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Surfactant-Solvent Flushing Process - Application to  
Decontaminate Excavated Soil and Debris

by  
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ABSTRACT

Solvent extraction of organic contaminants is one of the relatively low-cost methods currently under development for decontaminating excavated soil and abandoned waste. However, the application of this technology to excavated sediments, soils and debris presents unique challenges. The high moisture content, the low toxic contaminant concentrations and high fine-grain material characteristics require special attention to surfactant-solvent selection and processing flexibility. This describes the technical issues associated with surfactant-solvent extraction and recent bench-scale test results. These tests indicate that this technology is safe and cost-effective for further development and engineering design as part of a full-scale commercial plant.

1. Introduction

This paper discusses the technical issues of applying surfactant-solvent flushing to contaminated sediments, soil and debris, which exhibit high moisture content, low toxic contaminant concentrations, and high fraction of fines.

2. Technical Considerations for Applying Surfactant-Solvent Flushing

2.1. General

There are three fundamental technical considerations for applying surfactant-solvent flushing to treat contaminated soil and debris.

These are :

- the chemical and physical characteristics of the soil and sediment to be treated;
- the clean-up goal for the selected final product or treatment objectives for the process; and
- the process to achieve the goal.

The latter involves the development and application of the particular surfactant-solvent flushing process to convert the

contaminated raw materials to the desired final product.

## 2.2. CONTAMINATED SOIL Characterization

Although soil and sediment comes from numerous locations and differ in physical and chemical content, there are some general common characteristics. It is usually a black, sticky muck. It has a high water content in the range of 40 to 70% in situ, because of the high total surface area from the high percentage of hydrophilic fines (clays and silt). Carbon content is high (2 to 10% TOC on a dry basis), and a variety of heavy metals and organic contaminants can be found. These organic contaminants, which are the focus of this surfactant-solvent flushing process, are usually non-volatile, in-soluble in water, and not readily biodegradable. Among these, the hydrophobic organic contaminants of concern are usually low levels of dioxins, furans, PCBs, and polyaromatic hydrocarbons. If the soil and sediment is excavated from the nearby sea, the salinity in the water phase can be as high as 1%. In this case the objectionable organic contaminants are dioxins, furans, and PCBs, and polyaromatic hydrocarbons based on ecological studies. A few other contaminants in the pesticides and semi-volatiles groups may also be unacceptable. The odor and semi-solid/liquid state is also undesirable when placed upland and exposed to the atmosphere. Often heavy metals are not a problem for upland disposal. However, it may effect the suitability for reuse and should be stabilized.

## 2.3. Soil and Sediment Treatment Objectives and Surfactant-Solvent Flushing Process Objectives

The overall objective of a soil and sediment management program is to minimize cost over a given time horizon while satisfying various criteria specifications. Cost minimization also applies to treating the contaminated soil with the surfactant-solvent flushing process. Although a clean-up criteria has not been established for low but undesired levels of toxic compounds, reasonably safe goals can be proposed for useful products. For example, if the dioxin/furan levels are set at 1 ppt (total equivalent to 2,3,7,8 TCDD) and PCBs levels are set at 1 ppb, the required removal is usually 1-3 orders of magnitude. Other organics would also be removed using the solvent extraction process.

Depending on the type of product desired for beneficial reuse, the organic-free sediments can be stabilized with Portland cement or other agents to fix metals. This not only eliminates a disposal cost, but may provide a financial contribution if the product is sold at 30 pln per cubic meter.

After setting the overall goals, some of the desirable

objectives of the organic flushing plant are

- to treat a variety of organic contaminants at various concentrations;
- to pretreat soils to reasonable but flexible specifications;
- to design the commercial plant with flexible level of organics removal in order to attain the safe levels of the reusable product;
- to produce various desirable products to maximize reuse; and
- to integrate the surfactant-solvent flushing plant with a solidification plant and its requirements (i.e., produce organic contaminant-free soil with moisture content required by solidification plant).

