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Engineering Bulletin

Chemical Dehalogenation

Treatment: APEG Treatment

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Superfund

Purpose

Section 121(b) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) mandates the Environmental Protection Agency (EPA) to select remedies that "utilize permanent solutions and alternative treatment technologies or resource recovery technologies to the maximum extent practicable" and to prefer remedial actions in which treatment "permanently and significantly reduces the volume, toxicity, or mobility of hazardous substances, pollutants and contaminants as a principal element." The Engineering Bulletins are a series of documents that summarize the latest information available on selected treatment and site remediation technologies and related issues. They provide summaries of and references for the latest information to help remedial project managers, on-scene coordinators, contractors, and other site cleanup managers understand the type of data and site characteristics needed to evaluate a technology for potential applicability to their Superfund or other hazardous waste site. Those documents that describe individual treatment technologies focus on remedial investigation scoping needs. Addenda will be issued periodically to update the original bulletins.

Abstract

The chemical dehalogenation system discussed in this report is alkaline metal hydroxide/polyethylene glycol (APEG) which is applicable to aromatic halogenated compounds. The metal hydroxide that has been most widely used for this reagent preparation is potassium hydroxide (KOH) in conjunction with polyethylene glycol (PEG) [6, p. 461]* (typically, average molecular weight of 400 Daltons) to form a polymeric alkoxide referred to as KPEG [16, p. 835]. However, sodium hydroxide has also been used in the past and most likely will find increasing use in the future because of patent applications that have been filed for modification to this technology. This new approach will expand the technology's applicability and efficacy and should reduce chemical costs by facilitating the use of less costly sodium hydroxide [18]. A variation of this reagent is the use of potassium hydroxide or sodium hydroxide/tetraethylene glycol, referred to as ATEG, that is more effective on halogenated aliphatic compounds [21]. In some KPEG reagent formulations, dimethyl sulfoxide

(DMSO) is added to enhance reaction rate kinetics, presumably by improving rates of extraction of the haloaromatic contaminants [19][22].

Previously developed dehalogenation reagents involved dispersion of metallic sodium in oil or the use of highly reactive organosodium compounds. The reactivity of metallic sodium and these other reagents with water presented a serious limitation to treating many waste matrices; therefore, these other reagents are not discussed in this bulletin and are not considered APEG processes [1, p. 1].

The reagent (APEG) dehalogenates the pollutant to form a glycol ether and/or a hydroxylated compound and an alkali metal salt, which are water soluble byproducts. This treatment process chemically converts toxic materials to non-toxic materials. It is applicable to contaminants in soil [11, p. 1], sludges, sediments, and oils [2, p. 183]. It is mainly used to treat halogenated contaminants including polychlorinated biphenyls (PCBs) [4, p. 137], polychlorinated dibenzo-p-dioxins (PCDDs) [11, p. 1], polychlorinated dibenzofurans (PCDFs), polychlorinated terphenyls (PCTPs), and some halogenated pesticides [8, p. 3][14, p. 2]. This technology has been selected as a component of the remedy for three Superfund sites. Vendors should be contacted to determine the availability of a treatment system for use at a particular site. The estimated costs of treating soils range from \$200-\$500/ton. This bulletin provides information on the technology applicability, the types of residuals resulting from the use of the technology, the latest performance data, site requirements, the status of the technology, and where to go for further information.

Technology Applicability

This technology is primarily for treating and destroying halogenated aromatic contaminants. The matrix can be soils, sludges, sediments, or oils. If a waste site has contaminants other than halogenated compounds, other alternatives should be considered.

The concentrations of PCBs that have been treated are reported to be as high as 45,000 ppm. Concentrations were

* [reference number, page number]

reduced to less than 2 parts per million per individual PCB congener. Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have been treated to nondetectable levels at part per trillion sensitivity. The process has successfully destroyed PCDDs and PCDFs contained in contaminated pentachlorophenol oil. For a contaminated activated carbon matrix, direct treatment was less effective and the reduction of PCDDs/PCDFs to concentrations less than 1 ppb was better achieved by first extracting the carbon matrix with a solvent and then treating the extract [15, p. 1].

All field applications of this technology to date have been in various matrices and not on specific Resource Conservation and Recovery Act (RCRA) listed wastes. The effectiveness of APEG on general contaminant groups for various matrices is shown in Table 1. Examples of constituents within contaminant groups are provided in Reference 23, "Technology Screening Guide for Treatment of CERCLA Soils and Sludges". This table is based on the current available information or professional judgment when no information was available. The proven effectiveness of the technology for a particular site or waste does not ensure that it will be effective at all sites or that the treatment efficiency achieved will be acceptable at other sites. For the ratings used for this table, demonstrated effectiveness means that, at some scale, treatability was tested to show that, for that particular contaminant and matrix, the technology was effective. The ratings of potential effectiveness and no

expected effectiveness are based upon expert judgment. Where potential effectiveness is indicated, the technology is believed capable of successfully treating the contaminant group in a particular matrix. When the technology is not applicable or will probably not work for a particular combination of contaminant group and matrix, a no-expected-effectiveness rating is given.

