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A FEASIBILITY STUDY OF RESPONSE TECHNIQUES FOR DISCHARGES OF HAZARDOUS CHEMICALS THAT DISPERSE THROUGH THE WATER COLUMN

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July 1976

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16. Abstract

Certain hazardous chemical spills are soluble in water and may persist in the water column for long periods of time. In some cases, adverse environmental impacts of such spills may be ameliorated by a response method which either removes a major portion of the spilled chemical or which converts the chemical to a less harmful species.

In this program, the feasibility of four types of chemical treatment has been assessed for the amelioration of the effects of hazardous, water-soluble chemical spills. These treatments are: Neutralization, Solvent Extraction, Precipitation and Chelation.

For each technique, the treatment chemistry was studied, potential methods of application of the treating agent were evaluated and the environmental fate and consequences were assessed for the treatment options, including the possibility of misapplication of treating agent. In addition, future requirements for additional research and development needed to implement actual field response techniques and equipment are projected for each treatment method.

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METRIC CONVERSION FACTORS

Approximate Conversions to Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
in	inches	*2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
		AREA		
in^2	square inches	6.5	square centimeters	cm^2
ft^2	square feet	0.09	square meters	m^2
yd^2	square yards	0.8	square meters	m^2
mi^2	square miles	2.6	square kilometers	km^2
	acres	0.4	hectares	ha
		MASS (weight)		
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2000 lb)	0.9	tonnes	t
		VOLUME		
tsp	teaspoons	5	milliliters	ml
Tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft^3	cubic feet	0.03	cubic meters	m^3
yd^3	cubic yards	0.76	cubic meters	m^3
		TEMPERATURE (exact)		
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

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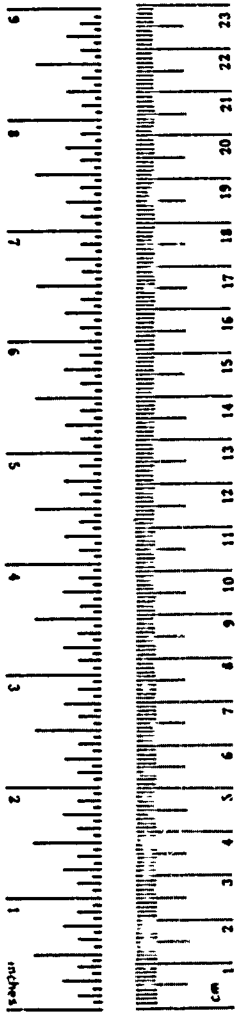
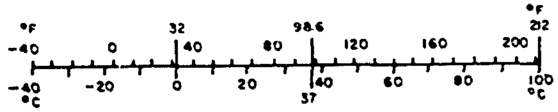
*1 in ≡ 2.54 (exactly). For other exact conversions and more detailed tables, see NBS Misc. Publ. 286, Units of Weights and Measures, Price $2.25, SD Catalog No. C13.10:286.



Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
		AREA		
cm^2	square centimeters	0.16	square inches	in^2
m^2	square meters	1.2	square yards	yd^2
km^2	square kilometers	0.4	square miles	mi^2
ha	hectares (10,000 m^2)	2.5	acres	
		MASS (weight)		
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	
		VOLUME		
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m^3	cubic meters	35	cubic feet	ft^3
m^3	cubic meters	1.3	cubic yards	yd^3
		TEMPERATURE (exact)		
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F



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SUMMARY

This report examines the feasibility of treating spills of chemicals which disperse throughout the water column and which are inherently more difficult to treat than those spills, such as oil, which form a separate phase in the water body. There are, at present, no effective methods to treat this type of spill and any proposed technique will encounter a number of theoretical and practical difficulties. In this work, we have examined in detail the feasibility of using four different methods as response techniques for amelioration of chemical spills which disperse in the water column. These are neutralization, solvent extraction, precipitation, and chelation. Each technique is applicable to a different class of compounds. For example, neutralization can only be applied to acids and bases; solvent extraction is potentially useful for organic compounds; and, precipitation and chelation are potentially useful for certain inorganic compounds, particularly toxic heavy metals.

In Chapter 1, we present the background, objectives and scope, and our approach to this problem. Each response technique is covered in a separate chapter-- 2 - neutralization; 3 - solvent extraction; 4 - precipitation; and, 5 - chelation. These chapters are organized to provide a description of the principles involved in the technique, the requirements to alleviate the ecological impact of the spill, the rationale for the screening of potential agents, and the final choice of the most appropriate agent(s). Potential deployment methods for the preferred agents are described and the fate and consequences of treatment considering both the effects of the spilled chemical and application or misapplication of the amelioration agent.

Chapter 6 describes our conclusions concerning each of the four treatment techniques. Neutralization appears to be a feasible and practical response technique for treatment of spilled chemicals which are acids and bases. We recommend treatment with sodium bicarbonate for acids and treatment with sodium dihydrogen phosphate for bases. With proper deployment, these agents can be expected to greatly ameliorate the effects of the spilled chemical without providing additional adverse effects on the environment.

Solvent extraction appears to be a feasible technique, but suffers from more practical limitations than neutralization. Vegetable oil appears to be the most satisfactory agent for this purpose and this material would have a limited effect on the environment due to its low toxicity and limited solubility in water. From the list of 75 organic chemicals considered in this report, about 20% appear extractable by vegetable oil. More than 25% of the chemicals are considered unextractable because of their highly polar nature. However, 35% of the chemicals listed have low toxicity limits and treatment is probably unnecessary.

The chemicals subject to amelioration by precipitation contain both cations and anions. Therefore, it is not theoretically possible for a single type of agent to be effective for both species. The number of agents which will reduce the concentration of the toxic element sufficiently is quite small and the most useful agent appears to be disodium hydrogen phosphate. This is the preferred precipitating agent for six out of the thirteen chemicals considered. The others require individual treatment and quantitative data to assess effectiveness of potential agents is lacking in the literature. No treatment is recommended for synthetic latex. Chelation has a limited applicability to the same group of thirteen chemicals. Two chelating agents have been identified, EDTA, (a sequesterant) and oxine, (a precipitant) which are applicable to five out of the thirteen chemicals studied. No suitable reagent was identified for the other eight chemicals.

In Chapter 7, we provide recommendations for future research on each of the four treatment techniques. Neutralization appears to be the most promising technique and should receive further support in the areas of additional laboratory testing, construction and testing of deployment equipment and field tests of the system in an actual or simulated spill situation. Solvent extraction also appears to warrant further development; but, first we suggest as a primary requirement, a careful comparison of solvent extraction with carbon adsorption to determine the relative efficiencies, areas of overlap and utility of these two techniques for ameliorating spills of organic chemicals. Both precipitation and chelation deserve further consideration because they are applicable to certain types of spills, e.g., toxic heavy metals, which can have extended adverse effects on the environment. There is a need to develop further data about specific chemical-agent interactions and the practical aspects of equipment, deployment techniques, modeling of spill amelioration and finally field testing in an actual or simulated spill situation. The long-term environmental impact also needs further consideration if the chemical precipitant and the chemical chelate are not removed from the aquatic environment.

