TREATMENT TECHNIQUES FOR SPILLS OF HAZARDOUS WATER-SOLUBLE CHEMICALS — A FEASIBILITY STUDY*

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Summary

   Spills of hazardous chemicals which are water soluble are more difficult to treat than other spills where the chemical forms a separate phase. There is a need to develop treatment techniques which are applicable to a range of chemicals, which reduce the adverse environmental effects of the spill and do not introduce any additional environmental problems.
   Four techniques are examined in this paper: neutralization is effective for acids and bases, solvent extraction is effective for some organic chemicals, and precipitation and chelation are effective against some toxic metals. Each technique has some important practical limitations if further adverse environmental effects from the treatment agent are to be avoided. However, for each technique, one or more reagents can be selected which are effective, non-toxic and readily available.

1. Introduction

   The United States Coast Guard is responsible for responding to spills of hazardous chemicals into U.S. waters. Effective treatment of chemical spills is inherently difficult and the Coast Guard has carried out an extensive program of research to develop improved treatment methods. One of the first steps was an earlier study [1] to survey 400 hazardous chemicals listed in CHRIS [2] and to classify them into a few categories, each of which is potenti ally treatable by a single method. One broad classification is between those chemicals which are soluble and mix with water and those which do not. Studies by Srinivisan et al. [3] and Bauer et al. [4] provided information on the latter category. The study described here was restricted to chemicals which are soluble and therefore present throughout the water column.
   Soluble chemicals comprise a significant fraction of the hazardous chemicals which are transported by water or likely to spill into water bodies. They produce spills which are usually invisible, dispersed, and which cannot be re-

*Presented at the 1980 Conference on the Control of Hazardous Material Spills, Louisville, Kentucky.

moved physically by booms, skimming, or settling. Bulk properties such as density, boiling point, etc. are largely irrelevant and effective treatment of the spill relies on specific chemical or physical properties. From the results of the earlier study, four treatment techniques were identified which appeared to be promising for the treatment of soluble chemical spills. These techniques are:

1. Neutralization — for acids and bases,
2. solvent extraction — for organic chemicals,
3. precipitation — for toxic metals,
4. chelation — for toxic metals.

The objectives of this program were to determine for each of the above treatment techniques:

1. The most effective treatment against a large number of chemicals.
2. The treatment required to reduce the chemical to an environmentally "safe" level.
3. The optimum agent to spill ratio.

2. Methodology

The procedure used for each of the four treatment techniques was firstly to review the theoretical principles and define the parameters for comparison of different agents. Secondly, the agents were screened using the criteria in Table 1 to find the most effective candidate. Thirdly, any broad practical

TABLE 1

Criteria for choice of treatment agent

1. The agent should reduce the concentration of toxic species in solution below (or within) water quality criteria limits.
2. The agent should be soluble in water. (This does not apply to solvent extraction.)
3. Excess or misapplication of the agent should not cause water quality criteria to be exceeded.
4. Excess agent should not produce other adverse environmental effects (e.g., large pH changes, biological oxygen demand).
5. It should be low cost, readily available, and safe to use.

limitations were noted, and finally availability, cost of treatment and overall usefulness in treatment of spills was estimated. For further background information on equipment for delivery of the agent and environmental impacts of treatment the original report should be consulted [5].

3. Results

Neutralization

Principles of neutralization
Neutralization can be defined as the interaction of an acid with a base and

so is only applicable to spills of acids or bases or to spills of compounds which react with aqueous solutions to form acids and bases. Quantitatively, acidity and basicity are conveniently defined in terms of pH where:

$$pH = -\log [H^+]$$

An acid in solution produces hydrogen ions and, therefore, has pH < 7. A base in solution produces hydroxyl ions and has pH > 7. An exactly neutral solution or pure water has pH = 7.

The pH produced in the water after a spill depends on the strength of the acid or base and on its concentration. Therefore, the dilution caused by mixing mitigates the effect of the spill and must be taken into account. The strength of an acid is defined in terms of pK_a values (similar to pH values) such that:

$$pK_a = -\log K_a \text{ where } K_a = \frac{[H^+][A^-]}{[HA]}$$

For strong acids $pK_a < 4$ and for weak acids $pK_a \approx 5$ to 8. The strength of bases can be defined in the same way. Polybasic acids ionize in stages and the dissociation constants (K_{a1}, K_{a2}, K_{a3}) decrease successively.

