Snow As an Expedient Adsorbent for Hazardous Waste Spills

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ABSTRACT

Laboratory tests indicated that snow can be an effective adsorbent for spills of insoluble hazardous waste materials. Fresh snow was most effective, followed by old snow and wet snow. The sorption ratios ranged from 0.24 g/g to 3.12 g/g depending on the type of snow and waste material. Also, a column study indicated that much of the adsorbed material drains out if it is not collected soon after it is mixed with the snow. A hypothetical spill scenario is presented that shows how snow might be used as an adsorbent in a typical spill situation.

INTRODUCTION

A hazardous material spill can constitute a severe threat to human health and the environment. However, if the spill occurs on land during winter, several factors come into play that can reduce this threat. First, the ground is usually frozen, so the material probably will not penetrate. Secondly, the lower temperatures lower the vapor pressure so that the downwind spread of toxic vapors is reduced. Finally, if the spill occurs on snow-covered ground, an effective and virtually free sorbent material is already available on site. This material is, of course, snow.

The main purpose of this study was to evaluate snow as an adsorbent material. Three types of snow were selected: a fresh snow, an old snow, and a wet snow. Each type of snow was tested on six hazardous wastes. Also, macroscopic observations were conducted to determine how the waste materials were being retained. These studies were conducted in coldrooms at the U.S. Army Cold Regions Research and Engineering Laboratory (CRREL) in Hanover, New Hampshire.

This paper also includes a typical spill scenario where snow might be used as an expedient sorbent material. A method of estimating the amount of snow needed is shown. Suggestions as to what could be done with the melted waste/snow mixture after collection are also presented.

LITERATURE REVIEW

The literature includes only a few reports of actual spills on snow-covered ground. One incident occurred on December 1977 when gasoline slowly leaked from a pipe at a small tank farm in Nenana, Alaska (Allen, 1979). By the time the leak was discovered, approximately 113,500 L (30,000 gallons) had been lost. Most of the gasoline was found within the bottom 10 to 15 cm of the snow cover. Penetration into the ground was less than 3 cm. The contaminated snow was picked up with aluminum shovels (to avoid sparks), thrown into lined dump trucks, and transported to an approved temporary storage site. The remaining gasoline on the ground was allowed to evaporate.

Another incident occurred in January 1983 near Warwick Lake, Ontario, when approximately 59,000 L of diesel oil leaked out of a fuel tank (Burns, 1988). A large portion of this fuel escaped through a damaged containment dike

and made its way under the snow to the frozen surface of a lake. Very little fuel, if any, penetrated the ice. Most of the fuel was soaked up in the lower 15 cm of snow. This oil-soaked snow contained 5 to 50 percent fuel by volume, depending on location. Cleanup crews were able to shovel up this snow and transport it to a rock basin where it was burned. It is interesting to note that burning was accomplished by melting a small amount of snow until a puddle of oil was formed. This puddle was then ignited using a blowtorch and the fire became self-sustaining as fuel was released from the melting snow.

In the early 1970s, exploitation of arctic oil reserves raised several questions as to what would happen if crude oil spilled on snow-covered ground. In tests conducted with a warm (15°C) North Slope crude oil, McMinn and Golden (1974) noted that the oil did not penetrate substantially below the surface of the snow. The downward percolation of the oil was stopped by an impermeable ice layer formed when meltwater produced by the warm oil refroze. However, this pooled oil was rapidly converted to an oil/snow "mulch" when blowing snow became mixed with the oil. The mulch was dry in appearance and could easily be shoveled as a cohesive material. Also, they found that unlike the snow-fuel oil mixture, the snow-crude oil mixture was difficult to ignite and burned poorly.

Allen (1979) experimented with small spills of Prudhoe Bay crude, Cook Inlet crude, and hydraulic/diesel oil on 25 cm of loose, dry, undisturbed snow. Samples of the oil/snow mulch were taken at various time intervals and thawed, which caused the oil to separate from the water. The volume of oil in samples taken soon after the spill varied from 40 to 70% of the total volume, but samples taken 24 hours later contained only 20 to 40%. Apparently some of the oil drained away by gravity.