I.0 INTRODUCTION

1.1 BACKGROUND

Chemicals which mix (dissolve) in water present one of the major current challenges to spill amelioration. Until recently, almost all research and development in spill clean-up has been devoted to those (insoluble) chemicals which are present in the water as separate phases; either floating (as oils) on the surface of the water, or deposited on the bottom. The deployment problems in removal of these chemicals are often difficult, particularly in rough waters, but the ability to physically separate the two phases significantly aids the detection, containment and removal of these spilled chemicals.

In contrast, soluble chemicals, which comprise a significant fraction of hazardous chemicals transported by water or likely to find their way into waterways, produce spills which are usually invisible, do not remain localized and cannot be removed by simple physical means such as booming, skimming or settling. Since the dissolved chemicals are present in the water body as separate molecules, rather than discrete phases, they disperse much more rapidly, and their treatment is made more difficult as they become more dilute and dispersed. Finally, since they are dispersed, the bulk properties of the chemicals (such as density, viscosity, freezing point, etc.) are largely irrelevant, and their removal depends upon the specific chemical or physico-chemical behavior of the particular chemical.

Because of these severe difficulties of rapid dispersion and chemical specificity, amelioration techniques for soluble chemicals have been largely neglected. At present, there is only one widely-used way in which the effect of soluble spills is moderated: dilution. Although this is an easy, and often most practical method on the open seas, it may not be adequate in enclosed bodies of water such as small ponds and lakes, in low current rivers, or for large spills in harbors and estuaries. It may also be undesirable to simply dilute very toxic spills, since the risk to the environment after dilution may still be considerable. Other techniques, particularly carbon and ion-exchange resin adsorption, are currently under study for removal of hazardous chemicals, but the utility of these techniques is restricted to a moderately small class of chemicals, and the feasibility of their deployment is limited.

The Coast Guard, in an effort to determine categories of chemical and physical treatments which might be useful for amelioration of hazardous chemical spills, has recently completed a program[*] in which 400 potentially hazardous chemicals were classified into physical and chemical categories. Considerable effort was devoted to dividing these chemicals into the minimum number of physical or chemical categories which would allow all chemicals in a given category to be treated by a single amelioration method. The objective was to eventually arrive at a minimum number of amelioration methods which would be generally applicable to wide classes of spills. For each of these physico-chemical classes, a number of potential spill amelioration techniques were suggested. Identification of these treatment methods was based on theoretical aspects of the chemicals and/or the treatment methods. No effort was devoted at that time to determining which of these theoretically feasible techniques could be translated into practical usable amelioration methods under the real-world constraints of rapid response, high volume, limited facilities, personnel with limited training, and most important, the practical limitations of working on the open seas or in a rapidly flowing river.

The Coast Guard has now identified four treatment techniques which appear, at least on the basis of theoretical and laboratory data, to be particularly promising for the amelioration of soluble chemical spills. These are neutralization of acids and bases, solvent extraction, precipitation and chelation of metal ions. Three classes of chemicals have been specified for treatment by each of these techniques. (A single class of chemicals has been assigned for potential treatment by either precipitation and/or chelation.) These chemicals are listed in Appendix A of this report.

Amelioration of a spill of a hazardous water-soluble chemical involves coping with two major elements of the spill: (1) the chemical

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[*] "Survey Study to Select a Limited Number of Hazardous Materials to Define Amelioration Requirements", Coast Guard Report CG-D-46-75, Vol. I, Vol. II, March (1974).

nature of the spilled material; and (2) the location of the chemical itself--not only at the point of the accident, but, equally important, at the points upstream and downstream of the accident location as the chemical disperses. It is this second element--dispersal (and concommitant dilution)--that is perhaps the most difficult aspect of the spill amelioration problem. Without adequate means for locating the spilled chemical and deploying the treatment agents where the chemical is actually located at a real point in time, the effectiveness of chemical treatment methods is considerably diminished except possibly for small lakes and ponds.

However, keeping in mind the difficulties anticipated in locating the contaminated zone in a flowing water body, it is necessary to first evaluate whether a particular chemical response is feasible and effective. For responses that are chemically feasible and which show potential for ameliorating the environmental consequences of a hazardous, water-soluble chemical spill, it is also necessary to ascertain whether the response can be effective in terms of U.S. Coast Guard spill control operations. This requires an evaluation of cost and availability of materials, methods of transportation for chemicals and treating equipment to the contaminated water zone, and methods of application.

1.2 OBJECTIVES AND SCOPE

The objective of this program was to determine, for each of the four treatment techniques (i.e., neutralization, solvent extraction, precipitation and chelation):

- The concentration range to which each class of chemical would have to be reduced in order to reach an environmentally "safe" level.
- A minimum number of high potential treatment agents in each class which would reduce the contamination level to a "safe" value.
- A minimum number of high potential methods for the effective deployment of these treatment agents.
- The optimum agent-to-spill ratio required to reduce contamination to the "safe" level.

- The ultimate environmental fate of the spilled chemical, the agent and the reaction products, and the possible environmental consequences of treatment.
- The preferred agent(s) and technique(s) for further development by the Coast Guard identified on the basis of efficiency, practicality of deployment and environmental consequences.
- The equipment and deployment methodology required and a research plan for the development of the proposed technique.

1.3 APPROACH

Levels of water quality required to be met by the proposed treatment methods are based on water quality standards from Governmental agencies (the Environmental Protection Agency and the National Academy of Sciences), where they exist. Where these criteria do not exist, we based our criteria on a literature search and on in-house experience.

Selection of desirable treatment agents was based on the known properties of the agents and spill chemicals, and on screening the effectiveness of the agents in reducing the contaminant to the required level, the practical properties of the spill agent (cost, density, physical state, etc.) and the environmental risks associated with using the agent.

Evaluation of deployment methods included consideration of equipment, means of transport to the response zone and in situ effects of treatment using spill dispersion modeling based on a model already developed by ADL.

In the study of deployment methods for solvent extraction, chelation, and precipitation, we also considered the relative merits of adding the treatment agent to the water body versus the alternative of pumping the water through a treatment station containing the treatment agent and post-treatment separation equipment. We also considered the relative merits of having the "treatment station" on shore or on board ship.

Selection of the preferred methods for further study by the Coast Guard was based upon the following criteria:

- Environmental Fate and Consequences: Ultimate fate of the spilled chemical, agent and reaction products, and their consequences on the environment including toxicity and other hazards; possible consequences of sub-optimum treatment such as overtreatment, undertreatment, and application at incorrect location; relative hazards of the original spill and the treatment agent and/or reaction products.

- Chemical Agent: Cost, availability, storage requirements, significant weight or volume differences, physical state, shelf life, and effectiveness in ameliorating chemical spills to the desired "safe" levels.
- Application Equipment and Personnel: Type of equipment, cost, availability, current state-of-the-art; difficulty of agent application, level of expertise required to operate equipment, manpower and other facilities required for deployment and operation of equipment, equipment delivery and deployment problems.

The research plan for the development of the preferred technique(s) includes:

- Description of further research needed to demonstrate the efficacy of the treatment agent on reducing spill chemical contamination to the required level in cases where the reaction chemistry is partly or largely unknown.
- Development of deployment methods (including dispersion modeling and detection methods), equipment, and procedures.
- Research into environmental consequences.

Priorities have been set on the basis of those areas most likely to yield practical results for chemical spills with high hazard ratings.