The pH during neutralization of a strong acid by a strong base can be calculated from the equation

$$[H^+] = a - b$$

where $[H^+]$ is the hydrogen ion concentration and a and b are the concentrations in moles/liter of acid and base, respectively, in the final mixed volume.

For neutralization of a strong acid with a weak base the equation becomes more complex:

$$[H^+]^3 + [H^+]^2 [(b-a) + K_{a1}] - [H^+] (aK_{a1} + K_w) - K_{a1}K_w = 0$$

where K_1 is the dissociation constant of the base and $K_w = 10^{-14}$ the ionic product of water.

These equations can be solved numerically, or approximately by hand, to estimate the amount of agent required to neutralize the spilled chemical.

Selection of neutralizing agent

The U.S. water quality criteria limits for pH are 6—9; neutralization to exactly pH 7 is not required. However extreme deviations of pH in either direction cause adverse environmental effects, therefore, the consequences of misapplication or use of excess reagent are particularly important.

The calculated amounts of various bases required to neutralize a spill of hydrochloric acid are shown in Table 2. Sodium hydroxide, a strong base, is efficient but excess use, or misapplication results in a high pH outside the water quality limits.

Sodium carbonate is only acceptable if most of the agent neutralizes the spilled chemical. Sodium bicarbonate is the preferred reagent. It is a weak

TABLE 2

Consequences of excess or misapplication of agent

Neutralizing agent		Amount required (kg*)	pH after adding 20% excess past pH = 6	pH for misapplication of the neutralizing agent
1. Neutralization of hydrochlorid acid				
1.0 *M*	Sodium hydroxide	4.0	12.0	14.0
1.0 *M*	Sodium carbonate	2.8	7.1	12.1
1.0 *M*	Sodium bicarbonate	15.2	6.2	8.3
1.0 *M*	Urea	2.4×10^6	6.1	7.1
2. Neutralization of sodium hydroxide				
1.0 *M*	Sulfuric acid	4.9	0.85	0.3
1.0 *M*	Acetic acid	6.0	5.46	2.4
1.0 *M*	Sodium dihydrogen phosphate	12.2	7.87	4.5
1.0 *M*	Sodium bicarbonate	158	9.0	8.3

*For neutralization of a spill of 100 moles (3.6 kg of hydrochloric acid and 4 kg of sodium hydroxide).

base and even complete misapplication would not cause any pH problems but larger quantities are required for neutralization. Urea is unsatisfactory because impossibly large quantities would be required.

Similar conclusions can be drawn for the neutralization of a spilled base (also shown in Table 2). Sulfuric and acetic acids are not acceptable because of pH deviations, Sodium dihydrogen phosphate is the preferred reagent. Sodium bicarbonate is not acceptable for bases because of the large amount required for neutralization.

Practical limitations of neutralization

There are no serious limitations to the use of the preferred agents. Sodium bicarbonate and sodium dihydrogen phosphate are readily available in solid form and are not toxic. They pose no problems in storage and handling. Both agents are very soluble in water and can be applied as a slurry or solution. Their low cost (26 cents U.S./kg for bicarbonate, 55 cents U.S./kg for phosphate) makes neutralization possible even for large spills.

Range of application

Neutralization with sodium bicarbonate would be effective against spills of 13 chemicals classified as acids and 16 chemicals which react in water to form acids. Neutralization with sodium dihydrogen phosphate would be effective against 22 chemicals classified as bases and 6 chemicals that react in water to form bases; 6 other weak bases which were evaluated did not exceed the water quality limits for pH and therefore would not need neutralization.