Limitations

The APEG technology is not intended as an in situ treatment. APEG will dehalogenate aliphatic compounds if the mixture is reacted longer and at significantly higher temperatures than for aromatic compounds, it is recommended that a related reagent KTEG be considered for these contaminants. KTEG has been shown at laboratory scale to be effective on halogenated aliphatic compounds such as ethylene dibromide, carbon tetrachloride, ethylene dichloride, chloroform, and dichloromethane (methylene chloride) [18, p. 2]. The necessary treatment time and temperature for KTEG use can be determined from laboratory tests.

Treatability tests should be conducted prior to the final selection of the APEG technology to identify optimum operating factors such as quantity of reagent, temperature, and treatment time. These tests can be used to identify such things as water content, alkaline metals and high humus content in the soils, glycol extractables content, presence of multiple phases, and total organic halides that have the potential to affect processing times and costs [19].

The treated soil may contain enough residual reagent and treatment byproducts that their removal could be required before final disposal. If necessary, such byproducts are usually removed by washing the soil two or three times with water. The soil will have to be neutralized by lowering the pH prior to final disposal.

Specific safety aspects for the operation must be considered. Treatment of certain chlorinated aliphatics in high concentrations with APEG may produce compounds that are potentially explosive (e.g., chloroacetylenes) and/or cause a fire hazard. The use of DMSO or similar reagents may lead to formation of highly flammable volatile organics (e.g., methyl sulfide) [18, §IV C]. Severe corrosivity can be a concern when DMSO is teamed with other APEG reagents. Alkaline reactive materials such as metallic aluminum will compete with the contaminants for the reagent and may produce hydrogen gas (explosive). Vapors from heating oily soils, which are often the matrix in which PCBs are found, can also create such potential problems as fires and noxious fumes. These problems can often be solved by taking appropriate corrective actions during elevated temperature processing.

The operation must also be conducted with care because of the elevated temperatures and production of steam, the use of caustics in the process, and the presence of acids that are used for neutralization. If DMSO is used, care must be taken to prevent its coming into contact with skin, for it enhances transport of PCBs through the skin, thus increasing the risk of exposure.

Table 1
Effectiveness of APEG Treatment on
General Contaminant Groups for Various Matrices

Contaminant Groups		Effectiveness			
		Sediments	Oils	Soil	Sludge
Organic	Halogenated volatiles	▼	▼	▼	▼
	Halogenated semivolatiles	▼	▼	▼	▼
	Nonhalogenated volatiles	□	□	□	□
	Nonhalogenated semivolatiles	□	□	□	□
	PCBs	■	■	■	■
	Pesticides (halogenated)	▼	■	■	▼
	Dioxins/Furans	■	■	■	■
	Organic cyanides	□	□	□	□
	Organic corrosives	□	□	□	□
Inorganic	Volatile metals	□	□	□	□
	Nonvolatile metals	□	□	□	□
	Asbestos	□	□	□	□
	Radioactive materials	□	□	□	□
	Inorganic corrosives	□	□	□	□
	Inorganic cyanides	□	□	□	□
Reactive	Oxidizers	□	□	□	□
	Reducers	□	□	□	□
■ Demonstrated Effectiveness: Successful treatability test at some scale completed					
▼ Potential Effectiveness: Expert opinion that technology will work					
□ No Expected Effectiveness: Expert opinion that technology will not work					

Technology Description

Figure 1 is a schematic of the APEG treatment process.

Waste preparation includes excavation and/or moving the soil to the process where it is normally screened (1) to remove debris and large objects and to produce particles that are sufficiently small to allow treatment in the reactor without binding the mixer blades.

Typically, the reagent components are mixed with the contaminated soil in the reactor (2). The material must be well mixed with the reagent to allow effective treatment. Treatment proceeds inefficiently without mixing. This mixture is heated to between 100° and 180° C. The reaction proceeds for 1 to 5 hours depending upon the type, quantity, and concentration of the contaminants. The treated material goes from the reactor to a separator (3) where the reagent is removed and can be recycled (4).

