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Savannah River Site
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**EVALUATION OF ABSORBENTS FOR COMPATIBILITY WITH
SITE GENERATED HARZARDOUS AND MIXED LIQUID WASTES**

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SUMMARY

SRS Solid Waste requested SRTC to perform a literature-based evaluation of sorbents, which are compatible with hazardous mixed waste being generated on site. Polypropylene-based materials and ground corn cob (Toxi-dry), because of their compatibility with the Consolidated Incinerator Facility (CIF) process, are the only two spill stabilization agents which are recommended for use on site (IS manual, Waste Acceptance Criteria 3.18). While ensuring minimal potential for undesired reactions between spills and spill control agents, Solid Waste wants to increase the number of site approved absorbents to give waste generators more flexibility in choosing liquid spill immobilization agents.

For simplicity, we have classified the basic types of spills expected at the site into the following three general categories: organic compound spills (pure hydrocarbons, solvents, PCB, mixed organic aqueous solutions), aqueous salt solutions and very dilute acids/bases/ organic, and concentrated acids and bases. Based on the review of available commercial literature for spill control sorbents for the three categories, we recommend the following sorbents:

- Imbiber Beads[®], Nochar[®] (A-A610 and A630) and Petroset[®] products for stabilization of petrochemicals and organic spills,
- Modified polypropylene and polyacrylate products (Quick-Solid[®], Sterego[®], Aqua-Sorb-HP[®], Universal Plus[™] and HA8010), Aqua Biber[®], Nochar-A660 and Aquaset[®] products for stabilization of aqueous spills and very dilute acids, bases and organics,
- Neutrakit-2[®]/Neutratorb[®] neutralization absorbents for some concentrated acids and caustic spills followed by stabilization of neutralized product with either Aqua Biber[®] or Nochar-A660.

The Imbiber Beads[®], and Nochar[®] products are proprietary polystyrene polymeric materials and the aqueous solution spill stabilizers are derived from various processing modifications of polypropylene and polyacrylates. Both Petroset[®] and Aquaset[®] materials are modified aluminosilicate minerals (Clays).

These polymers and modified clays are absorbents from which immobilized liquids can not be easily squeezed or leached out at room temperatures and thus are ideal for site spill control needs. However, the extent of their effectiveness in controlling large spills and producing acceptable final waste forms are dependent on several other factors and requires consultations with the product manufactures and vendors.

The EPA now requires that a procuring agency, when purchasing sorbents made from materials like polymer, inorganic and organic materials, purchase them made with recovered materials when these items meet applicable specifications and performance requirements.

Sorbent Selection Criteria.

Commercial sorbents used to control[^] or recover free liquids can act as adsorbents, absorbents or both. Absorption is defined as the retention of liquids within the molecular structure of the material and adsorption as the retention of liquids on the surface of particles/inner surface by capillary action and surface tension^{1,2}.

Adsorption materials usually have large surface areas on which the liquids are physically bound, and with uptake of the liquids there are, in general, a minimal overall volume change. Absorbents, on the other hand, because of changes in their internal structures, tend to show limited changes in volume* (swelling) when used for spill control.

The selection and application of spill immobilization agents is driven by Federal regulations, in particular, EPA's hazardous waste treatment standards/waste handling concerns^{3,4} and the waste acceptance criteria (WAC) of disposal facilities here on site. Required properties for these sorbent materials include the following⁵:

- Meet Federal, state and local regulations for eventual disposal,
- Absorb many times its own weight (low sorbent cubage factor; ratio of sorbent volume used to the liquid volume sorbed),
- Be non volatile and produce non volatile final waste forms,
- Be inert to the hazardous liquid spill to be immobilized,
- Quickly absorb free liquid waste with minimal changes in volume and density,
- Bind uniformly to aqueous and organic phases indefinitely without freestanding liquid,
- Be light weight (low weight by volume),
- Insoluble in excess hazardous spill to be immobilized.
- Must be non-toxic, non-hazardous, non-corrosive, non- pyrophoric or explosive in nature,
- Must be thermally stable and not disintegrate under normal humidity and pressures conditions,
- Final waste form, solidified or gelled matrix, must pass Toxic Characteristics Leachate Procedure (TCLP) test,
- Produce no respirable dust, such as silica dust,
- Low microbial susceptibility (non-biodegradable) including high resistance to fungal growth and
- Meet EPA -9096 test at a minimum of 20 psi in 40 to 1 ratio for aqueous matrices
(A measure of how easily the spill could be squeezed out under pressure).