2.0 NEUTRALIZATION

2.1 PRINCIPLES OF NEUTRALIZATION

Neutralization, for the purposes of this task, can be defined as the interaction of an acid with a base. Therefore as a corollary, neutralization is only applicable to spills of acids or bases or to spills of compounds which react in aqueous solution to form acids and bases. Neutralization adds further components to the aqueous environment unless the "salt" produced is volatile and escapes to the atmosphere or is insoluble and settles to the bottom. However, since excess acidity or basicity produced by a spill is harmful to the environment regardless of the specific nature of the compound, neutralization will produce a beneficial effect.

Pure water is very slightly dissociated into hydrogen and hydroxyl ions according to the equation,

$$H_2O = H^+ + OH^- \qquad 2.1\text{-}(1)$$

At room temperature, the concentrations of hydrogen ions $[H^+]$ and hydroxyl ions $[OH^-]$ are each equal to 10^{-7} mols/ℓ. Natural waters are generally not neutral due to the presence of naturally occurring acidic or basic substances in solution. An acid can be simply defined as a compound which dissolves in water to form hydrogen ions (H^+) and a base as a compound which dissolves in water to give hydroxyl ions (OH^-). Quantitatively, acidity and basicity are conveniently defined in terms of pH where

$$pH = -\log [H^+] \qquad 2.1\text{-}(2)$$

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 effects mitigates the effect of the spill and must be taken into account when considering the requirements for neutralization. In addition, exact neutralization to $pH = 7$ is not practical or even desirable in some cases and the extent of neutralization required is discussed in the context of the water quality criteria which are developed in section 2.3.

2.2 ELEMENTS OF ACID-BASE THEORY

2.2.1 Acids

An acid may be defined as a substance which when dissolved in water, undergoes dissociation with the formation of hydrogen ions according to the equation below for a monobasic acid:

$$HA = H^+ + A^-$$

with 2.2-(1)

$$Ka = \frac{[H^+]\ [A^-]}{[HA]}$$

where $[H^+]$, $[A^-]$, $[HA]$ are approximately equal to the concentrations of these components in <u>dilute</u> solution. Ka is the dissociation constant. Strong acids such as hydrochloric and nitric acids are almost completely dissociated in solution; thus Ka for these acids is very large.

Polybasic acids such as sulfuric or phosphoric acids ionize in stages with progressively smaller dissociation constants. For example, in sulfuric acid the first hydrogen ion is completely ionized while the second hydrogen ion is only partly ionized, i.e.,

$$H_2SO_4 = H^+ + HSO_4^- \qquad Ka_1 = \text{very large}$$

$$HSO_4^- = H^+ + SO_4^= \qquad Ka_2 = 10^{-2} \qquad 2.2\text{-}(2)$$

For the tribasic acid, phosphoric acid,

$$H_3PO_4 = H^+ + H_2PO_4^- \qquad Ka_1 = 7 \times 10^{-3}$$

$$H_2PO_4^- = H^+ + HPO_4^= \qquad Ka_2 = 6 \times 10^{-8}$$

$$HPO_4^- = H^+ + PO_4^{\equiv} \qquad Ka_3 = 5 \times 10^{-13} \qquad 2.2\text{-}(3)$$

Thus the <u>first</u> hydrogen ion of phosphoric acid is strongly hydrolyzed but the <u>third</u> hydrogen ion is weakly hydrolyzed.

In measuring the strength of acids it is convenient to define pKa values (similar to pH values) where

$$pKa = -\log Ka \qquad 2.2\text{-}(4)$$

A low value for pKa indicates a strong acid with a high degree of dissociation. Strictly speaking, the free hydrogen ion H^+ does not exist in aqueous solution; each hydrogen ion combines with a molecule of water to form a hydronium ion H_3O^+.

2.2.2 Bases

A base can be defined in an analogous manner as a substance which dissolves in water undergoing dissociation with the formation of hydroxyl ions

$$BOH \rightleftarrows B^+ + OH^-$$

$$K_b = \frac{[B^+]\,[OH^-]}{[BOH]}$$

$$pKb = -\log K_b \qquad 2.2\text{-}(5)$$

Strong bases such as sodium hydroxide and potassium hydroxide are completely dissociated in aqueous solution; ammonium hydroxide is a weak base which is only dissociated to a small extent.

2.2.3 Water

We have noted that in pure water

$$[H^+]\,[OH^-] = Kw = 10^{-14} \qquad 2.2\text{-}(6)$$

where Kw is defined as the ionic product of water. This relationship must still hold in acidic or basic solutions; therefore

$$Ka = Kw/Kb$$

$$pKa = 14 - pKb \qquad 2.2\text{-}(7)$$

2.2.4 Buffers

A buffer is a mixture of a weak acid (or base) and its salt which has the power to stabilize a solution around a predetermined pH during the addition of acid or base. Conversely, addition of excess buffer to an acid will give a pH close to the pH of the buffer itself. To understand buffer action, it is necessary to study the equilibrium between a weak acid and its salt. The dissociation of a weak acid is given by

$$HA \rightleftarrows H^+ + A^-$$

$$[H^+] = \frac{[HA]}{[A^-]} \cdot Ka \qquad 2.2\text{-}(8)$$

This equilibrium is also applicable to a weak acid even if there is salt MA present. If the initial concentrations of acid and salt are denoted [acid] and [salt] respectively, then the concentration of undissociated acid is [acid] -

$[H^+]$ and of anion is [salt] + $[H^+]$ at equilibrium. (The salt is assumed to be completely dissociated.)

Therefore,

$$[H^+] = \frac{[Acid] - [H^+]}{[Salt] + [H^+]} \cdot Ka \qquad 2.2\text{-}(9)$$

This equation can be solved as a quadratic but it may be simplified by assuming that the dissociation of the weak acid is suppressed by the common ion effect, i.e., $[H^+] <<< [Acid]$ or [Salt]. The above equation then reduces to

$$[H^+] = \frac{[Acid]}{[Salt]} \cdot Ka$$

$$pH = pKa + \log \frac{[Salt]}{[Acid]} \qquad 2.2\text{-}(10)$$

Similarly for a mixture of a weak base with its salt

$$[H^+] = \frac{Kw}{Kb} \cdot \frac{[Salt]}{[Base]}$$

$$pH = pKw - pKb - \log \frac{[Salt]}{[Base]} \qquad 2.2\text{-}(11)$$

Buffering capacity is maintained over the range of acid to salt ratios from 10:1 to 1:10; therefore, the approximate pH range for a buffer is

$$pH = pKa \pm 1 \qquad 2.2\text{-}(12)$$

2.2.5 Calculation of pH of Unneutralized Spill

If the concentration and dissociation constant for a spilled acid (monobasic) or base (monoacidic) is known (or can be estimated), then the pH may be calculated. An exact calculation (assuming pure water) would require the solution of Eq. 2.2-(13) for $[H^+]$, the concentration of hydrogen ions.

$$[H^+]^3 + Ka[H^+]^2 - [H^+](Kw + M_0Ka) - KwKa = 0 \qquad 2.2\text{-}(13)$$

M_0 - original concentration of acid (moles/liter)
Ka - acid dissociation constant
Kw - dissociation constant for water = 10^{-14} (25°C)

This cubic equation may be solved numerically or the approximations given in Table 2.2-1 may be used for the special cases indicated.

