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Project Summary

Methods/Materials Matrix for Ultimate Disposal Techniques for Spilled Hazardous Materials

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This study reviews and evaluates various conventional and novel methods for the ultimate disposal of spilled or released hazardous materials. The object was to use the data on actual spilled material characteristics as the basis for selecting the most appropriate ultimate disposal methods for residues from spill cleanups. The conventional methods reviewed are: biotreatment, chemical treatment (neutralization, oxidation, and reduction), incineration, pyrolysis, landfilling, and fixation. Novel processes considered are: wet air oxidation, improved thermal degradation, microwave and plasma destruction, selective biodegradation, high temperature physical and chemical fixation, and oxidation with aqueous bromine.

The report discusses the problems and requirements of applying each of these techniques to large and small hazardous substance spills and releases, particularly in situations where the spilled or recovered waste material is mixed with debris and various other chemicals.

An attempt was made to use chemical and physical properties to specify preferred disposal methods for a wide range of toxic and hazardous substances and wastes. The original matrix format proved to be too complex and required too many subclassifications to be useful. In its place, what was developed is a generalized matrix that used conventional classifications of the technology available in the mid-1970's. The matrix generated can assist on-site coordinators in making assessments of the preferred disposal routes for hazardous wastes and spill residuals. The more generalized matrix is subdivided according to the physical and chemical properties of the hazardous materials and the nature of the other wastes or debris present in the residue.

A second version of the matrix was also developed on the assumption that secured landfills would become unacceptable in the future and that certain novel techniques now under development could play a significant role at that time. The need for new disposal technology is addressed.

This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

This study was conducted during the late 1970's and contains dated information pertaining to U.S. Environmental Protection Agency regulations and policies. Consequently, the reader is reminded to retain the same perspective that would be appropriate in reading any document several years after its initial preparation. Particular care should be exercised when considering the cost data and references to "current and anticipated" regulations and Agency policies, many of which have now become much more demanding. It was decided to publish this report, even though portions are out of date, based on the potential benefits that could be derived from the technical content of the study.

Regulation and control of the transport and disposal of hazardous substances (and particularly hazardous wastes) have become a primary environmental issue. Though restrictions are intended to apply mainly to hazardous industrial wastes, they also apply to hazardous wastes and residues encountered at spill sites.

Cleanup procedures at spill incidents usually address the onsite collection, containment, and deactivation of specific wastes in a manner that minimizes damage to the immediate environment (air, land, water) and reduces the hazard to people, other living entities (animals, flora), and structures. Little attention has been devoted to the ultimate (final) disposal of the accumulated wastes after spilled or released hazardous substances have been collected, chemically modified to prevent damage to the local environment, and/or physically mixed with debris, sorbents, water, etc. Procedures that are appropriate for the destruction or disposal of pure or highly concentrated hazardous wastes are frequently not practical or even technically appropriate once a material has been retrieved from the environment, often under adverse conditions. Nevertheless, before a response activity can be considered complete, final destruction or disposal of the residual materials should be planned and implemented to ensure minimal long-term environmental impact. Such final action may be unnecessary in only a few cases, e.g., highly volatile spilled material, that has already entered the air column, releases that have been dissolved in a large volume river, hazardous substances that have been absorbed by soil in a manner that permanently immobilizes components of concern (heavy metals).

In the absence of specific guidance for cleanup personnel, best engineering judgement has been the only basis for selecting a final disposal process for spill residuals. The purpose of this study was to develop a system of preferred or ranked disposal, destruction, and treatment options that (1) would be based on the chemical and physical properties of the residues and (2) could be applied to a variety of spilled materials under a wide range of conditions. It soon became apparent that a complex matrix system that incorporated a detailed compilation of all the different factors and combinations could not be generated in a practical, useful form. A more generalized matrix was therefore developed for qualitative guidance for field personnel. The matrix does include factors such as reactivity, solubility, leachability, availability of sites, etc.

The generalized matrix was subsequently modified on the assumption that secure landfills (as used in the 1970's) would cease to be viable alternatives in the future. In addition, the modified matrix anticipated that treatment systems now under development (such as those discussed in the body of the report) would become commercially available and would expand the options open to the onsite coordinator.

