IMMOBILIZATION OF LOW-LEVEL OILY RADIOACTIVE WASTE

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The immobilization of low level nuclear contaminated oils has been a continuing problem. Rotating and sliding machinery require lubricants. Oils represent problems when present in water with both ion exchange and membrane systems used to concentrate and isolate aqueous contaminated liquids. It is our understanding that some of these oils are stored as liquids in drums and tanks. When stored in this way it is always possible for corrosion or a careless fork truck driver to cause a leak and a huge problem. This paper describes a way to prevent liquid loss and also protect the water run off from critical storage areas.

For any meaningful discussion we all should start with proper definitions. The list below are those that are particularly important to understand the following discussion.

DEFINITIONS

LOW-LEVEL OILS described in this paper are those that contain transuranics that emit 10 nanocuries/gram or less.

SORBENT is a general term that can mean either ADSORBENT or ABSORBENT.

ADSORPTION is a surface phenomena and in addition to outer surface can include inner surfaces such as pores and capillaries. The solid material does not swell and is insoluble.

ABSORPTION is a physical process where the solid matrix swells. The term IMBIBE is a synonym for ABSORB. This material does not dissolve but in a given fluid will swell to a certain size but no further.

THICKENERS are materials that may become soft and dissolve in excess solvent. If the molecular weight is high they will increase the viscosity of the fluid.

From: *The Chemical Dictionary*

ABSORPTION should be distinguished from ADSORPTION, in that the latter is a surface phenomenon, i.e., the material taken up is distributed over the surface of the ADSORBING material. In ABSORPTION, the material taken up is distributed throughout the body of the ABSORBENT.

The reason it is important that you recognize the difference between ABSORBENT and ADSORBENT is that most salesmen don't understand that there is a difference. Some that do know the difference call their products sorbents --- which doesn't give the customer a clue --- but you would be safe to assume that they are ADSORBENTS. Some properly advertise their materials as ADSORBENTS which is a descriptive term. Think of trying to do without an important ADSORBENT like activated carbon. All Physical Chemistry texts that I am acquainted with properly make the distinction between AD and AB. It has always been a surprise to find some Chemical Engineers (applied physical chemistry) who did not understand the difference. It took the EPA over 15 years to recognize that they had been using the wrong term and had improperly advised the Congress and Senate. The U.S. EPA now understands that there is a difference. See block below and they almost have the definition in correct form.

Sorbents, Adsorbents and Absorbents: What's the Difference?

As described in EPA's rule-makings, "ADSORBENTS" are materials that retain liquids on the surface of their particles by capillary action and surface tension. "ABSORBENTS", mean-while retain liquids within their molecular structure. This Fact Sheet and the rule itself use the term sorbent or "sorb" to refer to materials that are used to treat free liquids that are either adsorbents or absorbents, or both. (EPAI53O-F-92-030)

From: *"The World Catalog of Oil Spill Response Products"*
Robert Schulze, Editor l993

"Absorption only includes those cases in which the oil combines with the sorbent material in such a way that it neither leaks out nor can be squeezed out. Imbiber beads combine with the oil in a way that it cannot leak out or be squeezed out. This is presently the only known product that meets the strict definition of being a true ABSORBENT. All the (other) materials described in this report are adsorbents."

This brings us back to what we feel is "Best Available Technology" (BAT) to immobilize low-level oily radwaste. The Imbibing/Absorbing material we are describing to you is not new. It was originally made by the Dow Chemical Company and offered for sale to NRC licensed nuclear waste companies and/or to the Department of Energy over 15 years ago. Mr. Heyward G. Shealy, Chief of the Bureau of Radiological Health for the State of South Carolina (the Barnwell site in particular) in a letter Sept., 8, 1978 stated "---require oil composites be contained with Dow Imbiber Beads."

