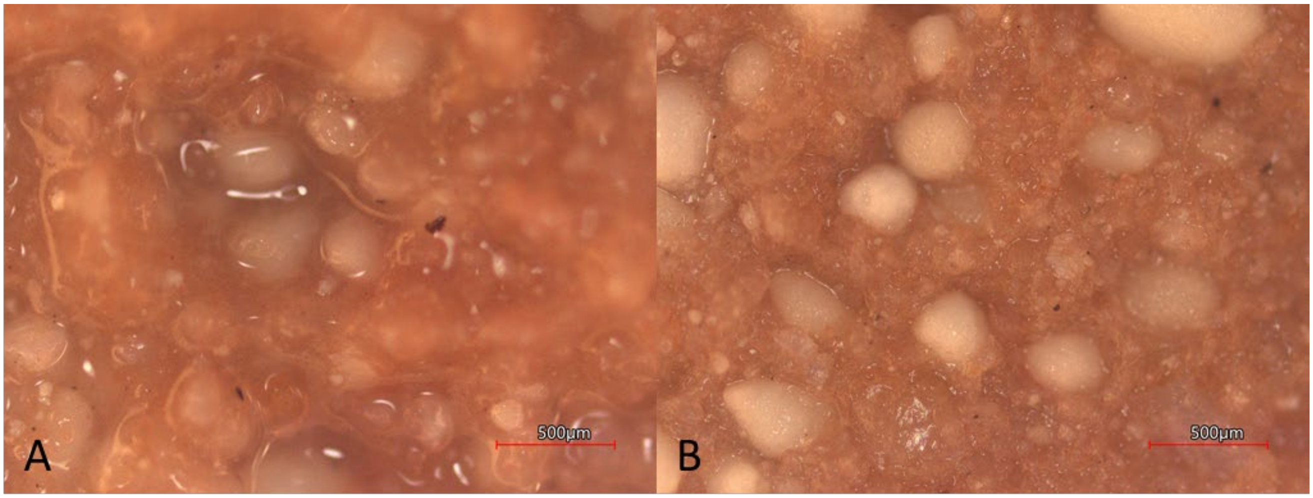

Figure 3-9. Visual microscopy of surrogate Spill-X-A material form before (A) and after centrifugation (B)

4.0 Conclusions

Four sorbents of the seven tested are promising for the solidification of the ARS liquid effluent. Of these, Aquaset II, the powdered form of Aquaset provides near immediate strong sequestration of the surrogate liquid effluent, however, may require a lost paddle or other more intensive mixing technique. Aquaset IIG can reach homogeneity without mixing but a 96 hr set time is recommended before all liquid is sequestered on and within the pore structure of the particle. Drierite® sets as gypsum, and seemingly incorporates liquid between the gypsum crystals. Drierite® was determined to require a 7-day set time, though this value may be skewed by the need to break the monolithic form apart for testing. Spill-X-A, which has the lowest liquid loading capacity of the sorbents, performed well with a 48-hr. set time but would likely require mixing. Absorb-N-Dry was ruled out as a primary absorbent at the liquid loadings defined by WIPP because liquid leached from the bottom of the mixture. However, Absorb-N-Dry may be useful in a mixture of absorbents (i.e., top coating to remove any liquid films before sealing) with its rapid incorporation of liquid. Finally, zeolites (4A and 10A) are not recommended as possible sorbents due to the heat produced during hydration of the sorbent.

5.0 Recommendations

Further testing is recommended to better categorize the performance and scale up requirements of the sorbents. Pursuant of this the following studies are recommended:

- Liquid loading capacity Tests: Set tests and mixture characterization testing for the retained sorbents at 90% loading should be performed. These tests would allow a safety factor for liquid incorporation and may quicken set times. For Aquaset II, increased capacity testing may also be beneficial.
- Other mixing methods: overall in situ mixing with a paddle/blade was the most efficient mixing techniques. However, this required the decontamination of the blade or a lost paddle design. During set and mixture characterization testing the sorbent/sodium nitrate mixture was physically shaken providing homogeneity and rapid incorporation of liquid. Therefore, closed vessel mixing may be feasible and more aggressive techniques could be tested (e.g., Acoustic or Turbula mixers).
- Full process testing: Due to time constraints mixing then allowing the mixture to set could not be tested. Therefore, further testing of the entire process to ensure the mixing method provides a surrogate solidified excess material with the required characteristics should be undertaken. Static, paddle, and end over end methods (and any other identified through the above recommendation) should be tested for mixture characteristics and reproducibility.
- Larger scale: larger scale (but not full scale) testing by using quantities and vessel scaled to the dimensions of 55-gallon drums should be performed.
- Complex excess material stream: Surrogate material to represent the expected radionuclide content should be incorporated into the surrogate effluent to understand how the each is sequestered by the solidification agents. The characteristics of the pore water over time should be determined to define radionuclide interactions with the sorbents.

6.0 References

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Appendix A. Photos of Dry Sorbents

Figure A-1. Absorb-N-Dry

Figure A-2. Aquaset II

Figure A-3. Aquaset IIG

Figure A-4. Drierite®

Figure A-5. Spill-X-A

Figure A-6. Pellet Zeolite 4A

Figure A-7. Granular Zeolite 10A (13X)

Figure A-8. Powder Zeolite 4A

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