Pollution Prevention and Reuse Alternatives for Crude Oil Tank-Bottom Sludges

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ABSTRACT

The U. S. petroleum industry annually produces large quantities of storage tank sludges. These wastes consist of sediments, water, and oil emulsions, which are periodically pumped or drained from the bottom of storage tanks containing crude oil, intermediate product, or refined product. The purpose of this paper is to discuss beneficial uses for this material. Results of an IPEC-funded research project will be summarized, along with other waste minimization techniques and alternatives for reuse: dust palliative on unimproved roads, fuel for cement kilns, crude distiller feedstock, and coking feedstock.

INTRODUCTION

The U.S petroleum industry annually produces about 1.5 million barrels of storage tank bottom sludges that settle out in production operation vessels. These wastes consist of sediments, water, oil emulsions, and heavy hydrocarbons such as asphaltenes. Typical crude oil tank bottoms contain more than 50% by weight oil, 30–45% water and 5 – 20% solids (http://www.scaltech.com/technica.htm). The composition of the sludge vary from facility to facility and from tank to tank within the same facility, and is dependent upon the composition of the stored product, the storage conditions, the length of the storage time, and the condition of the sludge tank. These tank bottoms are not taken to the refineries primarily because of the detrimental effect of fine sediments on pumps and pipelines at the refineries. Some state agencies (including the Oklahoma Corporation Commission) allow controlled application to lease or county roads, but sludges are usually considered waste and are removed for treatment or disposal.

Conventional physical and chemical methods of treatment for tank bottom sludges focus on the recovery and reuse of the organic content of the sludge. Sludge treatment at large facilities includes centrifugation to remove the heavy metals from the liquid, then separation of water from the hydrocarbons. The hydrocarbons are reused as process feed. The water is treated in the wastewater treatment plant, and the non-petroleum solids are landfilled. Alternate processing includes land farming, composting, and solidification and landfilling. However, the owners of small storage facilities may not find the limited options available to recycle the organic content of the sludge economically viable.

This paper reviews the results of an Oklahoma State University research project on reuse of tank bottom sludges as road base material for secondary roads. It also outlines the current state of the practice on other pollution prevention and reuse alternatives for tank bottom sludges. The U.S. Environmental Protection Agency (EPA) lists the waste management hierarchy as: ***Reduce, Reuse, Recycle***. We use the EPA hierarchy in this paper.

SUMMARY OF ROAD BASE RESEARCH PROJECT

Crude oil tank bottom sludges appear to compare most closely with cutback asphalts or emulsified asphalts with regard to general properties. Therefore, the tank bottom sludges were characterized using standard emulsified asphalt testing methods.

Currently, tank bottom sludges from primary field operations are specifically excluded from the definition of hazardous waste [40 CFR Part 261.4 (b) (5)]. Despite being exempt from RCRA, sludges can contain potentially hazardous materials, so this study examined the environmental impact of using tank bottom sludges as roadbase material. Ten sludges from varied geographical locations and geological formations within Oklahoma were sampled for this project.

Sampling Methods

A weighted metal sampler was tied to a 30ft nylon line and dropped through the storage tank thief hatch while holding to the other end of the line. As the sampler hit the bottom, it was allowed to fill for about 30 seconds before it was pulled out. To ensure a representative sample, the sampler was dropped at various points distributed uniformly over the bottom of the tank. The material retained in the sampler was then collected in a 30 cm dia x 36 cm height plastic bucket and shut air tight with a screw-type lid.

The samples collected from various tanks were then transported back to the OSU School of Civil and Environmental Engineering Laboratories, where they were stored at room temperature for future testing purposes.

Testing for Environmental Properties

The tests selected for environmental analysis included:

Waste characterization:

1. EPA SW 846 Method 3031 – Acid digestion of oils for metals analysis by atomic absorption or ICP spectrometry.
2. EPA SW 846 Method 9071B – n-Hexane extractable material (HEM) for sludge, sediment, and solid samples.
3. TNRCC Method 1006 – Characterization of C_6 to C_{35} petroleum hydrocarbons in environmental samples.
4. Fractionation of oils into saturates, aromatics, and asphaltenes – This is a non standard method outlined in a thesis study by Terry Smith titled "Geochemical Biomarker Study of the Woodford Shale in the Witcher Field, Oklahoma County, Oklahoma."