For dibasic acids H_2A with $Ka_1 > Ka_2$

$$[H^+] = \frac{[H_2A]\ Ka_1}{[H^+]} \cdot \left[1 + \frac{2Ka_2}{[H^+]} \right] \qquad 2.2\text{-}(14)$$

If $Ka_1 >> Ka_2$, then the appropriate equation for a monobasic acid may be used. In tribasic acids, e.g., H_3PO_4, the existence of a Ka_3 may generally be ignored.

2.2.6 Calculation of pH During Neutralization

If the volume, V_0, and concentration, M_0 (moles/liter), of the spill are known*, then the pH of a partially neutralized spill of a strong acid or strong base may be obtained. The relevant (approximate) equations are given in Table 2.2-1. When weak acids and weak bases are involved, an exact solution for $[H^+]$ becomes quite complicated, requiring the solution of a set of seven simultaneous equations with seven unknowns. The approximations given in Eq. 2.2-(1), 2.2-(15), and 2.2-(16) are only useful when (1) the initial concentration M_0, is large compared with the acid or base dissociation constant (Ka or Kb) of the spilled material, and (2) the neutralization is some distance from the equivalence point. For the partial neutralization of a dibasic acid by a strong base BOH the following equations are valid:

$$[H^+]^3 + [B^+]\ [H^+]^2 - [H^+]^2\ [H_2A]\ K_1 + Kw - 2[H_2A]\ K_1K_2 = 0 \qquad 2.2\text{-}(15)$$

$$\text{where} \quad [B^+] = M_1V_1/(V_1 + V_0) \quad \text{and} \quad [H_2A] = M_0 - [H^+] \qquad 2.2\text{-}(16)$$

Calculation of the pH at the equivalence point and beyond may be done with the equations given in Table 2.2-1. However, the approximations start to break down when weak acids or weak bases are used as neutralizing agents and more complex equations may be necessary depending on the accuracy required. A more comprehensive treatment of the formulas involved in such calculations may be found in Ricci.[26]

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* V_0 and M_0 refer to the volume and concentration of the contaminated water, not the raw spill material.

TABLE 2.2-1

CALCULATION OF pH DURING SPILL NEUTRALIZATION

$pH = -\log_{10}[H^+]$

Type of Spill	$[H^+]$ of Unneutralized Spill	$[H^+]$ of Spill During Treatment	$[H^+]$ at Neutralization Point	$[H^+]$ with excess Neutralizing Solution Added
Strong Acid $Ka > 10^{-4}$ (monobasic)	$[H^+] = Mo$	$[H^+] = \frac{VoMo - V_1M_1}{Vo + V_1}$	$[H^+] = \sqrt{Kw}$	$[H^+] = \frac{Kw(Vo+V_1+Vex)}{Vex\ M_1}$
Strong Base $Ka > 10^{-4}$ (monoacid)	$[H^+] = \frac{Kw}{Mo}$	$[H^+] = \frac{Kw(Vo+V_1)}{VoMo+V_1M_1}$	$[H^+] = \sqrt{Kw}$	$[H^+] = \frac{Vex\ M_1}{Vo+V_1+Vex}$
Weak Acid $Ka = 10^{-5}$ to 10^{-8} (monobasic)	$[H^+] = \sqrt{MoKa}$	$[H^+] = Ka\left(\frac{VoMo - V_1M_1}{V_1M_1}\right)$	$[H^+] = \sqrt{\frac{KaKw}{c}}$	$[H^+] = \sqrt{\frac{KaKw}{c}} + \frac{Kw(Vo+V_1+Vex)}{Vex\ M_1}$
Weak Base $Kb = 10^{-5}$ to 10^{-8} (monoacid)	$[H^+] = \frac{Kw}{\sqrt{MoKb}}$	$[H^+] = \frac{Kw}{Kb}\left(\frac{V_1M_1}{VoMo - V_1M_1}\right)$	$[H^+] = \frac{\sqrt{Kwc}}{\sqrt{Kb}}$	$[H^+] = \sqrt{\frac{Kwc}{Kb}} + \frac{Vex\ M_1}{Vo+V_1+Vex}$

NB Equations are only valid for strong neutralizing agents Ka or $Kb > 10^{-4}$

Ka, and Kb are the dissociation constants for the acid, and base, $Kw = 10^{-14}$ at 25°C

Mo = concentration of spilled material (in moles/liter) in the untreated water

Vo = volume of water contaminated by the spill (liters)

M_1 = concentration of neutralizing agent (in moles/liter) in neutralizing solution being added

V_1 = volume of neutralizing solution added (liters)

Vex = volume of excess neutralizing solution added (liters)

$c = Mo\left(\frac{Vo}{Vo+V_1}\right) - Kw/[H^+]$; in general, second term here, $Kw/[H^+]$, may be neglected if the first term is greater than about 100 Kw/Ka for neutralization of acids, or 100 Kw/Kb for neutralization of bases.

2.3 WATER QUALITY CRITERIA FOR pH

2.3.1 The pH Range in Natural Waters

TERRESTRIAL - The acidity-alkalinity range of terrestrial waters varies over nearly the entire pH range. The waters of Kata-numa, a volcanic lake in Japan, are essentially fairly concentrated sulfuric acid with a pH of 1.7. Another crater lake, Kawah Idjen, in Indonesia, may even have a pH of less than 0.7. Such highly acid waters are by no means restricted to volcanic regions. Biological activity and the decay of dead vegetable material can produce high acidity. For example, the sphagnum-mat-edged pools around Mud Lake, Michigan, can have a pH as low as 3.3. Biological acidification of fresh water can be greatly aggravated by human activity, as in the well-known case of acid mine drainage. Waters in the bituminous coal region near Elkins, West Virginia, for example, have pH values close to 3.

On the other extreme, highly alkaline waters are also formed in nature, especially in arid regions such as the American Southwest. Lake Nakura, an alkaline lake in Kenya, Africa, has a pH of 12.

But such highly acid and alkaline waters are the exception rather than the rule and "normal" terrestrial waters have pH values usually within 1 unit of neutral; pH 7. Lake Erie, for example, is slightly alkaline with pH of 7.7. A series of streams reviewed by Stumm and Morgan (1970)[30] fell in the pH 6.6-8.0 range, and a series of ground waters, pH 6.8-8.0.

MARINE. - In contrast to terrestrial waters, the pH of seawater is restricted to a narrower range (Table 2.3-1). Surface values in the Western Pacific, for example, stay pretty much within the range pH 8.0-8.4. Within this range, however, the deep-sea pH profile can exhibit some significant features. As in terrestrial waters, biological activity, notably photosynthesis, can affect the pH of seawater, giving rise to interesting diurnal and seasonal fluctuations. For example, in a shallow Texas bay, Park et al[22] observed that on a summer day the pH rose from about pH 8.2 in the morning to pH 8.9 in the afternoon, and that in winter the pH ranged about 0.5 units less. In biologically rich tropical water even greater diurnal ranges of pH 7.3 to 9.5 are not uncommon.