During the reaction, water is vaporized in the reactor, condensed (5) and collected for further treatment or recycled through the washing process, if required. Carbon filters (7) are used to trap any volatile organics that are not condensed. In the washer (6), the soil is neutralized by the additions of acid. It is then dewatered (8) before disposal.

Process Residuals

There are three main waste streams generated by this technology: the treated soil, the wash water, and possible air emissions. The treated soil will need to be analyzed to determine if it meets the regulatory requirements for the site before final disposition can be made. The soil's pH must be

adjusted before disposal. The chemistry of this technology is specific to halogenated organics and, based upon a test conducted by the EPA in 1985, results in byproduct compounds that appear to be neither toxic nor of concern. In that test the EPA checked for 1) mutagenicity, 2) toxicity, and 3) bioaccumulation/bioconcentration of the byproducts of two different contaminants: tetrachlorobenzene and 2,3,7,8 - TCDD that had been treated by the process [3, p. 80]. The individual byproduct chemical compounds were not determined. These compounds and the residual levels of reagent or catalyst did not present a serious health or environmental problem [12, p. 2].

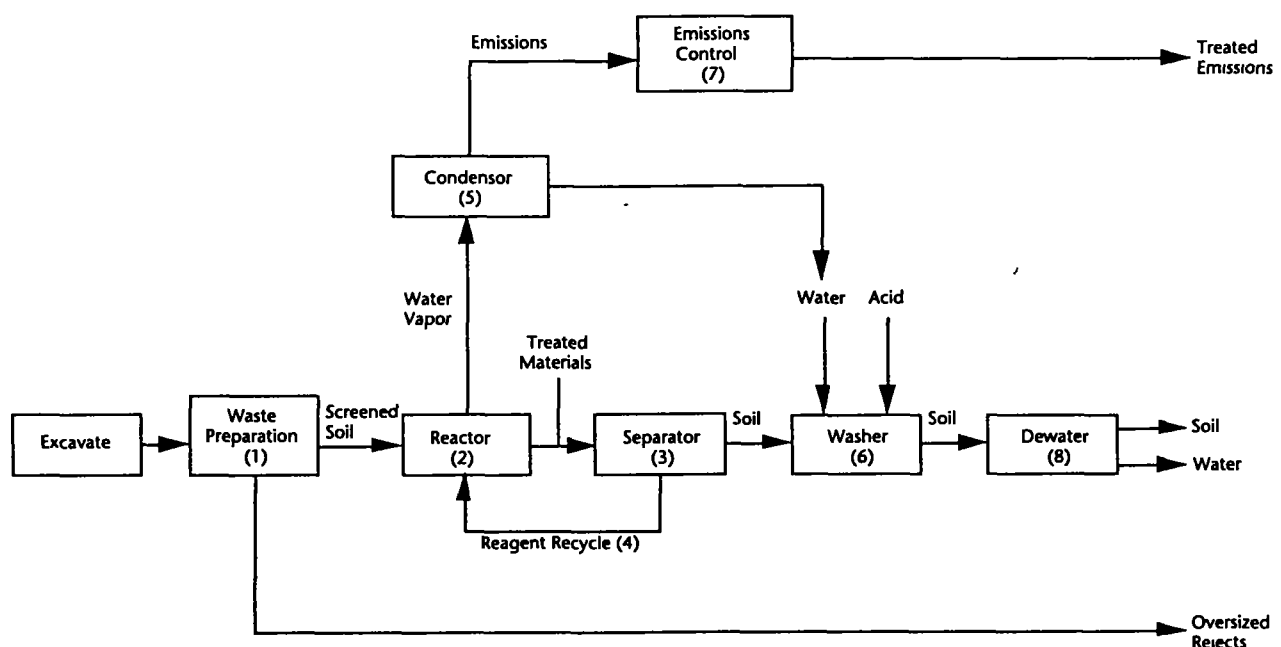
Waste wash water contains only trace amounts of contaminants and reagents and would be expected to meet appropriate discharge standards, enabling it to be discharged to a local, publicly owned treatment works or receiving stream. Volatile air emissions can be released due to the heating and mixing that occurs with the process. They are usually captured by condensation and/or on activated carbon. The contaminated carbon is usually incinerated.

Site Requirements

APEG treatment units are transported by trailers [13, p. 54]. Therefore, adequate access roads are required to get the unit to the site. The system that operated in Guam, which used a 1.5-ton batch reactor, required an area of 100 feet by 100 feet.

Energy requirements involve heating the reactor and removing the water by volatilization. For the reactor used in Guam, a standard 440V, three-phase electrical service was required along with a diesel steam-generating plant rated at

Figure 1
APEG Treatment Process



600 lb/h and 80 psi [13, p. 53]. A standard municipal water supply, or equivalent, is adequate for this process.