[^] Sorbents are used here for spill control and not for stabilization to attain acceptable final waste forms for disposal.

* Swelling decreases in most cases with increase in ionic strength.

Site Sorbent Needs

If the liquid spill to be contained or immobilized is mixed low-level waste with low activity (radioactivity), as may be the case here on site, one other requirement, in addition to the ones enumerated above, is that the sorbent material resist radiolytic decomposition under low-level radioactive conditions. The sorbent material may also be required to be a universal absorbent, one that is capable of absorbing both aqueous and organic phases.

The site's emergency spill response goals[#] are to immobilize hazardous liquid spills with an appropriate sorbent material to restrict the spreading of the spills and thus enhance follow-up cleaning operations. Absorbent materials are preferred for site immobilization needs over adsorbent materials because of the following characteristics:

- They absorb many times their own weight.
- Immobilized liquid spills are not easily squeezed out from absorbents as a result of changes in environmental conditions (freeze/thaw), vibrations and external pressure.
- They show a minimal evaporation or leaching out of bound liquids with changes in temperature.

Although some swelling or changes in volume may be encountered when working with absorbents, it is possible to overcome this disadvantage by engineering the spill-bearing absorbent containers to accommodate or account for volume changes.

Commercial sorbents that may meet site hazardous liquid spill control needs can be classified into three categories, organic, inorganic and cross-linked hydrolyzed synthetic polymers. Most of the natural sorbents that fall in the inorganic and organic classes are mainly adsorbents, such as vermiculite and diatomaceous earth. These inorganic materials, like all adsorbents, can only hold or bind to a small amount of liquid spills.

Our emphasis on the selection of site immobilization sorbents is on the high molecular weight synthetic polymers, excluding, of course, polymers designed to degrade naturally and ones derived from biological materials. We also include modified aluminosilicates such as petroset® and aquaset® and some modified inorganic clay absorbents like Zorbite® and dehydrated organic peat like HSSSorb® and Corpex-980A/B® in this class of preferred sorbents. These materials can be formulated to be used as absorbents or adsorbents (See summary Table 4 for commercial contacts).

Polymeric Absorbents

These classes of absorbents are designed to immobilize hazardous chemicals or low level-radioactive mixed hazardous liquid including ordinary aqueous waste by providing a solid waste form, limiting surface area available for leaching, and limiting the solubility of the constituents of the waste. In some cases the polymeric materials are modified with other inorganic or organic additives, which serve as chemical bonding agents or enhance performance of final waste forms.

[#] Spill containment methods here deal only with liquid spills and slurries. It does not address the containment of gases or other phases of hazardous spills.

In general, these types of polymers meet almost all the required properties needed for spill control absorbents as outlined above. Some of the draw backs in the use of the polymers include swelling and increase in volume of the waste form produced and reduction in their abilities to resist microbial attacks and thus microbial deterioration when they are extensively modified with organic/inorganic additives. However, these short falls can be controlled by engineering polymeric absorbents to meet specific goals with the help of product manufacturers and vendors.

For spill controls, these commercial polymer-based absorbents can be classified into three main groups:

- Polymer absorbents for oils, solvents and petrochemicals
- Polymer-based universal absorbents for aqueous and organic/petrochemicals and
- Polymer-based absorbents for aqueous liquids only.