Mackay et al. (1975) conducted several experimental spills of crude oil on snow. They found that snow acted as an excellent adsorbent and the area contaminated in a winter oil spill was only about one-eighth the area affected by a summer spill. However, they concluded that a winter spill-contaminated area could exceed the summer spill area if the snow could not be collected before thaw.

Johnson et al. (1980) studied the effects of two experimental 7570-L spills of hot Prudhoe Bay crude oil on two similar plots in subarctic interior Alaska. One spill was conducted in the summer while the other was conducted in the winter. Because of the snow cover, the winter spill covered only 62% of the terrain covered by the summer spill. Also, oil movement stopped after only one day and remained immobilized until snowmelt.

Kawamura et al. (1986) concluded that snow will adsorb only chemicals that are immiscible in water. Miscible chemicals such as glycol, low-weight alcohols, and acids will dissolve the snow and become diluted. Also, a strong acid could release heat on contact with the snow, causing even more snow to melt. After the snow has melted, the easiest chemicals to separate should be those that are the least soluble.

MATERIALS AND METHODS

The effectiveness of an adsorbent material can be determined by measuring its sorption ratio, which is a ratio of the weight of waste adsorbed to the weight of sorbent (Cheremisinoff, 1989). For example, a sorption ratio of 1.0 means that 1.0 kg of waste can be sorbed by 1.0 kg of sorbent.

A modified American Society for Testing Materials (ASTM) procedure (F726) was used to measure the sorption ratio of snow. However, this procedure was modified to accommodate snow. The snow and waste material were set at $0 \text{ or } -5^{\circ}\text{C}$ rather than $23 \pm 4^{\circ}\text{C}$, and the drainage time was increased from 30 to 90 seconds. Basically, this procedure closely simulated a cleanup operation in which the sorbent is mixed with the spill and collected as soon as it became saturated. The detailed steps in this procedure were as follows:

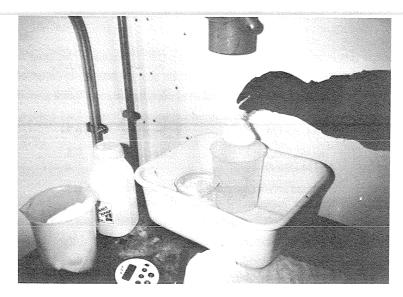


Figure 1. Submerging snow sample in gasoline during sorption ratio tests.

- 1. A piece of cheesecloth and string was soaked in the hazardous waste, removed, and drained. A 30-×30-cm piece of cheesecloth and a 15-cm piece of string were found to be adequate. The cheesecloth was spread on an aluminum pieplate and the string placed on top. The pieplate was placed on a scale and tared to eliminate the wetted cheesecloth and string from being included in the weight of snow or hazardous waste.
- 2. About 50 cm³ (three heaping tablespoons) of snow was placed in the center of the cheesecloth, weighed, and recorded as the weight of snow, W_s . After taring the scale, a bag of snow was formed by collecting the ends of the cheesecloth and tying them with the piece of string.
- 3. The bag was submerged in a container of waste (see Fig. 1) until the snow was completely saturated. Generally, saturation was complete within a few seconds. However, to ensure saturation the sample was soaked for about 40 seconds. The sample was withdrawn and allowed to drain for 90 seconds. The sample was placed on the pieplate, weighed, and recorded as the weight of waste, $W_{\rm w}$.
 - 4. The sorption ratio was calculated by dividing $W_{\rm w}$ by $W_{\rm s}$.

Using the above procedure the sorption ratio was measured for three types of snow: a fresh dry snow, an old dry snow, and an old wet snow. These three types of snow were selected because they should be easily recognizable by cleanup personnel at an actual spill event.

The fresh snow was collected on 26 December 1990 immediately after a snowstorm. The crystals were plate-like in shape and ranged in size from 0.7 to 2.0 mm. The snow was placed in a covered cardboard carton and stored in a coldroom at -5°C. Tests using this snow were conducted at -5°C over a 7-day period.

The old snow came from a sample collected during the previous winter (1989–90) and stored in a coldroom at -29°C. Because of the long storage time, the snow crystals had been transformed from flakes into well-rounded crystal grains ranging from 0.2 to 1.0 mm in diameter. Sorption tests with this snow also were conducted at -5°C.