#### 2.4. Surfactant-Solvent Flushing Technology

Applying solvent extraction for treating sediments is more complex than the two standard types found in textbooks: liquid-solid extraction or liquid-liquid extraction. The excavated soils and sediments are already two phases (liquid and solid) in the form of an aqueous slurry, and the introduction of a partially miscible solvent creates a second liquid phase. One approach is to eliminate the aqueous phase by drying the sediment and thereafter conduct the conventional liquid-solid extraction. This is practiced in many industrial applications. The second approach is to keep the water, view the aqueous slurry as the "dense" liquid phase, and use a partially miscible solvent or surfactant-solvent solution as the second phase of the liquid-liquid extraction. This is practiced widely in the separation of aromatics from aliphatics, sulfur compounds from oil and pollutants from wastewaters. Selectivity for specific contaminants can still be achieved by using partially miscible acetate/alcohol solvent blends.

There are two possible mechanisms for the contaminants to transfer from the solid particle to the solvent layer. The first mechanism is for the organic contaminant to first dissolve in the new aqueous/organic layer and then transfer to the organic layer/droplets. This is probably effective because the new solvent blend can penetrate the sediment particles. The second mechanism is for the organic phase solvent blend to contact the solid particles with proper mixing, and to extract the organic contaminant directly. This is effective in solvating molecules such as PCBs, which are also non-polar.

Solvent choice is influenced by the interactions of the structure of the chemicals. The main contaminants of concern are the non-polar to slightly polar polyaromatic hydrocarbons, and multi-chlorinated hydrocarbons such as PCBs, dioxins, furans and pesticides. The surfactant-solvent solution offers both a slightly polar and non-polar group and provides affinity for the

contaminants. The solubility of the solvent increases as the aliphatic group increases. To increase solubility of the solvent in water, a surfactant is added. This blend also provides the additional benefit of increasing the solubility of other contaminants selective to the surfactant. This blend also exhibits higher than expected solubility and penetration into the sediments. The sensitivity of solubility to solids content is very high. This is favorable as it occurs in the 30 to 35% solids range, where the two low viscosity liquid layers readily mix and quickly separate for decanting.

The surfactant-solvent blend has several important properties that reduce processing cost. First, some combinations form heterogeneous minimum azeotropes with water. This allows the removal of essentially all the solvent from sediments without removing most of the water. Second, the heterogeneous azeotrope improves the solvent recovery distillation step. Third, the density of the surfactant-solvent blend is significantly less than water or aqueous slurry and makes the separations easy. Fourth, the solvated sediment mixture flows well and is non-sticking to materials of debris such as carbon steel, plastics, and glass.

#### Thermal Stability and Non-Reactivity

The surfactant-solvent blends are thermally stable and non-reactive at the processing temperatures (maximum temperature expected at distillation reboiler is <140°C) and neutral conditions. The concern that the solvent hydrolyze is minimal as the pH of the sediment is near neutral.

#### Safety and Environmental Considerations

The selected surfactant-solvent blend is nontoxic to workers and the NDS exposure threshold levels are relatively high. Some of these compounds are used in household products and are considered safe. Unfortunately, in the purer nonaqueous state, these solvents are flammable and present an explosion hazard. This is overcome by inerting and specifying explosion-proof equipment systems. Dust releases are also limited by keeping the sediments wet with water during operation. The surfactant-solvent blend does not pose environmental problems. The solvents are biodegradable if trace quantities are left in the sediment. The compounds selected are not listed under land disposal restrictions and are not hazardous. Atmospheric emissions are controlled by enclosure of unit operations. The wastewater effluent is evaporated to solvent levels for acceptance by the POTW or in-plant treatment.

#### Costs

Cost is an important consideration when selecting solvents for two reasons. One, the solvents should be commercially available and relatively inexpensive. Although the solvent is

recovered, some makeup is needed to replenish the amount lost from fugitive emissions and the amount left in the waste oil to maintain fluidity. Two, the solvents are recovered efficiently from downstream operations. The energy cost is minimized by not removing all of the water from the sediments. The high volatility and minimum azeotrope with water also helps to keep energy costs low during the distillation and steam stripping steps.

### 3. Bench-Scale and Pilot-Scale Tests

#### 3.1. Test Program and Objectives

SAKAR completed both bench-scale and pilot-scale tests to evaluate its Mobile Soil Decontamination System (MSDS) using soil mixed with some contaminant compounds.

The MSDS system, shown in Figure, consists of three sequential technologies:

##### Step I SEx :

A solvent extraction process to remove organics contaminants and produce organic contaminant-free sediments and a fuel or waste oil for on site combustion or off-site disposal (incineration). The solvent is recovered by partially drying the soil, distilling the waste oil and steam stripping the wastewater.