TABLE 2.3-1

pH Ranges in Natural Waters

	pH Range
TERRESTRIAL WATERS	
Exceptional	1-12
"Normal"	6.5-8
MARINE WATERS	7.5-8.4

The oceans of earth are a highly buffered aquatic system and this controls the pH to within narrow limits. The carbon dioxide-carbonate system (Figure 2.3-1) is believed to be responsible for this control; however, in recent years the importance of the contributions of ion-exchange and other equilibria, especially involving silicate minerals, has gained growing recognition. The salt content of the seas is in fact the consequence of a gigantic titration or neutralization taking place throughout geological time of alkaline crustal material mobilized by weathering and acidic outgassing of the earth's crust. This global neutralization is also occurring locally in terrestrial waters but because of their transitory nature, the "end point" is often never approached.

Change of pH is a product of more critical biological stress than a sustained pH level. Natural rates of change in pH are probably fairly slow. In the case of the shallow Texas bay cited above, the pH changed by about 0.7 within a 12 hour period, due to photosynthetic activity; this probably represents a fairly drastic change in a natural environment. Solar warming could also contribute to the afternoon peak in pH since the solubility of atmospheric CO_2 in water (Figure 2.3-1) decreases with increasing temperature.

2.3.2 Water Quality Standards for pH

The Committee on Water Quality Criteria of the Environmental Studies Board of the National Academy of Sciences, National Academy of Engineering,[34] has recommended that, for marine waters, (1) "the normal range (presumably of the site in question) of pH in either direction should not be extended by more than 0.2 (pH) units", that (2) "within the normal range the pH should not vary by more than 0.5 units", and that (3) "addition of a foreign material should not drop the pH below 6.5 or raise it above 8.5". How the value 0.2 was arrived at is unclear. Presumably recommendation 1 or 3 should be applied, depending upon which is the most (?) restrictive. The 0.5 unit change in recommendation 2 is, as we have seen, less than the range of rapid natural changes but may nevertheless be reasonable. Comparison with Table 2.3-1 suggests that, in recommendation 3, the lower limit of 6.5 may be much too low, especially when one remembers that the synergistic effects of high acidity may be considerable.

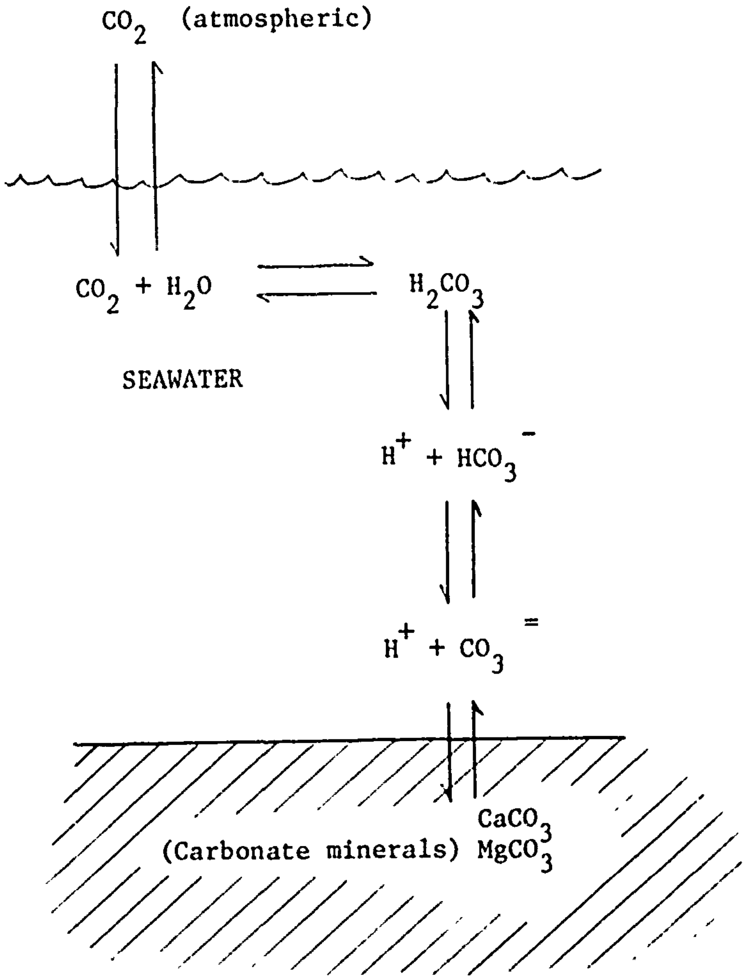

FIGURE 2.3-1

Buffering Seawater pH by the Carbon Dioxide - Carbonate System

Recommendations for terrestrial waters are in terms of level of protection (Table 2.3-2). Comparison with Table 2.3-1 suggests that the recommendations for a "high level" of protection are reasonable and also seem to correspond roughly to the same degree of protection that is recommended for marine waters. Whether terrestrial waters need the same, a greater, or lesser level of protection than marine waters is subject to debate.

Some uses are less restrictive than others. A pH range of 4.5 to 9.0 has been proposed as acceptable for irrigation and 5.0 to 9.0 for public drinking water, as compared to 6.0 to 9.0 for fresh water and 6.5 to 8.5 for marine aquatic life.[24]

2.3.3 The pH Limits for Aquatic Life

Organisms have adapted to environments that are astonishingly extreme with respect to pH. Acid pools and alkaline lakes can teem with life. pH 2-10 appear to be the extreme limits for living organisms. The cells of a stomach are undamaged by the gastric juices - a hydrochloric acid solution - and acid-mine drainage, it might be noted, is the consequence of the activity of micro-organisms. Natural, unbuffered terrestrial waters with pH 4 derived from carbon dioxide and natural organic acids can support flourishing biocommunities, and waters with a pH as high as 9.5 can support fish but tend not to be highly productive. Table 2.3-3 summarizes some of the known effects of pH on terrestrial water biota. It should be noted that not only do different species exhibit different tolerances to pH, but also the tolerance of a given species can be different for different stages in its life cycle. Reproduction, for example, can be seriously reduced by pH's which do not appear to adversely affect the adult organisms. In as much as terrestrial waters, being relatively unbuffered, generally exhibit greater pH ranges and fluctuations than sea water, fresh water organisms have adapted correspondingly and tend to be more tolerant of pH change than marine organisms. Oysters appear happiest in brackish waters of about pH7.0, but at only a half a pH unit lower, at pH 6.5, their activity is very significantly reduced. Not unexpectedly, organisms can tolerate relatively large pH changes within the normal ambient range, whereas relatively small changes at the limits of these ranges can be harmful.