Polymeric absorbents for oils are multi-component polymers engineered to absorb a broad range of oily products from hexane, gasoline, diesel fuel, chlorinated solvents, polar materials likes acetates, ether, 2-butanone, and other low viscosity fluids. The universal absorbents are designed to immobilize spills consisting of oil in water or petrochemicals in water or vice versa.

These polymeric absorbents are commercially available in different forms ranging from particulate, boom, blanket sheet/cushion, and pillow forms. The two most referenced commercial classes of polymeric absorbents are Imbiber Beads^{TM6} and the Nochar[®] products. Both polymeric materials are polystyrene-based absorbents and their manufacturing techniques are dependent on various processing techniques to render them micro-porous. These products come in various types and are designed to immobilize from petroleum/hydrocarbon based spills, acid/pure aqueous based spills, to petroleum/non-petroleum based spills. Some of these materials can also be used to immobilize oily low-level radioactive waste⁷ and may meet EPA requirements for immobilization of compatible hazardous materials for landfills. The methods of application or using these proprietary materials can be obtained directly from the vendors or manufactures.

Commercially, there is another class of high-density polymer materials, which are modified in various ways to handle only aqueous waste and aqueous chemicals waste streams. These include commercial products such as Stergo[®], Quick-Solid[®], Aqua Sorb-HP[®], Universal PlusTM and Waste Lock[®]. These are reported by the manufacturers to meet EPA-9096 tests and have good spill-to-absorbent ratios. See Table 4 for product summary and commercial vendor information.

It is worth noting that the sorption capacities or load capacity of spills onto these absorbents varies significantly and is dependent on the types of spills to be controlled or immobilized. Vendors and manufactures will usually provide general loading capacity information.

These and other polymeric absorbents should not be exposed to oxidizing agents like ozone and bleach (See reference 9).

Modified Inorganics and Organic Absorbents.

Some classes of modified inorganic materials, especially the quarternary ammonium amine modified aluminosilicates⁸ commercially labeled PetrosetII[®] for oils and Aquaset[®] for aqueous liquids, are of interest for use on site. Since inorganic materials are less susceptible to radioactive degradation⁹, these materials are especially of interest in dealing with low-level radioactive spills on site. Commercial organic sorbents of interest include those already mentioned above. They are derived from dehydrated organic materials and as such may only be useful in treating spills containing no oxidizing agents and radioactive agents.

Cost of Absorbent Materials

Based on information provided by vendors, the polymeric products ImbibersBeads[™] and Nochar[®], in bulk form, cost an average of \$8.00 per pound. Prices per pound for the modified polypropylene and polyacrylate products average \$3.50. Petroset[®] and other inorganic sorbents, cited above as potential absorbents, tend to be significantly cheaper with prices ranging from \$1.20 to just under \$2.00 per pound. In general, the higher the quantity of material purchased the lower the cost of material per pound.

General Spill/ Absorbents Selection Guide

Tables 1, 2 and 3 provide a general guide in the matching of potential spills to absorbent materials, which could be used to contain a spill.

Column one shows a general classification of possible spills and potential liquids and wastes which could be spilled here on site. The other three columns to the right show the recommended absorbing agents. The letter "X" is used to indicate an acceptable compatible absorbing agent.

The four columns in Tables 1, 2 and 3 show absorbing agents which have been considered, based on literature search, to be suitable for use on hazardous and mixed liquid or slurry spills here on site. The information should be applied with caution, as there are factors to be considered in the use of any individual absorbent for spills and waste stabilization, such as disposal and final fate of waste form produced. These factors can not be covered within the limits of these tabulations. Also, the amount, rate and method of application of each individual absorbent in relation to the type and size of anticipated spill or waste, to a large extent, depends on the manufacturer's recommendations, which must be followed in most cases. These and other factors must be carefully considered and may call for special engineering judgement, particularly in large-scale applications. More information on each absorbent can be obtained from manufacturers.

Table1 Absorbent immobilization selection guide for hazardous/mixed waste liquid Spills.