Shortly after this approval from the state of South Carolina, The Dow Chemical Company began a program of de-commercialization of the project. The project had always been a technical success (1R- 100 Award 1974) but the marketing department of the Dow department in charge decided that the potential markets did not warrant the investment to take the project from experimental to full scale commercial development. The project was then licensed to an outside company and finally licensed to the Imbibitive Technologies Corporation (ITC) in March 1994. Imtech is owned by ITC. ITC is the exclusive worldwide Imbiber Bead® and owns a production plant for the product and is making the Imbiber Beads®. This unique product is the one that, we believe, offers the best available technology to immobilize low-level radioactive oily products.

Two different methods of using the Imbiber Beads® for immobilization allow you a choice. Imbiber Beads are a high molecular weight non-biodegradable polymer and meet the USEPA requirements for immobilization of compatible hazardous materials for landfilling.

In method one the Imbiber Beads® are mixed with an organic wicking material. There is also a small amount of aqueous immobilizing material to handle up to 0.5% of incidental water in the liquid. It is important with both methods to remove water to at least this level. It is far more economical (and easy) to separate any water layer and immobilize the aqueous material with a cementitious material. The advantage of method one is that the final material can be immobilized and land filled – but if it becomes practical to use incineration to concentrate oily radwaste material, this system is completely combustible.

In method two the Imbiber Beads® are used to immobilize the oil and then mixed into a cementitious material and cast for curing of the cement. This then gives a structural material like cement with the oil contained in the Imbiber Beads and not available for leaching through the pores in the concrete. This method will make incineration much more difficult but it may give a comfort level to those that have confidence in cement.

The first testing of Imbiber Beads® for use in this oil application involved a radiation test to investigate any effect on the polymer structure that might cause chain scission.

We obtained a typical gamma scan of reactor waste from Richard LaRhette of the Maine Yankee Atomic Power Co., to make the assumptions and calculations below.

If we could arrive at an average yearly dose rate taken over seven half-lives it would approach 5.714 RADS/YR for ^{60} Cobalt and 2.00 RADS/YR. for ^{137} Cesium. If we assume no decay for the isotopes or constant emission at these average levels it would require 262,513 years to dose a single central milliliter of oil (in the center of a 55 gallon drum) to 1.5 megarads with ^{60} Cobalt, or 750,000 years with ^{137} Cesium.

We then exposed Imbiber Beads® containing oils at various oil/bead ratios from 1 to 1, 2 to 1, and 3 to 1 to a dose level of 1.5 megarads over 24 hours (^{137} Cesium - 100,000 curies).

Oil/Bead Ratio	**Solvent**	**Initial Appearance**	**Appearance After 1.5 Megarad**
3/1	Toluene	Loose GEL - No Free Oil	Unchanged
3/1	#2 Fuel Oil	Gel -No Free Oil	Unchanged
3/1	50% #2 Fuel Oil! 50% Toluene	Gel -No Free Oil	Unchanged

The Imbiber Beads® used for immobilization are 500 micron in size or less. Since all the fluid must diffuse into the solid polymer structure the small size gives sufficient surface area for a rapid imbibition. The polymer is a multicomponent polymer engineered to imbibe a broad range of oily products from hexane, gasoline, diesel fuel, chlorinated solvents, polar materials, like acetates, ether, methylisobutyl ketone and many others. The absorbing/imbibing Imbiber Beads® work best and fastest with low viscosity fluids that the adsorbents work poorly with. In a good solvent, the Imbiber Beads® with proper molecular architecture will imbibe up to 27 times their original volume and swell up to 3 times their original diameter. The polymer particles are solid with no pores or capillaries. Once imbibed into the molecular structure the liquid cannot be squeezed out and even if cut in two nothing will leak out. The only thing that will come out is vapor and the amount of the vapor loss is dependent on the vapor pressure of the liquid --- and the amount of outer surface area exposed. As any engineer knows -- if you mix a solid high modulus material like the Imbiber Beads® with a low modulus material liquid then the resulting material will probably have a modulus (or rigidity) between those two and so do the Imbiber Beads®. The swollen Imbiber Beads® are solid but rubbery. They can if forced be extruded by pressure (as the unimbibed Imbiber Beads® could) -- but as the USEPA reports, “Such extrusions, however, are not releases of liquids and should not be so interpreted”.