The wet snow was obtained on 5 February 1991 during a midwinter thaw period. The crystals were typically rounded and gathered into small clusters. The mean grain size was 0.8 mm at the time the snow was collected but this increased

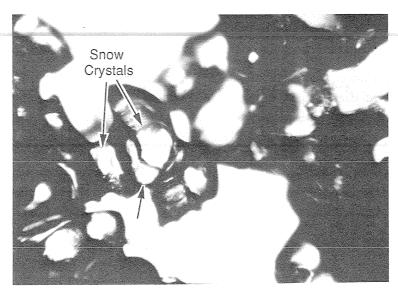


Figure 3. Location of fuel oil on snow crystals.

One explanation for the variation in sorption ratios between wastes could be the difference in viscosities. The high-viscosity wastes such as fuel oil and kerosine also had the higher sorption ratios. This would seem reasonable because liquids with a high viscosity will probably be retained for a longer period at the adsorption sites. Mackay et al. (1975) also noted the importance of viscosity in his experiments with crude oil spills on snow. This generalization could help estimate the sorption ratios of other materials.

HYPOTHETICAL SPILL SCENARIO

Suppose a fuel delivery truck has an accident and spills $11,355 \, L$ (3000 gallons) of no. 2 fuel oil in a remote location (see Fig. 4). The ground is frozen and covered with 15 cm of old snow. Most of the oil flows off the pavement and into a ditch that drains into a stream. It melts a path through the snow until it cools to $0^{\circ}C$, and then it flows beneath the snow. When the emergency spill response team arrives, the fuel oil is flowing slowly beneath the snow toward the stream. The air temperature is $-6^{\circ}C$.

In this case, the recommended plan of action would be:

- 1. Locate the leading edge of the spill in the drainage ditch. With a shovel, mix snow with the oil until it forms an oil/snow mulch. Progressively move upstream towards the source of the spill, mixing snow with the oil. This action will slow and should eventually stop the further spreading of oil. Based on an oil density of 0.876 and a sorption ratio of 0.83, the weight of snow needed to sorb 11,355 L of oil is 11,984 kg. If an average snow density of 300 kg/m³ is assumed, the volume of snow needed is approximately 40 m³. With 15 cm of snow on the ground it would take all the snow from a 266 m² area to sorb the spill. As shown in Figure 4, this area is well within gathering distance from the spill. Trucks with plows could be used to gather snow and push it toward the oil.
- 2. Remove the oil/snow mulch by shoveling it into garbage cans or bucket loader. Dump the mulch into a leakproof container such as a dumpster. For this spill it would take approximately nine 4.6-m³ (6-yd³) dumpsters.
- 3. Transport the containers to a heated warehouse or leave the containers at the site until spring. Allow the oil/snow mulch to thaw and siphon or decant as much oil as possible from the containers. Recycle the oil and discharge the water onto the fuel contaminated ground or to a sewage treatment plant if approved. In this case the volume of water discharged would be approximately 11,984 L (3166 gal.).

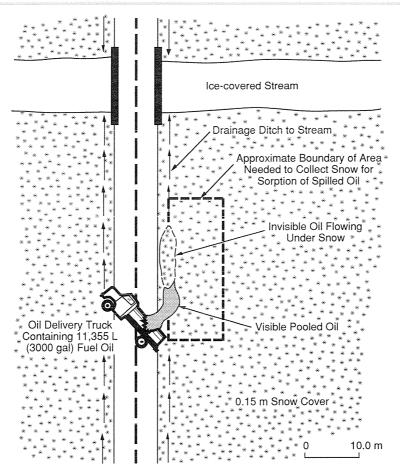


Figure 4. Sketch of hypothetical oil spill situation where snow is used as an expedient adsorbent material.

One option that should be considered in such a scenario is to remove any pooled oil by pumping it into a tank truck or container as soon as possible. This will not only expedite the cleanup but it will reduce the amount of snow required.

CONCLUSION

Snow is an effective adsorbent for cleaning up spills of insoluble hazardous wastes. It works best as either a fresh or old snow under below-freezing conditions. An important operational technique in using snow effectively is to collect the snow/waste mixture as soon as possible after mixing. Not only does the snow adsorb the spill but it can be easily separated from the waste by melting and decanting. Also, snow can be handled with simple hand tools and conventional snow removal equipment.

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