The information presented here and in the full report reflects the status of the soil treatment and waste disposal industry as it existed in the late 1970's. In the intervening years, significant changes have occurred in technology, promulgation of regulations, definition of social demands and impact of economics.

Treatment Options

For a variety of reasons, not every spill receives or requires cleanup. In addition, not every spill cleanup generates residues that are hazardous, even by current standards. For example, of a random sampling of 78 hazardous material spills occurring from December 1975 to May 1977, 28 (36%) received "no cleanup". The cleanup techniques for the others (64%) were as follows:

Item	No. of Incidents
Water wash	19 (24%)
Chemical treatment	9 (11%)
Recovery	6 (8%)
Landfill	2 (3%)
Biotreatment	1 (1%)
Nothing reported (excludes "no cleanup")	13 (17%)

Of course, these data are not necessarily representative of all spill incidents.

To develop a basis for a matrix of treatment options for various wastes, the authors reviewed a wide range of technologies for the ultimate disposal of hazardous wastes and made qualitative judgements about the applicability of these technologies to spill residues. Key comments considered during development of the treatment matrix are noted in the following paragraphs.

Biological Processes

Without further treatment, even the upper level of removal achievable with biological treatment processes (about 90%) may not be adequate for hazardous or toxic substance releases. Approaches such as trickling filters, activated sludge systems, etc. are used for hazardous wastes (intentionally and otherwise) but land application is probably the method most cost-effective and most readily applicable to spill residuals. More than half of the hazardous materials defined by various Federal agencies and tabulated in the appendix of the full report are expected to be susceptible to biodegradation. Note that other constituents of a spill residue may also play a role in the success of a particular process.

Incineration

The basic process technology for incineration is well-developed and well-suited to the ultimate disposal of organic hazardous wastes although the nature of the ash remaining from specific wastes may need special attention. Various systems can handle viscous liquids, tars, solids, etc. These systems include multiple hearths, rotary kilns, fluidized beds, catalytic combustors, and others. Cost and accessibility of the appropriate equipment are the key factors in selecting an incinerator for disposal of the residuals from a hazardous spill (or release) cleanup. Certain wastes such as PCB's, require extreme conditions to achieve the required destruction. The incineration of chlorinated wastes at sea is a special case receiving increasing attention for its ability to avoid the air pollution problems inherent in land-based incineration. More than half of the hazardous materials listed in the report appendix are appropriate candidates for incineration (in general, the exceptions are the inorganic materials).

Neutralization

Neutralization with strong or weak acids and bases is widely used in the cleanup of hazardous chemical spills. This process can also contribute to the insolubilization of other hazardous components such as chromic ions (Cr-III).

Precipitation

Precipitating agents are often used during cleanup procedures to separate inorganic hazardous species from other spill components. Once precipitated as oxides, carbonates, or sulfides, many metals are sufficiently insoluble to be disposed of as nonhazardous wastes.

Chemical Oxidation and Reduction

Though a number of oxidants and reductants are used in chemical processing, only a few are suitable for field use. These include sodium and calcium hypochlorite, hydrogen peroxide, sodium sulfite, ferrous sulfate, and sulfur dioxide.

Fixation

Organic fixation agents such as tar, asphalt, polyolefins, and epoxy resins can be used to immobilize (encapsulate) residuals, but many of the products are sensitive to disintegration by the ultraviolet component of sunlight, indigenous microorganisms, weathering, etc. Inorganic silicates have been used, primarily, to retard the movement of heavy metals in landfilled sludges.

Sanitary Landfills

Without protection (use of liners or collection of leachate) against the migration of hazardous or toxic waste constituents, sanitary landfills are unsuitable for hazardous wastes. But, when spilled material has been detoxified or otherwise deactivated, ultimate disposal in a sanitary landfill may be acceptable if it meets Federal, state, and local regulations.

Secured Landfill

Secured landfills equipped with impervious liners and leachate collection systems may meet future requirements for the storage of hazardous wastes. Separate cells for reactive wastes can prevent chemical interactions that could solubilize otherwise immobile materials. Besides technical requirements, a secured landfill must also meet strict permitting and reporting requirements. The long-term integrity of such sites is an ever-present question.