TABLE 2.3-2

Recommendations for Terrestrial Waters

Level of Protection	pH Range	pH Change
Nearly Maximum	6.5-8.5	0.5
High Level	6.0-9.0	0.5
Moderate Level	6.0-9.0	1.0
Low Level	5.5-9.5	1.5

TABLE 2.3-3
Some Known Effects of pH on Terrestrial Water Biota

11.5-12.0	Some caddis flies (Trichoptera) survive but emergence reduced.
11.0-11.5	Rapidly lethal to all species of fish.
10.5-11.0	Rapidly lethal to salmonids. The upper limit is lethal to carp (Cyprinus carpio), goldfish (Carassius auratus), and pike. Lethal to some stoneflies (Plecoptera) and dragonflies (Odonata). Caddis fly emergence reduced.
10.0-10.5	Withstood by salmonids for short periods but eventually lethal. Exceeds tolerance of bluegills (Lepomis macrochirus) and probably goldfish. Some typical stoneflies and mayflies (Ephemera) survive with reduced emergence
9.5-10.0	Lethal to salmonids over a prolonged period of time and no viable fishery for coldwater species. Reduces populations of warmwater fish and may be harmful to development stages. Causes reduced emergency of some stoneflies.
9.0-9.5	Likely to be harmful to salmonids and perch (Perca) if present for a considerable length of time and no viable fishery for coldwater species. Reduced populations of warmwater fish. Carp avoid these levels.
8.5-9.0	Approaches tolerance limit for some salmonids, whitefish (Coregonus), catfish (Ictaluridae), and perch. Avoided by goldfish. No apparent effects on invertebrates.
8.0-8.5	Motility of carp sperm reduced. Partial mortality of burbot (Lota lota) eggs.
7.0-8.0	Full fish production. No known harmful effects on adult or immature fish, but 7.0 is near low limit for Gammarus reproduction and perhaps for some other crustaceans.
6.5-7.0	Not lethal to fish unless heavy metals or cyanides that are more toxic at low pH are present. Generally full fish production, but for fathead minnow (Pimephales promelas), frequency of spawning and number of eggs are somewhat reduced. Invertebrates except crustaceans relatively normal, including common occurrence of mollusks. Microorganisms, algae, and higher plants essentially normal.
6.0-6.5	Unlikely to be toxic to fish unless free carbon dioxide is present in excess of 100 ppm. Good aquatic populations with varied species can exist with some exceptions. Reproduction of Gammarus and Daphnia prevented, perhaps other crustaceans. Aquatic plants and microorganisms relatively normal except fungi frequent.
5.5-6.0	Eastern brook trout (Salvelinus fontinalis) survive at over pH 5.5. Rainbow trout (Salmo gairdneri) do not occur. In natural situations, small populations of relatively few species of fish can be found. Growth rate of carp reduced. Spawning of fathead minnow significantly reduced. Mollusks rare.
5.0-5.5	Very restricted fish populations but not lethal to any fish species unless CO_2 is high (over 25 ppm), or water contains iron salts. May be lethal to eggs and larvae of sensitive fish species. Prevents spawning of fathead minnow. Benthic invertebrates moderately diverse, with certain black flies (Simuliidae), mayflies (Ephemerella), stoneflies, and midges (Chironomidae) present in numbers. Lethal to other invertebrates such as the mayfly. Bacterial species diversity decreased; yeasts and sulfur and iron bacteria (Thiobacillus-Ferrobacillus) common. Algae reasonably diverse and higher plants will grow.
4.5-5.0	No viable fishery can be maintained. Likely to be lethal to eggs and fry of salmonids. A salmonid population could not reproduce. Harmful, but not necessarily lethal to carp. Adult brown trout (Salmo trutta) can survive in peat waters. Benthic fauna restricted, mayflies reduced. Lethal to several typical stoneflies. Inhibits emergence of certain caddis fly, stonefly, and midge larvae. Diatoms are dominant algae.
4.0-4.5	Fish populations limited; only a few species survive. Perch, some coarse fish, and pike can acclimate to this pH, but only pike reproduce. Lethal to fathead minnow. Some caddis flies and dragonflies found in such habitats; certain midges dominant. Flora restricted.
3.5-4.0	Lethal to salmonids and bluegills. Limit of tolerance of pumpkinseed (Lepomis gibbosus), perch, pike, and some coarse fish. All flora and fauna severely restricted in number of species. Cattail (Typha) is only common higher plant.
3.0-3.5	Unlikely that any fish can survive for more than a few hours. A few kinds of invertebrates such as certain midges and alderflies, and a few species of algae may be found at this pH range and lower

Source: Reference 34

A spill of an acidic substance, for example, is not a single impact; it is a barrage of environmental stresses (Figure 2.3-2) presenting, in the cases where the spill is combated by neutralization, at least 10 critical aspects. There is first the natural pH level (1) and the natural fluctuation of the pH level (2) which define the pH range to which the impacted biota are accustomed. Both the change of pH resulting from the spill (3) and the rate of this change (4) are important. Rapid changes in the ambient environment tend to be especially traumatic and one might expect a gradual movement, even amounting to a greater pH increment, to be less disruptive than a rapid but somewhat smaller increment. Similarly, the duration of exposure (6) to the stress may be as important as the magnitude of the stress (5). Very little appears to be known about the effect of exposure duration. However, while some species may have some capability to adapt to an extended exposure stress, generally one expects the larger the exposure the greater the damage. The neutralization of the spill (7) is another traumatic environmental impact which could in itself be very damaging even if there is no overshoot (8) of the neutralization. This raises a question which needs a great deal more reflection. Will a second rapid traumatic event, the neutralization, do more damage than persistent, but slow diminution by dilution of the original impact? Even after recovery (9) and the pH range of the waters has been restored to its former value (10), damage, for example in the form of the altered biopopulation distributions, may persist.

Response to a pH-altering spill must also take into consideration the mixing and flow characteristics of the impacted water to minimize biological damage. If the water is quiescent and the spill has destroyed biota in a water volume, the expansion of lethality (by dilution) can be slow and of diminishing intensity. However, in the case of a river, a moving lethal slug will travel downstream exposing further aquatic environment to damage. In the latter case, neutralization may spare more organisms from destruction than the former.

2.3.4 The Environmental Impact of pH on Aquatic Systems

It is probably safe to assert that most of chemical equilibria in terrestrial and marine waters are pH dependent. Crustal weathering (with consequent erosion and increased silting), cation exchange with mineral species, precipitation and colloid chemistry, and of course, the