Solvent extraction

Principles of solvent extraction

A two-phase ternary mixture of water, solvent and one other component may have a wide range of properties. The theoretical background is quite complicated [6, 7]. However, this study was not concerned with all possible combinations of three components, only with the extraction of one relatively dilute component from water into a solvent. For this simple case, the equilibrium properties of the system can be described in terms of the partition coefficient (Pc).

$$Pc = \frac{\text{wt. fraction of chemical in solvent}}{\text{wt. fraction of chemical in water}}$$

Selection of solvent

All organic chemicals which have a low solubility in water are candidate solvents, but of 22 solvents screened, only four (heptane, vegetable oil, oleyl alcohol and octanol), were acceptable on the basis of the first criteria, i.e. a solubility less than the toxic limit (see Table 3). Heptane was eliminated from

TABLE 3

Data on promising solvents for extraction of hazardous chemicals from water

	Density (g/cm³)	Interfacial tension (dynes/cm)	Boiling point (°C)	Range of partition coefficients
Heptane	0.68	40	98.4	0.001 — 1
Vegetable oil	0.92	50	high	0.0004 — 80
Octanol	0.83	8.5	195	0.01 — 250
Oleyl alcohol	0.83	35	300	0.02 — 200

further consideration because of its low boiling point, appreciable fire hazard and low partition coefficients for the chemicals of interest in this solvent.

Octanol shows the most favorable range of partition coefficients, with values as high as 250, although some compounds still had coefficients much less than 1. The low interfacial tension for octanol would make separation somewhat more difficult. Oleyl alcohol, with a higher interfacial tension, higher boiling point and very similar range of partition coefficients, looks more attractive than octanol, although the available data on use of oleyl alcohol as a solvent are much more limited. Overall, vegetable oils appear to be the most attractive because of their low toxicity.

Practical limitations of solvent extraction

Thermodynamic equilibrium may be closely approached with efficient mixing and separation, but partition coefficients greater than 10 would be

required for a single stage operation to remove most of the hazardous chemical. Multistage operation must generally be employed. Each extraction removes a smaller quantity of hazardous chemical from the aqueous layer. However with a partition coefficient equal to, or greater than unity, a five-stage extraction (the limit of most equipment) would give over 95% recovery.

The mass transfer rate of a chemical from water to a solvent is generally limited by the extent of the interfacial contact between the two phases. Therefore, procedures for solvent extraction must be designed to maximize the area and rate of contact of the water and solvent phases to achieve a rapid extraction.

Rapid separation of solvent and water phases after mixing is also an important criterion. This property is a compound function of the difference in densities and the difference in interfacial tension between the two phases. For example: if the density difference between the two phases is 10—20%, then a relatively low interfacial tension of 5—10 dynes/cm^2 can be tolerated; conversely, if the density difference between the two phases is only 1—5%, then a high interfacial tension, 40—50 dynes/cm^2 is essential to achieve an adequate separation. In practice, the interfacial tension is often the critical property because small amounts of impurities, particularly those with detergent properties, can modify the surface film severely and prevent efficient separation.

Recovery and re-use of solvent is essential for any but the smallest spills. Therefore, a high boiling solvent allows the chemical to be removed without evaporating and condensing the solvent. Soybean oil is a typical vegetable oil which is produced in high volume, is widely available and costs 45—50 cents U.S./kg. It is stored in closed containers (to prevent oxidation and bacterial attack) and is stable to heat, with a flashpoint above 280°C. The difference in density between vegetable oil and water is only 10%, but this is compensated by a high interfacial tension.

Range of application
75 water soluble organic chemicals were evaluated in the original study [5] for potential treatment by solvent extraction with the following results:
1. 26 chemicals required no treatment because of low toxicity to aquatic organisms.
2. 23 chemicals were not extractable with vegetable oil because the partition coefficient was less than unity. Typically these were hydrophilic compounds with more than one hydroxyl group.
3. 18 chemicals were extractable with vegetable oil.
4. 8 chemicals could not be classified because the partition coefficient data are not available.