Contaminated soils or other waste materials are hazardous and their handling requires that a site safety plan be developed to provide for personnel protection and special handling measures.

A means of containing and cleaning up accidental spills must be provided. The reagents (KOH, acids, etc.) should be stored in drums with containment beneath and provisions to pump any spills to a holding area for neutralization [19, p. 2].

The process residuals normally must be stored until their level of contaminants are verified to be below those established for the site. Depending upon the site, a method to store waste may be necessary. Storage capacity will depend on waste volume.

Onsite analytical capabilities are highly desirable. Extraction equipment and gas chromatography/mass spectrometer capabilities should be available to measure contaminants of interest and to provide information for process control.

Performance Data

This technology's performance has been evaluated from bench-scale tests to field tests in large reactors. Table 2 summarizes the results of several more important applications of the technology and their results.

RCRA Land Disposal Restrictions (LDRs) that require treatment of wastes to best demonstrated available technology (BDAT) levels prior to land disposal may sometimes be determined to be applicable or relevant and appropriate requirements (ARARs) for CERCLA response actions. The APEG treatment technology can produce a treated waste that meets treatment levels set by BDAT, but may not reach these treatment levels in all cases. The ability to meet required treatment levels is dependent upon the specific waste constituents and the waste matrix. In cases where APEG treatment does not meet these levels it still may, in certain situations, be selected for use at the site if a treatability variance establishing alternative treatment levels is obtained. EPA has made the treatability variance process available in order to ensure that LDRs do not unnecessarily restrict the use of alternative and innovative treatment technologies. Treatability variances may be justified for handling complex soil and debris matrices. The following guides describe when

Table 2
APEG Field Performance Data

Site/Date	Contaminant/ Waste Form	Concentration Before	Concentration After	Volume Treated
Signo Trading NY/1982	dioxin/liquid	135ppb	<1 ppb	15 gallons
Montana Pole Butte, MT/1986 (16, p. 838) [5, p. 1]	dioxin furans/oil	147-83,923 ppb	<1 ppb	10,000 gallons
Western Processing Kent, WA/1986 [16, p. 838]	dioxin/liquid and sludge	120 ppb	<0.3 ppb	7,550 gallons
Wide Beach Erie County, NY/ 1985	PCBs (Aroclor 1254)/soil	120 ppm	<2 ppm	1 ton
Guam U.S.A./1988 793 gal. reactor [13, p. 43]	PCBs/soil	2500 ^a ppm with hot spots as high as 45,860 ppm	<1 ^{ab} ppm	22 tons soil 3.4 tons crushed rock
Bengart & Memel Buffalo, NY/1986 55 gal. drum [10, p. 13]	PCBs/soil	51 out of 52 drums, 108 ppm	<27 ppm	52 fifty-five gallon drums
Economy Products Omaha, NE/1987	TCDD, 2, 4-D, 2, 4, 5-T/liquid	1.3 ppm 17,800 ppm 2,800 ppm	ND 334 ppm 55 ppm	20 gallons

^a = value is an average value

^b = per resolvable PCB cogener

and how to seek a treatability variance for soil and debris: Superfund LDR Guide #6A, "Obtaining a Soil and Debris Treatability Variance for Remedial Actions," (OSWER Directive 9347.3-06FS) [20]; and Superfund LDR Guide #6B, "Obtaining a Soil and Debris Treatability Variance for Removal Actions" (OSWER Directive 9347.3-07FS) [17]. Another approach could be to use other treatment techniques in series with APEG treatment to obtain desired treatment levels.

Technology Status

The APEG process has been selected for cleanup of PCB-contaminated soils at three Superfund sites: Wide Beach, New York (September 1985), Re-Solve, Massachusetts (September 1987), and Sol Lynn, Texas (March 1988). Wide Beach is expected to start operation in the summer of 1990 [9, p. 99] [19].

This technology has received approval from the EPA's Office of Toxic Substance under the Toxic Substances Control Act for PCB treatment.

Significant advances are currently being made to the APEG technology. These advances employ water rather than costly PEG to wet the soil and require shorter reaction times and less energy. These advances should greatly enhance the economics of the process. Performance information on this modified process is not available at this time for inclusion in this bulletin [18].

This technology uses standard equipment. The reaction vessel must be equipped to mix and heat the soil and reagents. A detailed engineering design for a continuous feed, full-scale system for use in Guam is currently being completed. It is estimated that a full-scale system can be fabricated and placed in operation in 6 to 12 months. Costs to use APEG treatment are expected to be in a range of \$200-\$500/ton.

EPA Contact

Technology-specific questions regarding APEG technology may be directed to:

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