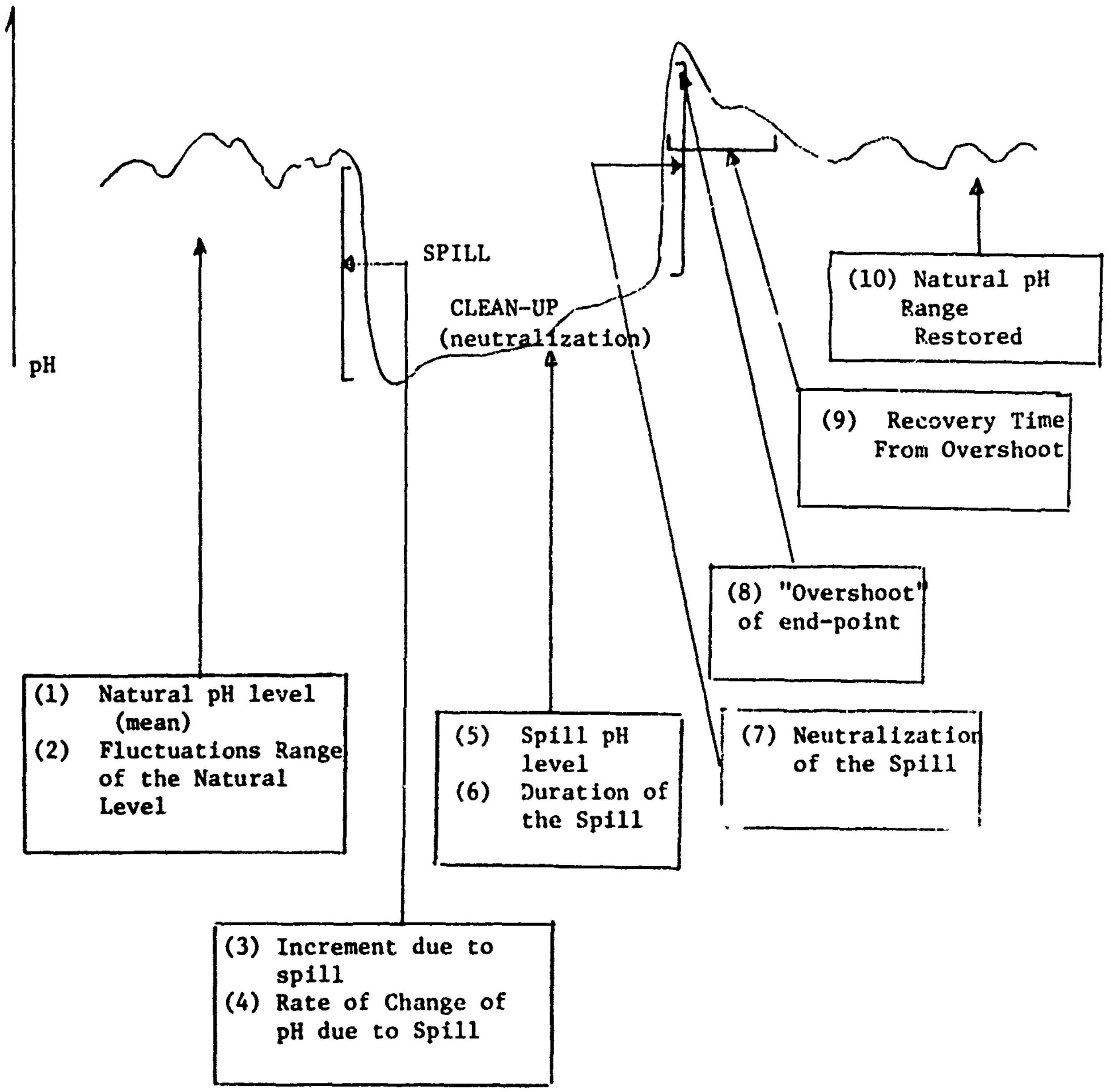

FIGURE 2.3-2

Aspects of Spill and Spill Clean-up

$CO_2 \leftrightarrow CO_3^{=}$ system are only a few examples of major pH-dependent geochemical processes.

The same may also be said of biochemical reactions. Many of the fundamental life processes are so pH dependent that the pH of blood and other body fluids is strictly regulated by the organism.

Chemical speciation of many dangerous pollutants is pH dependent. The solubility of toxic heavy metals often increases with decreasing pH; the toxicity of pulp and paper mill effluents is strongly pH dependent, as are also metal plating and finishing industry effluents, especially cyanides

$$H^+ + CN^- \rightleftarrows HCN \qquad 2.3\text{-}(1)$$

Sulfides are found in industrial effluents and are also formed in poorly aerated anoxic waters, both marine and fresh, and again the equilibria involved are pH dependent

$$2H^+ + S^= \rightleftarrows HS^- + H^+ \rightleftarrows H_2S \qquad 2.3\text{-}(2)$$

Thus a spill which causes a change in pH, particularly an acid spill, may solubilize other toxic components in the water body with far-reaching effects.

To complicate matters still further, the response of organisms to other environmental stresses such as oxygen level, temperatures, and tolerance to a host of chemical species encountered in natural waters can be pH dependent.

Finally, it should be noted that, in general, because of the strong dependence of aquatic organisms on chemical sensation for predator and prey detection, for environmental identification, and for intra-species identification and breeding, chemical pollution of waters can be a particularly disruptive form of environmental stress. In addition to damage to an individual organism's health, chemical pollution by confusing intra-species identification can (as in the case of catfish) destroy community relationships and structure, and by the confusion of environmental identification can disrupt migratory habits. The role of pH changes in aggravating these stresses is largely unknown.

2.3.5 Required Reduction of Contaminant

From the evidence available and the proposed water quality criteria, it seems that any treatment agent should act so as to return the pH to within the range of 6.0-9.0. Because of the potential adverse effects caused by rapid changes in pH, the problem of pH changes caused by misapplication of the neutralization agent or excess of the neutralization agent must be carefully evaluated.

2.4 IDENTIFICATION OF POTENTIAL NEUTRALIZING AGENTS

2.4.1 Initial Screening

An initial list of potential neutralizing agents was assembled for Table 2.4-1. It was prepared by choosing representative (strong, weak, and very weak) acids and bases, and buffers that are effective in the pH range of 6-9. Some of the buffers (first component listed) could also have been listed as very weak bases (e.g., borax) or as very weak acids (e.g., potassium dihydrogen phosphate).

The 22 potential neutralizing agents listed in Table 2.4-1 were initially screened to reduce the number requiring detailed examination. The reasons for the elimination of various chemicals as neutralizing agents are given below.

- Strong Acids: Hydrochloric acid and nitric acid were eliminated. Both of these chemicals are stronger vapor irritants than sulfuric acid (this was considered to be a significant problem), and both are more expensive and less readily available than sulfuric acid, which is the highest volume chemical produced in the U.S.

- Weak Acids: Phosphoric acid was eliminated primarily because it has a relatively low pKa compared with acetic acid (2.12 vs. 4.75) and thus was considered to be too strong an acid to be representative of "weak" acids. Another factor in favor of acetic acid is that it is less toxic to aquatic life than phosphoric acid.

- Very Weak Acids: Carbon dioxide was eliminated because it is too difficult to dissolve in water and to handle and deploy. The handling and deployment problems associated with the use of either gaseous or solid (i.e., dry ice) carbon dioxide would require specialized equipment and present storage problems.

- Strong Bases: Potassium hydroxide was eliminated because sodium hydroxide is quite similar in all the properties of interest and is less expensive. Sodium hydroxide is produced in much larger quantities in the U.S. and would thus be more readily available.

- Weak Bases: Ammonium hydroxide is eliminated primarily on the basis that it is a strong vapor irritant and thus would be difficult to handle.

- Very Weak Bases: None were eliminated.

TABLE 2.4-1

POTENTIAL NEUTRALIZING AGENTS

A. For the Neutralization of Bases

1. Strong Acids

Hydrochloric (HCl)
Sulfuric (H_2SO_4)
Nitric (HNO_3)

2. Weak Acids

Phosphoric (H_3PO_4)
Acetic (CH_3COOH)

3. Very Weak Acids

Carbon dioxide ($CO_2 \rightarrow H_2CO_3$, carbonic acid)
Boric (H_3BO_3)

B. For the Neutralization of Acids

1. Strong Bases

Potassium hydroxide (KOH)
Sodium hydroxide ($NaOH$)

2. Weak Bases

Ammonium hydroxide (NH_4OH)
Lime ($CaO \rightarrow Ca(OH)_2$, calcium hydroxide)
Sodium carbonate (Na_2CO_3)

3. Very Weak Bases

Urea (NH_2CONH_2)
Limestone ($CaCO_3$)

C. Buffers with Capacity in pH Range of 6-9

Sodium bicarbonate ($NaHCO_3$)
Potassium dihydrogen phosphate (KH_2PO_4) + Sodium hydroxide ($NaOH$)
Tris (hydroxymethyl) aminomethane + Sodium hydroxide ($NaOH$)
Borax ($Na_2B_4O_7 \cdot 10H_2O$) + Hydrochloric acid (HCl)
Disodium hydrogen phosphate (Na_2HPO_4) + Citric acid ($C_6H_8O_7$)
Disodium hydrogen phosphate (Na_2HPO_4) + Potassium dihydrogen phosphate (KH_2PO_4)
Disodium hydrogen phosphate (Na_2HPO_4) + Sodium dihydrogen phosphate (NaH_2PO_4)
Potassium chloride (KCl) + Sodium hydroxide ($NaOH$) + Boric acid (H_3BO_3)
Sodium diethylbarbiturate + Hydrochloric acid (HCl)

Buffers: The following three buffers are retained for further screening (1) sodium bicarbonate; (2) borax; and, (3) sodium dihydrogen phosphate + disodium hydrogen phosphate. The first two would be used preferentially for acid spills, and the latter for either acid or base spills. The other buffers were eliminated primarily on the grounds of duplication.