Precipitation

Principle of precipitation
Chemical precipitation occurs when two water soluble reagents react and

form an insoluble compound which then precipitates as a solid in the water column. For example, copper can be precipitated from a solution of copper sulfate by the addition of a stoichiometric amount of sodium sulfide:

$$CuSO_4 + Na_2S = Na_2SO_4 + CuS\downarrow \text{ (precipitated)}.$$

The primary chemical reaction is generally followed by a secondary physical reaction known as coagulation where the solid particles form larger aggregates which makes them more easily separable from water by techniques such as sedimentation, centrifugation, filtration or flotation.

The primary concept in precipitation reactions is that of solubility product. This concept states that the product of the concentrations of the ions (in solution) which form the "insoluble" compound is a constant. In a very dilute solution the substance can be assumed to be completely ionized; thus $MA \rightarrow M^+ + A^-$. If S_0 is the solubility of MA in moles/liter, then

$$S_0 = [M^+] = [A^-].$$

Hence, for the solubility product K_s:

$$K_s = S_0^2 = [M^+] [A^-]$$

For example, the solubility product of silver chloride is 1.2×10^{-10} (moles/liter)^2. Thus, the mixing of sodium chloride and silver nitrate will form a precipitate of silver chloride and reduce the concentration of silver ion in solution to a very low value. Since the solubility product must hold under all conditions, the addition of excess reagent, e.g., excess chloride ions, will further reduce the concentration of silver ions in solution. This is known as the common ion effect.

Selection of precipitation agent

For many toxic metals, the carbonate, hydroxide, phosphate and sulfide and oxalate salts are generally insoluble in water. Therefore, using solubility products of the various metal salts obtained from the literature [8], calculations were made to determine the equilibrium concentration of toxic metals in solution after treatment with a stoichiometric amount or slight excess of reagent.

Comparison of the results with the water quality criteria limits for each metal then allows a determination of acceptability (i.e., concentration lower than the water quality limits) or unacceptability (concentration higher than the water quality limits). See Table 4. The metal ion concentration is lowest in a saturated solution containing sulfide. For each of the metals, the concentration is well below the recommended allowable limits. The next most effective agent is phosphate ion which will reduce all the toxic metals except silver to acceptable levels. The remaining anions decrease in effectiveness in the following order: hydroxide > carbonate > oxalate. Thus, on the basis of the initial screening (Table 4), sulfide and phosphate reagents appear to be strong potential candidates.

TABLE 4

Applicability of precipitating agents for toxic metals

Metal	Metal salt				
	Sulfide	Hydroxide	Carbonate	Phosphate	Oxalate
Cadmium	A	NA	NA	A	NA
Copper	A	A	NA	A	NA
Iron	A	A	NA	A	NA
Nickel	A	NA	NA	A	—
Zinc	A	NA	NA	A	NA
Antimony	A	—	—	—	—
Silver	A	NA	NA	NA	A

A = Acceptable.
NA = Not acceptable.

Hydrogen sulfide is not an acceptable agent because it is gaseous and very toxic. With the exception of sodium sulfide, metal sulfides are insoluble in water. However, sodium sulfide is strongly basic with a pH close to that of sodium hydroxide and misapplication of the reagent would produce a pH outside of the acceptable range of pH 6—9. Therefore, although it is a very effective precipitating agent, sodium sulfide is not recommended for the mitigation of spilled chemicals.

Phosphate ion is non-toxic and the preferred agent is dibasic sodium phosphate which is slightly alkaline with a pH of about 9.5. Moreover, it could be modified, if necessary, by the addition of a small quantity of phosphoric acid to reduce its pH to below 9. Dibasic sodium phosphate is a solid, widely used as a water treatment chemical and in the food industry. It costs 48 cents U.S./kg. An application rate of 0.3—1.0 kg of agent per kg of spilled chemical (depending on the toxic metal) is necessary for complete reaction. Since most heavy metal spills are small in size, the cost of reagent is not the most important factor.

Practical limitations of precipitation

If the toxic metal precipitated is not removed from the water body, then dilution by natural flow or mixing may cause some of the precipitate to dissolve. This effect would be more evident in a fast flowing river. An alternative method would be to treat the contaminated water in a mixer/settler system and contain the precipitate. Dissolved solids naturally present in the water may affect the reaction. For example, calcium ions form insoluble salts with many reagents and, if present in the water body, would reduce the efficiency of precipitation unless excess reagent was applied.