Deep-Well Injection

The injection of liquid wastes into strata isolated from potentially usable groundwater is an attractive option for wastes that are difficult to treat by other routes. The use of this method will continue to be severely restricted by the need to assure that a well is truly isolated from groundwater.

Ocean Disposal

Though dumping into the ocean has been used for disposal of various wastes and while the ocean does have a buffering capacity unmatched by any land-based system and possesses significant biodegrative capacity, ocean disposal is now encountering heavy public resistance.

Matrix Development

Even after a cleanup, a hazardous material spill may leave a residue that must still be regarded and disposed of as a hazardous material. In other cases, dilution with soil or water will change the character of the spilled material so that it may be disposed of as a nonhazardous material.

The character of a spilled material often derives from its condition after capture, collection, and clean-up. The waste may be essentially unchanged and mixed with only small amounts of extraneous material; or it may be diluted with water, mixed with other combustible materials or mixed with other noncombustible materials such as soil, debris, and organic detritus. The actual nature of the residue often dictates the choice of disposal method.

Recovery should be the first option considered, particularly where the waste is unchanged and only slightly contaminated with other material. Mixtures with water are generally approached as waterborne wastes and are treated with neutralization, precipitation, bio-oxidation, and adsorption. When some components of the mixture are combustible, incineration may be the preferred route. But, when the other components are noncombustible, the mixture requires careful selection of separation and treatment processes to assure that all the components are disposed of safely.

As noted, it was impractical to develop a matrix for specific compounds or even for families of compounds on the basis of their chemical or physical properties. Many other factors, related to physical state, chemical composition, location, etc., affect the final choice of a treatment process for spill residues.

The alternative approach (Table 1) divides hazardous waste into organic and inorganic categories. Organics are further divided into reactive, unreactive, and highly toxic/persistent classes. Inorganics are categorized as reactive and highly toxic persistent. In these designations, reactivity refers to the ease of biochemical or chemical deactivation. Nonreactive organics are those that are not responsive to such chemical or biochemical processes and must, consequently, be incinerated, disposed of in a secured landfill, or otherwise detoxified or destroyed. The toxic/persistent category is defined to include compounds that are not degraded in the environment in less than a year and for which water solubility is greater than 1 mg/L (pesticides are examples).

When options are selected for deactivating spill residues, chemical or biochemical degradation and incineration, even with its high cost, are preferred to disposal in secured landfills. Deep-well injection and ocean disposal are not included in the matrix because of anticipated restrictions on their use.

Table 1 presents the preferential treatment options for spill residues when other materials of different character are present. For residues that are primarily organic, the preferred method is biochemical degradation or, if necessary, chemical treatment or pretreatment. Incineration is preferred when the waste is nonreactive and when any extraneous material is combustible and manageable in available equipment.

Secured landfill disposal is the preferred route where the spill residue is highly toxic or persistent and contains noncombustibles.

In the case of inorganic wastes or residues, fixation followed by placement in a secure landfill replaces incineration

Table 1. *Matrix For Conventional Disposal Methods*

Type of Residue Mixture with Other Materials	*Hazardous Organic Waste*			*Hazardous Inorganic Waste*	
	Reactive	*Unreactive*	*Highly Toxic/ Persistent**	*Reactive*	*Highly Toxic/ Persistent**
Mixture with minor amounts of extraneous matter	*B O S*	*O S*	*O S*	*B*	*F-S*
Mixture with substantial amount of water	*A-B A-O A-S*	*A-O A-S*	*A-O A-S*	*B*	*A-F-S*
Mixtures with combustible solids	*B O*	*O S*	*O S*	*B*	*F-S*
Mixtures with small non-combustible solids	*B S*	*S*	*S*	*B*	*F-S*

* = *Toxicity characteristics given in full report*
B = *Treatment (chemical or biochemical)*
O = *Incineration*
S = *Secured landfill*
F = *Fixation*
A = *Concentrate and remove from water*

for those materials that cannot be removed from the environment by chemical treatment.