	ABSORBENT	ABSORBENT	ABSORBENT	ABSORBENT	
LIQUID WASTE/ SPILL	IMBIBLER BEADS® (Regular or Nuclear grade)	NOCHAR® -A610	NOCHAR® -A630	(1) Quick Solid® (2) Sterego® (3) AquaSorb-HP® (4) NOCHAR®-A660 (5) Aquaset® products (6) Aqua Biber® (7) Universal Plus™ (8) HA8010	COMMENTS
PURE HYDROCARBON: Gasoline, Benzene Diesel, Oils	X	X			
HALOGENATED SOLVENTS: polychloro-ethene Trichloro-ethene Methylene Chloride and others alkyl halogenated solvents	X	X			For polymers, the desired degree of solidification and the viscosity of the spill being stabilized determines the amount of product required.
Non-Halogenated Organic Solvents: Acetone,2-butanone, formaldehyde (37% soln.) Antifreeze (50% conc.) Xylene, Toluene	X	X		X Aqua Biber® for antifreeze and formaldehyde	
Inorganic Aqueous solutions: Sodium/potassium /chromate/dichromate Sodium Nitrate, Sodium Nitrite, Zinc Bromide, Lead Salts, Calcium Salts			X	X Aquaset® and Nochar- A660 products only	Extent of absorption will depend on the ionic strength of the aqueous ionic solution and possibly pH of the solution. Check with manufactures/vendor.
Aqueous Organic Solution : For example Pyridine	X		X	X Aqua Biber®	Imbibler NG® *
Dilute Acid Solutions: sulfuric acid, Hydrochloric acid, Hydrobromic acid				May requires pre- neutralization treatment with Nuetrasorb® X	Aqua Biber® and Nochar-A660 can be used without pre-treatment for up to 37 % concentration.

* Post absorption volume changes may be quite significant with Imbibler NG®.

Table 2 Absorbent immobilization selection guide for hazardous/mixed waste liquid Spills (continued).

LIQUID WASTE/ SPILL	IMBIBLER BEADS	NOCHAR -A610	NOCHAR -A630	(1) Quick Solid® (2) Sterego® (3) Aqua-Sorb-HP® (4) NOCHAR-A660 (5) Aquaset products (6) Universal Plus™ (7) Aqua Biber® (8) HA8010	COMMENTS
Concentrated Acid solutions: Hydrochloric (>37%) Sulfuric acid (30%) Hydrobromic Acid Phosphoric acid Hydrofluoric(> 48%)				Use only after effective neutralization treatment with Neutrasorb® X Nochar-A660® can be used with sulfuric acid (95%), perchloric (70%) and Hydrofluoric (> 48%) acids	See guide lines on Neutrasorb® use ¹ <u>Exclude perchloric and Hydrofluoric acids, fuming acids and peroxy organic acids in this category if Neutrasorb® is to be used for neutralization.</u>
Dilute Caustic Solutions: Sodium Hydroxide Potassium Hydroxide Calcium Hydroxide, Ammonium Hydroxide, Dissolved Salt Simulants				May requires pre-neutralization treatment with Neutrakit-2® Aqua Biber® can be used w/o pretreatment For up to 25% conc. X	Nochar-A660 will stabilize selected caustics. Verify with vendors.
Concentrated Caustic solutions: Sodium Hydroxide, Potassium Hydroxide, Ammonium Hydroxide, Dissolved Salt Simulants				Use only after neutralization treatment with Neutrakit-2® X	Neutrakit-2® Use: : Manufacturer recommendations: Not more than 25 wt.% NaOH solutions or 45% KOH solutions.
Concentrated Caustic solutions: Synthetic sludge with: mercury Nitrophenols			X	Aquaset products X	Desired degree of solidification, the viscosity of the spill being stabilized and the inorganic ion content of the spill determine the amount of product required.
PCB and PUREX	X	X			See reference 9

¹ J.T Baker Inc. Phillisburg, NJ. (800-JTBAKER)

Table 3. Absorbent immobilization selection guide for hazardous/mixed waste liquid Spills: Nitric and perchloric Acids.