Range of application

Of 12 chemicals evaluated, 6 can be effectively treated with disodium

hydrogen phosphate. Silver also forms an insoluble phosphate but it is more effectively treated with sodium chloride forming highly insoluble silver chloride. (In marine waters, silver obviously needs no treatment.) Titanium tetrachloride hydrolyses in water to form non-toxic titanium dioxide and hydrochloric acid, therefore, it should be treated by neutralization. The phosphate reagent is not effective against soluble chromium or manganese compounds; spills of these chemicals can be treated to some degree by sodium sulfite or ferrous sulfate, preferably in a closed system.

Chelation

Principles of chelation
Chelating agents are compounds or ligands (generally organic) that coordinate, or bind, a metal ion in more than one position. This binding prevents the metal from reacting chemically and therefore reduces its toxicity. For example, the chelation of a copper ion by the tetrasodium salt of ethylene diaminetetraacetic acid (EDTA) can be represented by:

$$Na_2(EDTA) + Cu^{2+} \rightarrow Cu(EDTA) + 2Na^+$$
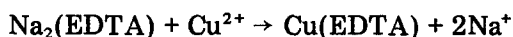
Copper displaces two of the sodium ions from the ligand and bonds the carboxyl groups, at the same time coordinating with the amino nitrogens.
The theory of chelation is described in reference works by Dwyer and Mellor [9] and Chaberek and Martell [10]. Effectiveness of a chelating agent for the reaction $M + L \rightleftharpoons ML$ is measured in terms of its stability constant K_1:

$$K_1 = \frac{[ML]}{[M][L]}$$

Using the Cu—EDTA chelate as an example, $K_1 = 6.3 \times 10^{18}$, so $[ML] = 6.3 \times 10^{18}[M][L]$, i.e., the concentration of metal chelate is over 10^{18} times the product of free metal and ligand concentrations in neutral solution.
Organic chelating agents may be divided into two classes, sequestrants and precipitants. In both cases, the metal ion is firmly bound and does not exhibit its normal toxicity. Sequestrants form chelate complexes which are soluble in water; therefore the compound still remains distributed throughout the water body. Precipitants, as the name implies, form insoluble chelates which may remain in suspension or collect at the bottom of the water body.

Selection of chelating agents
Sequestrants. Amino acids (glucine, cystein), hydroxy acids (citric and gluconic) and polyphosphates are all used as chelating agents, but they do not form sufficiently stable complexes with heavy metals and would not be very effective against spills. Amine derivatives of acetic acid which are also widely used do form stable chelates with most heavy metals and the stability constants are generally high enough ($K_1 > 10^8$) to reduce the toxic metal ions below the water quality criteria limits. Of this group, EDTA represents the pre-.

ferred agent because: it is widely used in industry food and medicine; it has a low toxicity; and it effectively chelates metals in the pH range 6—9. It is sold as a powder, generally as a sodium salt. The disodium salt has a pH in solution of 5—6. It costs about $7/kg and from 1 to 3 kg of EDTA are required to treat 1 kg of spilled chemical.

Chelating precipitants. These find their primary use in analytical chemistry for the separation and determination of metals [11]. Three reagents were selected for a preliminary evaluation.

Dimethylglyoxime is very effective in precipitating nickel, but not as effective in complexing other metals. Cupferron is a water soluble precipitant that chelates copper and titanium but is not as effective with other metals. Oxine (8-hydroxyquinoline) can precipitate a wide variety of metals but it is not very soluble in water, thus solutions are usually prepared in alcohol or acetic acid. Its effectiveness approaches that of EDTA if excess agent is used. All the precipitating agents examined have severe limitations. Oxine is probably the best choice because of its effectiveness with a range of metals (see Table 5). A major disadvantage is its low solubility in water. Oxine costs $14/kg and 0.5 to 2 kgs of agent are required to treat each kg of spilled chemical, it is thus more economical than EDTA on a weight basis (due to its lower molecular weight), but the cost of treatment is comparable.