Waste toxicity (Performed by EPA-certified private contract laboratory):

1. Toxic characteristics leaching procedure (TCLP) – 40 CFR 136, 261 Method for Chemical Analysis of Water and Waste EPA-600/4-79-020, March 1983. Test Method for Evaluating Solid Waste, SW-846, Final Update III, 1986. Standard Methods (18th Edition) for the Examination of Water and Wastewater. Performed by Accurate Labs & Training Center, Stillwater, OK.
2. Toxicity screening procedure – Methods for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms; EPA/600/4-90/027; 48-Hr. definitive acute toxicity test with *Ceriodaphnia dubia*. Performed by Stover Environmental Consulting Operations Management Analytical/Toxicology Laboratories, Stillwater, OK.

Testing for Engineering Properties

The tests selected to evaluate materials engineering properties were:

1. AASHTO - T166-83 Bulk Specific Gravity of Compacted Bituminous Mixtures
2. AASHTO - T209-82 Maximum Specific Gravity of Bituminous Paving Mixtures

3. AASHTO - T246-82 Resistance to Deformation and Cohesion of Bituminous Mixtures by Means of Hveem Apparatus
4. Freeze-Thaw test – A variation of ASTM Standard Test Method D 4842 – 90 for Determining the Resistance of Solid Wastes to Freezing and Thawing

Analysis of Petroleum Hydrocarbons

The Total Petroleum Hydrocarbon (TPH) of each sample was measured to estimate the ability to form a stable road base material. Since conventional asphalt is high in asphaltenes, a high percentage of aphaltenes in the sample, in relation to its TPH, was assumed to be a fair indicator of its ability to substitute asphalt. The TPH measured then served as the total when calculating the percentages of its major constituents of asphaltenes, paraffins, aliphatic and aromatic hydrocarbons. It was also used at the beginning of the study to give an estimate of its aggregate-coating capacity, as a less oily sample may not easily compact into a stable mold. Performing this step is crucial to deciding if the material could be used at all as a road base.

The results of this study indicated that the sampled sludges had low asphaltene content, which may not be enough to integrate the aggregates used in the sample. Aromatics and non-saturates did not indicate either a positive or a negative effect in this study. Saturated hydrocarbon content was slightly correlated with positive material properties. .

Analysis of Material Properties

The sludges did not prove suitable as a binder for roadbase materials. Four of the sludges were formed into molds using two different aggregates, as discussed in the previous section. Completed molds were analyzed for material properties according to the AASHTO tests cited above. The minimum HVEEM stability for roadbase material is 35 (Texas Department of Transportation standard). None of the roadbase molds met this criterion.

Analysis of Environmental Impacts

Roadbase molds were leached according to EPA Toxic Characteristics Leaching Potential protocols (EPA SW 846). Leachate was analyzed for toxic metals by EPA Method 6010. None of the metal extractions met the RCRA definition of hazardous.

Molds were also analyzed for RCRA toxic organics (except pesticides, which were not expected to be present) by EPA methods 8260 and 8270. All samples were below the practical quantitation level (BPQL).

Toxicity tests were performed on leachate from the molds, using *Ceriodaphnia dubia*, according to EPA protocols under the Clean Water Act. All the samples met the definition of toxic. This finding indicates that leachate should not be allowed to enter surface waters. State and federal regulations already prohibit this.

Conclusion

The results of this research indicate that the sludges tested do not make acceptable roadbase materials. However, the sludges do not contain hazardous materials in hazardous amount. Thus, beneficial reuse of the sludges should not pose an environmental hazard.

OTHER POLLUTION PREVENTION AND REUSE ALTERNATIVES

Several alternatives exist for the handling of tank bottom sludges; the best alternative varies with local economics and the properties of the sludge. Some of the candidate alternatives are conventional waste minimization techniques, materials reuse, recycling, and disposal. The alternatives discussed below adhere to EPA's goals for pollution prevention:

- pollution should be prevented or reduced at the source whenever feasible;
- pollution that cannot be prevented should be recycled in an environmentally safe manner whenever feasible;
- pollution that cannot be prevented or recycled should be treated in an environmentally safe manner whenever feasible; and
- disposal or other release into the environment should be employed only as a last resort and should be conducted in an environmentally safe manner.