	IMBIBLER BEADS	NOCHAR -A610	NOCHAR -A630	NOCHAR-A660 Aquaset products Aqua Biber Quick Solid® Universal Plus™ Steregeo® Aqua-Sorb-HP® HA8010	Comments
Concentrated Perchloric Acids				Nochar-A660® can be used with perchloric acid (up to 70%).	
Concentrated Nitric Acid				<u>Use only after effective neutralization treatment with Neutrasorb®</u>	Neutralize and then Immobilize with any of the aqueous spill stabilizers. DO NOT USE WITH FUMING NITRIC ACID.
Dilute Nitric Acids Perchloric Acids				Dilute nitric acid requires neutralization with Neutrasorb® before use of any of these materials. Nochar-A660® can be used with perchloric acid (up to 70%).	

Conclusions:

We recommend the following sorbents:

- Imbiber Beads®, Nochar® products (A-A610 and A630) and Petroset® products for stabilization of petrochemicals and organic spills,
- Modified polypropylene and polyacrylate products (Quick-Solid®, Steregeo®, Universal Plus™, HA8010 and Aqua-Sorb-HP®), Aqua Biber®, Nochar-A660 and Aquaset® products for stabilization of dilute aqueous spills and
- Neutracid-2®/Neutrasorb® neutralization absorbents for some concentrated acids and caustic spills followed by stabilization of neutralized product with either Aqua Biber® or Nochar-A660. Both Aqua Biber® and Nochar-A660 can be used directly with selected concentrated acids.

The stabilization of concentrated acids and caustic spills may require pre-treatment with commercial neutralizers like Neutrasorb[®] and Neutrakit-2[®]. The resulting neutralized spill can then be stabilized with any of the products for immobilization of aqueous spills.

Nitric and perchloric acids have some unique characteristics and as a result are excluded from the general immobilization method for other acids described above. **Manufacturers of Neutrasorb[®] acid neutralization agents exclude the neutralization of concentrated perchloric acids with this product and Nitric acid spills, at any concentration, should not be immobilized with Aqua Biber[®].** We have, therefore, summarized the best approaches for immobilizing these two acids separately (Table 3).

Manufactures of Aqua Biber[®] and Nochar-A660 claim that these materials can be used directly to immobilize concentrated acids like perchloric acids, sulfuric acid, hydrochloric acid and hydrofluoric acid. Although vendors for Nochar-A660[®] claim it can be used for nitric acid spill controls, this still needs to be verified. The recommended approach for dealing with nitric acid spills is to neutralize with Neutrasorb[®] and then contain with any of the aqueous spill immobilizers mentioned above.

These recommended proprietary polymers and inorganic materials are designed for immediate use in spill control or immobilization of various site liquid spills. The final waste forms generated, as a result of the use of these materials for spill control, may not qualify for incineration or direct disposal. If the stabilized waste form is determined to meet disposal requirements, Jenkins packaging information guide¹⁰ or other similar approaches should be consulted.

Sorbent materials have now been added to the EPA's Comprehensive Procurement guideline (CPG) items, and thus, Sorbents may be required to meet EPA's Recovered Materials Advisory Notices (RMANs), which recommends the use of sorbents that meet a recycled-content level greater than 25%. The impact of EPA's RMANs and CPG guidelines on the site's procurement, technical specifications and prices for sobents may require a thorough review of related EPA technical background documents¹¹.

In summary, EPA requires that a procuring agency, when purchasing sorbents made from materials like polymer, inorganic and organic materials, purchase them made with recovered materials when these items meet applicable specifications and performance requirements.

Table 4. Contact Information for Commercial Vendors and Manufacturers.