A modified matrix (Table 2) was also developed for future use and is based on two assumptions: (1) a secure landfill will ultimately be unacceptable and (2) certain novel technologies now under development will become commercial and will expand the range of deactivation options available.

The following novel techniques are cited in the full report as under development at the time of the study:

1. Thermal destruction of polychlorinated biphenyls in cement kilns
2. Dehalogenation of chlorinated hazardous wastes with elemental sodium
3. Chemical oxidation of combustible organic waste and waste mixtures with aqueous bromine
4. Highly energy decomposition of hazardous wastes and waste mixtures with microwave irradiation
5. Biochemical destruction of wastes with specific microorganisms
6. Wet air oxidation of hazardous wastes

Of these, all but microwave irradiation and bromine/water oxidation are still being actively considered.

Conclusions

Currently available technologies are often satisfactory for the ultimate disposal of the residues resulting from spills or releases of hazardous materials of low toxicity and persistence. But, at this time, no basis exists to assure that the most suitable method will be used in each spill situation. The use of recognized (licensed) hazardous waste management firms and facilities will help to ensure that appropriate methods are used.

Conventional technology is inadequate for the ultimate disposal of highly toxic and persistent materials, particularly when the residues from a spill are mixed with various extraneous materials. Differing forms of thermal destruction, including incineration, are well-suited to the destruction of highly toxic organics, but the distribution of suitably designed installations across the country may be inadequate to handle spill residuals. Disposing of toxic heavy metals in spill residues presents a special problem. Since these metals cannot be destroyed, various forms of fixation, as in glasses or minerals, become attractive for long-term immobilization.

Recommendations

Continued development of new disposal methods is required to close gaps in the capability of current technology and to overcome the lack of adequate disposal facilities.

Specific efforts should be focused on the total destruction of hazardous organic materials and the long-term immobilization of inorganic wastes, such as toxic "heavy" metals both in their cationic and anionic forms.

The use of landfill disposal for highly toxic and persistent materials should be phased out if the long-term integrity of such sites cannot be assured.

Though various thermal destruction systems are quite acceptable for the destruction of hazardous organic wastes, the distribution and availability of such facilities must be increased.

Alternative destruction methods are needed for: (1) localities where incineration systems are not available or expected soon, (2) low-volume wastes, and (3) residues containing various types of debris. Such alternatives include mobile incinerators and chemical destruction units for specific wastes (e.g., pesticides), modest volumes of mixed wastes, and residues from all but major spills and releases.

Much more work is needed on the fixation of inorganic wastes to assure long-term immobilization of toxic ("heavy") metals.

Spill cleanup personnel must be kept familiar with evolving hazardous waste regulations since these regulations apply to the complex residues from spill cleanups.

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Table 2. *Revised Matrix Using Novel Disposal Methods*

Type of Residue Mixture with Other Materials	*Hazardous Organic Waste*			*Hazardous Inorganic Waste*	
	Reactive	*Unreactive*	*Highly Toxic/ Persistent+*	*Reactive*	*Highly Toxic/ Persistent+*
Mixture with minor amounts of extraneous matter	*B* *O*	*O*	*O*	*B*	*F-S***
Mixture with substantial amount of water	*A-B* *A-O*	*A-O* *A-B*	*A-O* *A-B*	*B*	*A-F-S***
Mixtures with combustible solids	*L*-B* *O*	*O* *L-B*	*O*	*B*	*F-F-S***
Mixtures with small non-combustible solids	*L*-B* *L*-O*	*L-O* *L-B*	*L-O* *L-B*	*B*	*L-F-S***

+ = Toxicity characteristics given in full report
** = Optional*
*** = Not required if fixed product no longer meets hazardous waste criteria*
B = Treatment (chemical or biochemical)
O = Incineration
F = Fixation
A = Concentrate and remove from water
L = Leach
S = Secured landfill

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The complete report, entitled "Methods/Materials Matrix for Ultimate Disposal Techniques for Spilled Hazardous Materials," (Order No. PB 85-116 853; Cost: $28.00, subject to change) will be available only from:
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