EPA's fact sheet on pollution prevention for refineries lists several techniques that are also useful for crude tank bottom sludges; these are discussed below. Of primary importance is waste segregation (**http://es.epa.gov/techinfo/facts/chmi/strtgy7.html**).

The *Industrial Pollution Prevention Handbook* (McGraw-Hill, 1995) devotes a chapter to pollution prevention in the petroleum refining industry. Many of the techniques cited in the handbook are applicable to tank bottom sludges from production sites. The handbook lists solvent extraction, coking, thermal processing and thermal oxidation as potential management alternatives for petroleum sludges. The section below discusses the more commonly available of these options, along with waste minimization opportunities.

Waste Minimization Opportunities

Waste minimization is the preferred waste management alternative of the U.S. Environmental Protection Agency. It is usually, also, the least expensive alternative. The technique is not a single solution to tank bottom sludges, since crude oils contain substances that will settle out as sludges in production and storage tanks. However, waste management problems are lessened by good housekeeping. Of critical importance is the strict segregation of production wastes (nonhazardous by law) and hazardous wastes. If any hazardous waste is commingled with crude oil tank bottom sludges, the entire batch of waste is considered hazardous waste. Good housekeeping is listed by EPA as a critical part of any waste minimization program.

Another item listed by EPA is the addition of tank agitators, where economically feasible. Tank agitation can also be achieved with addition of air or steam. The *Industrial Pollution Prevention Handbook* cited above also lists in-tank mixers as a good waste minimization technique for storage tanks. Other techniques cited in the handbook are:

- Minimize intermediate tankage.
- Minimize contact between crude oil and air by using inert blanketing or floating roofs.
- Separate oil and water phases of tank bottoms using filters or centrifuges.
- Add emulsifiers.
- Use warm oil circulation with dispersant for tank bottom sludge cleanout to recover entrapped oil.

Material Reuse Opportunities

The research project discussed earlier in this paper was an attempt to find beneficial materials reuse opportunities for crude oil tank bottom sludges. As with waste minimization, this is usually a low-cost alternative.

The simplest reuse alternative for crude tank bottom sludges at production sites is application to lease or low-volume public roads as a dust palliative. The State of Oklahoma permits such application, as long as permit requirements are followed. The permits are issued by the Oklahoma Corporation Commission, the state regulatory agency for petroleum production. Two separate permit types are issued: one to the lease holder for lease roads, and one to County Commissioners for county roads. Landowner permission is required for application to lease roads, and any application to roads requires measures to ensure that surface waters are not contaminated. Some other states probably have similar permits.

Sludge reuse as feedstock for coking operations is an option frequently mentioned by EPA and other sources. Not all refineries have coking processes, but an increasing number do. Newer coking technologies are able to use a wider array of feedstocks, including tank bottoms. One patented process actually generates a “clean” fluid and low-BTU gas, rather than conventional coke (**www.exxonmobil.com/refiningtechnologies/fuels/mn_fluid.html**).

Crude sludges can also be used as fuel at cement or aggregate kiln operations. For sludges that contain hazardous materials and therefore cannot be managed as non-hazardous waste, kiln operations are ideal. In a rotary kiln operation, temperatures are carefully regulated so that organic contaminants are completely oxidized prior to release of gases to the atmosphere. Any metals contained in the fuels are chemically bound into the cement or aggregate and cannot be released to the environment (Gossman, D. 1992.

"Petroleum and Petrochemical Waste Reuse in Cement Kilns." *Environmental Progress,* **11**, 1).

Another point to remember is that any heavy petroleum stock can be "cut" with a lighter petroleum stock. A "cut," or less viscous, sludge is potentially applicable in a wider range of reuse opportunities than those listed above.

SUMMARY

Recovery of the sludge and processing to make a usable feedstock can be expensive. However, the value of the recovered product can make the entire process cost-effective (even generating a small profit, in some cases). It is critical to analyze the quality and quantity of sludge in the tank. If the sludges have a high percentage of recoverable hydrocarbons and no hazardous components in hazardous amounts, the sludges can be recovered as feedstock. Economics will dictate if this option is feasibile. A local tank cleaning/sludge recycling company must be contacted to get the cost data.