Brand Name⁺	Vendor	Contact	Comments
AquaSorb-HP[®]	Aquadox/ Rob Wright	630-964-1300 http://www.aquadox.com	Reported to meet EPA liquid release test (EPA-9096 test) at 20 psi in 40 to 1 weight ratio for clean water to absorbent.
Stergo[®] Radpads and Radsorbs	Corpex Technologies	(919) 942-0847	For pH ranges of 4.5 to 9. Reported to meet EPA-9096 test at 20 psi in 30 to 1 weight ratio water to absorbent.
Universal PlusTM	Sorbent Products Co. 206-623-0621	http://industry.net/sorbent.products	Universal absorbent
Quick-Solid[®]	Colloid Environmental Technologies	800-527-9948 http://www.cetco.com	Reported to meet EPA-9096 test at 20 psi in 25 to 1 weight ratio water to absorbent.
WaterWorks crystals Superabsorbent	WaterWorks America, Inc.	440-209-1440	Reported to meet EPA-9096 test at 50 psi in 10 to 1 weight ratio clean water to absorbent.
Waste Lock [®]	M2 Polymer Technologies	847-836-1393	Polyacrylate Reported to meet EPA-9096 test at 50 psi in 25 to 1 weight ratio liquid to absorbent.
IMBIBLER BEADS/Blends	Imbibitive Technologies	1-888-843-2323 www.imbiberbeads.com	For recent studies with this material see reference 9
Nochar	Nochar 317-613-3046	www.nochar.com	For recent studies with this material see reference 9
Petroset & Aquaset Products	Fluid Tech, Inc. 702-871-1884		For recent studies with this material see reference 9
Zorbite [®]	612 Meyer Lane, #8 Redondo beach, Ca 90278-5261	Captfred@aol.com 310-374-0167	Based on volcanic clay mineral. Universal absorber: all liquids oil, oil and water, etc.
Corpex-980A/B [®]	Corpex technologies, Inc	919- 388-2300	For absorption of oils and organic solvents
HA8010	NewPig company	NewPig.com 800-468-4647	
HSSSORB [®]	3554 Coco Lake Drive Coconut Creek, Fl.33073	954-725-9428 HSSSORB@aol.com	Dehydrated peat moss. Used for absorption of crude oil, gasoline, fuel oil

⁺ Recommended products in bold phase.

REFERENCES

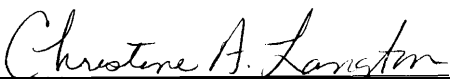
- ¹ ASTM F-716-93-“ Standard Methods of Testing Sorbent Performance of Absorbents”
- ² ASTM F-726-99-“ Standard Methods of Testing Sorbent Performance of Adsorbents”
- ³ 40 CFR 264.314 sections (e)(1) and (e)(2)
- ⁴ US Environmental Protection Agency Final Rule-Hazardous waste management; EPA/530 Z-92-019.
- ⁵ ASTM F1127 “ Standard Guide for Containment by Emergency Response Personnel of Hazardous Material Spills.”
- ⁶ Richard H. Hall and John S. Brinkman, “Immobilization of Low-Level Oily Radioactive Waste,” 16th Annual U.S. Department of Energy Low-Level Radioactive Waste Management Conference- Phoenix, Arizona, December 12, 1994.
- ⁷ R. S. Garcia, “ Commercially Available Low-Level Radioactive and Mixed Waste Treatment Technologies,” INEL, DOE/LLW-240, October 1996.
- ⁸ US patents Numbers 4775494 and 33915.
- ⁹ C. A. Langton, G. Iversen and L. N. Oji “ PUREX Waste Stabilization” WSRC-TR-2001-00526, November 2001.
- ¹⁰ C. F. Jenkins and T. E. Skidmore “ Compatibility –Wastes & 55 Gallon Storage Containers” SRT-MTS-2000-40027, February 16, 2000.
- ¹¹ EPA Document 530-R-00-002 (See <http://www.epa.gov/epaoswer/non-hw/procure/products/sorbents.htm>).

Approvals

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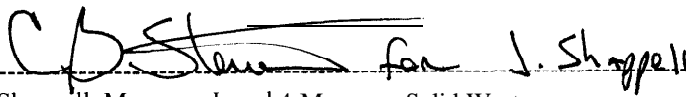
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