TABLE 5

Acceptable chelating agents for treatment of spilled hazardous chemicals

Metal	$\log_{10}$ (Stability constant)	
	EDTA (sequestrant)	Oxine (precipitant)
Copper	18.8	12.0
Nickel	18.6	10.0
Zinc	16.5	8.5
Cadmium	16.5	8.2
Iron	14.3	8.0
Calcium	10.6	4.5
Magnesium	8.7	5.2

Practical limitations of chelation

Optimum treatment with EDTA should reduce the concentration of free metal cations to very low levels, but other metal cations present will be chelated to some degree (i.e., those from the spill and those present naturally), though the complexes with heavy metals which are more stable will be favored The extent to which EDTA will combine with heavy metals from sediments or suspended particles is uncertain, but may result in the solubilization of additional toxic material; the transfer of metals from sediments to solution in this manner has been shown to occur in the presence of NTA for example. EDTA (and presumably its complexes), has a finite lifetime in the aquatic en-

vironment. Both chemical oxidation and biochemical oxidation will slowly break down the organic molecule and result in the slow release of metal ion. The chelation of metals will increase their residence time in solution by impeding the natural removal processes such as precipitation and/or cation exchange. Oxine's low solubility may prevent addition of sufficient agent to treat a spill effectively. If the resulting oxine—metal complex did not settle well, a colloidal suspension of it would diffuse or be transported by flow in the affected water body.

The beneficial effects of reducing the toxic metal concentration will be offset by any toxic effects of the chelation complex. No information was found describing the aquatic toxicity of oxine and its complexes, but oxine (in the presence of copper or iron) is a powerful bactericide and fungicide which suggests that its toxicity to aquatic life may be quite high. Other potential adverse effects include: mobilization of other metals from sediments increases in BOD associated with slow degradation of the oxine and eventual release of metals back into the water column.

One possible way to avoid some of the limitations of oxine (limited solubility in water and toxicity) would be to employ the reagent in a closed loop solvent extraction system. The procedures and equipment would be similar to those described previously for solvent extraction of organic compounds. Oxine would remain in the solvent phase while extracting the toxic metal ion from the water.

Range of application
Chelation is effective against the same seven toxic metals which can be treated by precipitation but the cost of treatment is higher. Thus in most cases precipitation would be the first choice. EDTA may have a potential advantage in some situations where it is necessary to detoxify the spill without removing the metal from solution.

4. Conclusions

Neutralization
Spilled chemicals can be treated by neutralization. Strong acids and bases which are chemically the most efficient are not the preferred agents because of the adverse environmental effects of using excess agent or application of agent in the wrong place. These are very real difficulties in an actual spill situation where the amount of the spill, its location, and its extent must be estimated quickly and usually with inadequate information.

Solvent extraction
Solvent extraction of water soluble organic compounds is inherently difficult in a spill situation. Most potential solvents are unacceptable because their solubility in water is higher than their aquatic toxicity level. However vegetable oil is non-toxic and can potentially remove about 20% of the organ-

ic chemicals which were considered. It is not practical to add the solvent to the water body and therefore the contaminated water must be pumped throug mixing and separating equipment. This limits the number of spill situations where solvent extraction might be used. In some situations other methods, for example absorbents, might be more effective.

Precipitation

Precipitation is useful to treat a number of toxic metals. The preferred agent is non-toxic disodium hydrogen phosphate. In situ treatment of a spill is possible, and will diminish the immediate adverse environmental impacts from the spill. If the precipitate then settles to the bottom, dredging may be necessary. If it remains in suspension and disperses, there is a possibility of dissolution again, but at much lower concentrations than the original spill.

Chelation

Chelation is analogous to precipitation in that the complexes formed with toxic metals have a much lower toxicity than the original spilled chemical. If a sequestrant is used, the complex remains in solution and becomes diluted and dispersed. If a precipitant is used, the complex may settle to the bottom and need further treatment to remove it. Sequestrants offer some potential advantages over precipitation with phosphate, chelating precipitants probably do not. One disadvantage is the high unit cost of chelating agent, but this is offset to some extent by the fact that spills involving heavy metals are genrally small.

Acknowledgement

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