As fluid viscosity increases and the corresponding lights fraction is low the imbibing process is slowed to a time that may be longer than practical or desired. When this happens the addition of a small quantity of a low viscosity fluid will speed up the rate of imbibition to a practical level. The chart on page 8 illustrates this procedure using #2 fuel oil with high viscosity refined oils.

For method one the Imbiber Beads® are blended with an organic wicking agent. The wick keeps the beads separated so they don't gel on the surface before all Imbiber Beads® have contacted the fluid, this allows the process of imbibition to take place without mixing. At less than equilibrium (maximum) swell, the Imbiber Beads® are sticky. Since the recommended loading levels are less than 3 parts oil to 1 part Imbiber Beads® the resultant mass is fluid free and coherent. The surface area is drastically reduced compared to any adsorbent material. Solids will not imbibe into the polymer structure. However, if a solvent that will imbibe is used to dissolve the solid --then both will imbibe. Even insoluble particulates can be trapped in the coherent mass of wick and Imbiber Beads®

The leach resistance of the Imbiber Beads® Wick system was checked using a study to simulate water infiltration into a shallow burial system. The oil used was 91% Mobil DTE Turbine oil with 9% #2 fuel oil. The solids used were Imbiber Beads® wick mix and Silica Sand adsorbent for the control.. All dissolved oil numbers are reported as total organic carbon (grams of methane).

Total oil in sample 60 ml
Total water flow ~ 4000 ml
Average Water Flow 140 ml/nr -Intermittent
Total Solid 40 ml

	Control Sand-Oil	Imbiber Beads® Wick Mix
Total Surface Area	Not Determinable	~16 in^2
Total Free Oil Leached	~20 ml	None Visible By Sheen
Total Dissolved Oil Leached	0.22 g	0.0086 g
Average 18 Day Leach Rate	0.01375 g	0.000477 g
Minimum Leach Rate 18 Days	Significant Loss Thru 18th Day 0.0166 g	No Significant Loss After 2nd day less than 0.0003 g

The loss of oil from the sand is 33.79% compared to the loss of 0.0179% from the Imbiber Beads® wick mixture. There was no visible sheen (6-10 ppm for #2 fuel) on the water from the bead/wick mixture.

The oil used in the water leach study (91% DTE with 9% #2 fuel) was mixed with approximately 100 ppm of cobalt nitrate salt (oil insoluble-water soluble). Leachate samples were analyzed for cobalt by Flame Atomic Absorption with a detection limit of 1 ppm. Over a 20 day period no cobalt was detected from the water leaching off the Imbiber Beads®/wick immobilized oil. However, the unimmobilized sample leached over 35% of the available cobalt during the first ten days.

We believe that the new availability of Imbiber Beads® will enable engineers in the power industry to design hardware to solve many of their "oily" problems. These applications include the use of gravity drainage devices to protect diked storage areas, spill control units, packages for safe shipping and improved safety and handling of oily wastes. All of these procedures can now be improved.

It is the aim of IMTECH AMERICA to provide the best imbibing polymers to industry. IIMTECH Research & Development will develop new formulations and new materials to answer problems that as of yet do not have answers. We welcome the chance to work with you for the good of the environment and the safety of people in industry.

References:

ASTM F-716-93 - "Performance Standard for Absorbents"

ASTM F-726-93 - "Performance Standard for Adsorbents"

ASTM F-1127-88 - "Standard Guide for Containment by Emergency Response Personnel of Hazardous Materials Spills"

ASTM Manual 10 - "A Guide to the Safe Handling of Hazardous Materials Accidents"

"US Environmental Protection Agency Final Rule - Hazardous Waste Management; Liquids in Landfills". Federal Register Vol. 57/No. 223/Wed., Nov. 18, 1992 PGS 54452 54461. 40 CFR Parts 260, 264, 265, and 271. EPA/530 Z-92-019

"World Catalog of Oil Spill Response Products"-Robert Schulze, Editor Chapter 3 Sorbents

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IMMOBILIZATION CHART

- Using Diluent to Control Time of Immobilization