##### Step II SWash :

A soil washing process to produce clean sediments. It consists mainly of separating solvent and surfactant residuals. Dewatering is not necessary if solids content is greater than 30%.

##### Step III SFix :

A solidification/stabilization process that adds Portland Cement to the cleaned soils and sediments to improve the leaching properties of inorganic contaminants and to improve the mechanical/physical properties.

After completing bench-scale treatability studies that showed promise of decontamination and production of potential useful products, a pilot plant was operated at War Harbour in Gdynia to treat 3 cubic meter of soils. The objectives of the test program were:

- to demonstrate how most of the steps of the technologies can decontaminate a significant quantity of actual soil feedstock, and produce products with desirable physical properties; and
- to collect process data for the preliminary design of a commercial facility.

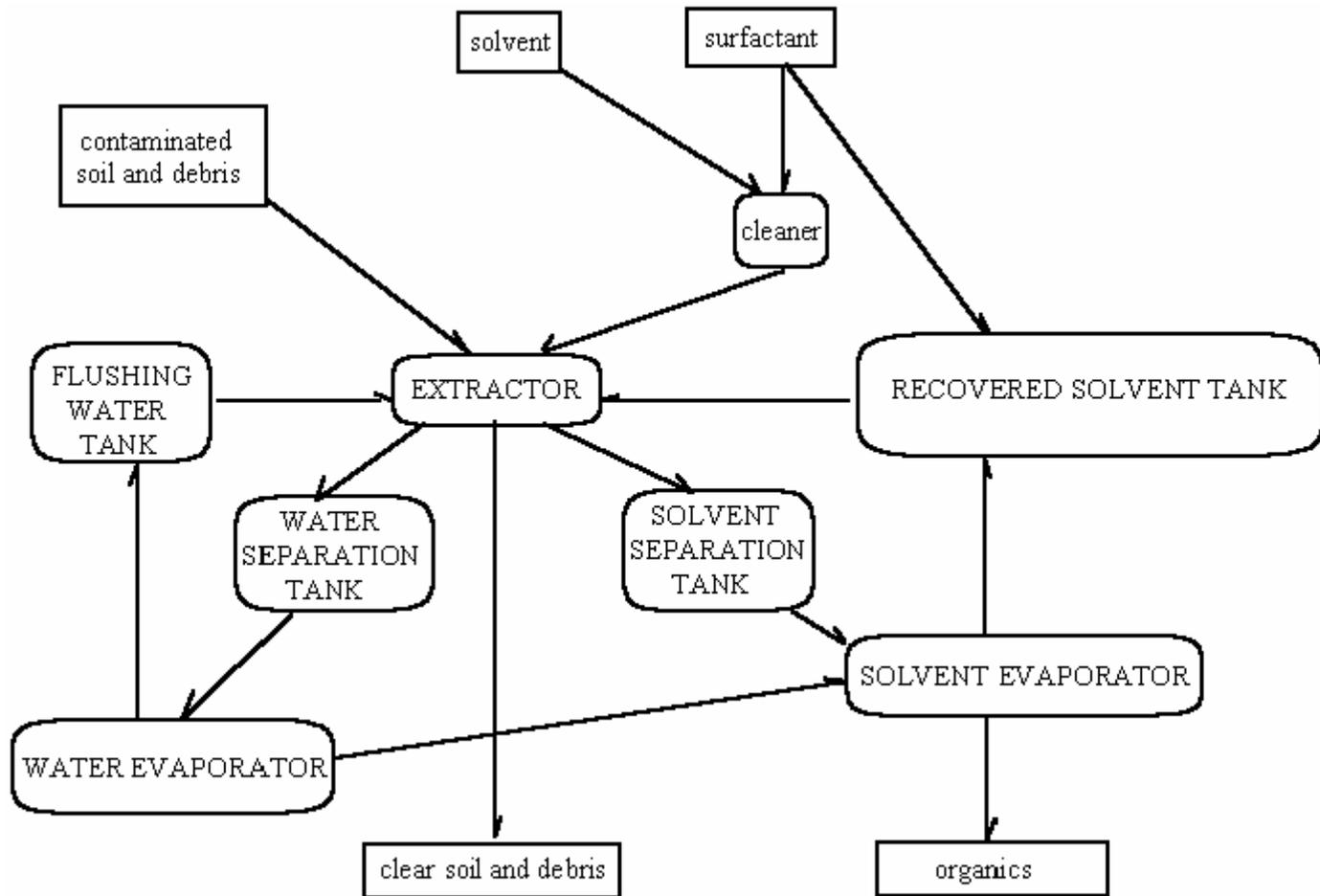


Figure 1: Block flow diagram of MSDS process

The test program focused on these tests:

- removing organics contaminants using a batch surfactant-solvent flushing and semi-continuous solvent recovery process. The solvent was a blend of cold surfactant/oil/acetate/alcohol believed to offer high removal at reasonable cost. The main operating variables were 1:2 solvent to sediment ratio for each extraction that was agitated for 10 minutes and settled for 90 minutes prior to recover the solvent phase with extracted contaminants. Organic contaminant removal was investigated for 1, 3, and 5 extractions.
- recovering the solvent for repetitive reuse; drying the decontaminated soil and debris; concentrating the waste oil; and steam stripping the wastewater.
- stabilizing/solidifying the organic-free sediments to produce end-products with improved physical properties. The organic-free soil with 30 to 50% water was mixed with 0.15 parts and 0.30 parts cement.

### 3.2. Test Results from Surfactant-Solvent Flushing Process

The performance of the SEx surfactant-solvent flushing plant is presented for the bench treatability study using the surfactant-acetate solution. The percent removal with three extraction stages was moderate (low 90s%) for most organic contaminants.

Difficulty was encountered in two areas:

- Penetration of the solvent into the sediment required intensive mixing and a long period.
- The sediment was difficult to handle as it adhered to debris.

In order to overcome these difficulties and seek greater organics contaminant removal, the pilot-plant program was improved by using a mixture of fuel oil/acetate/alcohol as the solvent. The sensitivity of organics removal was measured versus the number of extraction stages.

The pilot-plant performance improved considerably: the reduction in total group PCBs increased by almost one order of magnitude to the high 90s%. The reduction improves as the number of extractions increases, but is not very sensitive after 3 extractions. Further laboratory work is recommended to potentially improve removal performance to 90-99%.

The performance of the SFix solidification/fixation process is presented. The heavy metals already meet the upland disposal criteria. The reduction in amount of total group PCB extracted is significantly greater with the flushing-and-stabilized materials than the stabilized-only.

### 4. Physical Properties and Product Uses

The SWash process produces a viscous, flowable slurry at the optimal moisture content (40-50%) for solidification with Portland cement in a pugmill. If heavy metals are not a problem, the SWash product can also be used directly with other dry materials to produce a landscape soil or construction fill.

Solidification of the sediments with Portland cement (or other weaker binding agents such as gypsum) also changes the physical properties of the products made. By varying the amount of water and cement, different properties can be attained. The addition of a small proportion of cement (0.1, 0.15 and 0.2 parts to 1 part soil) produces a light and soft agglomerated material that can be crushed to various sizes. The soil-like material meets the specifications for operational landfill cover or construction fill for depressions areas. It can also be blended with other materials such as compost, sludge, other soils to produce a landscaping soil. The addition of larger proportions of cement (0.3 and 0.4 parts) produces a cured block of material that is stronger with the unconfined compressive strength. The cured material can be crushed to various sizes to resemble

crushed stone or aggregate. However, it does not meet the specifications for use as a road sub-base. For the same reason, it appears that producing other more expensive structural concrete-like products may not be practical.

## 5. Process Design

The operation of the batch and semi-continuous pilot plant generated some process data to design a full-scale automated plant with some confidence. The full-scale plant should be fully continuous, with large flexibility to accommodate soil and sediment with varying granulometry and contaminants. The best extractor type appears to be the mixer-settler, widely used in the industry because of their reliability, flexibility, and high capacity. The large volume of inventory is another advantage. It can provide the residence time (many hours) that may be required for the extraction of contaminants with slow diffusion rates.

The solvent can be evaporated from sediments in a steam jacketed ribbon dryer. Packed distillation columns are appropriate for recovering the solvent and concentrating the waste oil. Packed columns are appropriate for stripping organics from wastewater with direct steam. The wastewater can be treated with conventional techniques to meet the POTW or other direct discharge requirements.

## 7. Conclusion

Surfactant-solvent flushing is a promising technology for removal of organic contamination from sediments. The surfactant-solvent blend is highly effective in removing most organic contaminants without dewatering/drying the sediments. The treatment costs are comparable with landfill disposal and are probably less for large-scale plants.