2.4.2 Factors Influencing the Choice of Neutralizing Agent

The ideal neutralizing agent should have the following characteristics:

- It should return the pH to the range of 6-9 without a large overshoot (in pH) if a small excess of the agent is added by mistake or it is applied outside the area of the spill.
- It should be relatively non-toxic to aquatic life, and not form more toxic compounds in the neutralization reaction.
- Its biological oxygen demand (BOD) should be small.
- It should have a high solubility in water.
- It should be safe to use by Coast Guard personnel (i.e., have low flammability, high TLV, etc.).
- It should be easy to handle and store.
- It should be commonly available in bulk quantities and be low in cost.

Important properties of the remaining neutralization agents are summarized in Table 2.4-2. Sulfuric acid and sodium hydroxide do not seem promising because of their high aquatic toxicity rating and hazards in handling. Both lime and limestone present serious problems because of their low solubility in water and they have no advantage over sodium carbonate except in price.

TABLE 2.4-2

POTENTIAL NEUTRALIZING AGENTS - IMPORTANT PROPERTIES

Agent	Physical Properties			Aquatic Toxicity Code[1]	Human Hazard			Handling, Cost, Availability		
	Type of Agent	Physical State	Solubility (Wt.%)		Vapor/liquid-solid/flammability[2]			Handling Problems	Approx. Cost (¢/lb)	Production (1,000 ton)
Sulfuric Acid	Strong Acid(very low)	Aqueous Solution		3	2	4	0	Moderate	2.5	32,357
Acetic Acid	Weak Acid (4.75)	Liquid or Aqueous Solution		2	2	3	2	Moderate	15.	1,214
Boric Acid	Very Weak Acid(9.14)	Solid or Aqueous Solution	4.8	1	0	-	0	Minor	11.	(1971) 59
Sodium Hydroxide	Strong Base(Very large)	Solid or Aqueous Solution		3	0	4	0	Moderate	8.5	10,719
Lime	Weak Base (11.57)	Solid	0.18	2	0	1*	0	Minor Settles in water--may cake	1.5	19,882
Limestone	Very Weak	Solid	0.0015	0	0	0	0	Minor Powder may float	1.5	>500,000
Sodium Carbonate	Weak Base	Solid	6.6	2	0	0	0	May cake	3.2	7,550
Urea	Very Weak Base(0.18)	Aqueous Solution or Solid	54	0	0	0	1	Minor	8.3	3,635
Sodium Bicarbonate	Buffer	Solid	6.4	2*	0	0	0	May cake	7.	225
Borax	Buffer	Solid	1.6	1-2	0	0	0	May cake	11.	640
Sodium Dihydrogen Phosphate	Buffer	Solid	>50	0*	0	0*	0	Minor	17.	39

1. Acetic acid and Urea have a BOD_5 demand of 0.6 and 0.1 lbs/lb respectively
2. For explanation of various codes see notes on following pages.
3. Chemical Marketing Reporter, August 1975.

*Estimated

NOTES TO TABLE 2.4-2

1. Aquatic toxicity code. This relates to the aquatic toxicity of the neutralizing agent only; the products of neutralization are not considered here. The code given represents the threshold level or range for acute toxicity based usually on data from studies with fish. The code used is as follows:

Code	Toxicity
0	Practically non-toxic. Acute threshold limit >10,000 ppm.
1	Threshold range 1,000 - 10,000 ppm.
2	Threshold range 100 - 1,000 ppm.
3	Threshold range 1 - 100 ppm.
4	Threshold range < 1 ppm.

2. Biochemical Oxygen Demand (BOD). Only two chemicals listed, acetic acid and Urea have a measurable BOD. Their BOD values are 0.6 lb/lb and 0.1 lb/lb (pounds of oxygen consumed per pound of chemical in 5 days).

3. Flammability Code. The National Research Council flammability rating scheme was used in this classification. It defines flammability classes as follows:

Code	Level of Flammability
0	Chemicals that are essentially non-combustible, considered to represent no fire hazard.
1	Chemicals representing a minimum fire hazard having a closed cup flash point above 140°F.
2	Chemicals having a closed cup flash point below 140°F and above 100°F.
3	Flammable chemicals having a closed cup flash point below 100°F and a boiling point under standard conditions above 100°F.
4	Flammable chemicals having a closed cup flash point below 100°F and a boiling point below 100°F.

NOTES TO TABLE 2.4-2, continued

4. Threshold Limit Value (TLV). The TLV is defined as the concentration of the substance in air that can be breathed for five consecutive eight-hour workdays (40-hour work week) without adverse effect. Sulfuric acid has a TLV = 1 mg/M^3 and acetic acid has a TLV of 10 ppm. The other chemicals listed do not have published TLV values.

5. Vapor irritant code. The code assigned (National Research Council code) is based on the likelihood of developing injury and the severity and persistence of that injury, including a consideration of volatility and injurious concentrations. The injured area may be the skin or mucous membranes of the eyes, nose, throat, or lungs.

Code	Irritant Nature
0	Chemicals that are non-volatile, or the vapors from which are non-irritating to the eyes and throat.
1	Chemicals that cause a slight smarting of the eyes or respiratory system if present in high concentrations.
2	Chemical vapors that cause moderate irritation, such that personnel will find high concentrations unpleasant. The effect is temporary.
3	Moderately irritating volatile chemicals, such that personnel will not usually tolerate moderate or high vapor concentrations.
4	Severe eye or throat irritants, vapors from which are capable of causing eye or lung injury, and which cannot be tolerated even at low concentrations.

6. Liquid or solid irritant code. The code (also a National Research Council code) relates to the tendency of a chemical to chemically "burn" or irritate human skin from contact in the liquid or solid state. Dermal effects from prolonged or repeated contacts are not considered.

NOTES TO TABLE 2.4-2, continued

Code	Irritant Nature
0	No appreciable hazard; chemicals are practically harmless to the skin.
1	Minimum hazard. Usually includes chemicals that, if spilled on clothing and allowed to remain, will cause smarting and reddening of the skin.
2	Chemicals that cause smarting of the skin and first-degree burns on short exposure and may cause second-degree burns on long exposure.
3	Fairly severe skin irritants, usually causing pain and second-degree burns after a few minutes contact
4	Severe skin irritants, causing second-and third-degree burns on short contact and very injurious to the eyes.

2.4.3 Final Selection of Potential Neutralizing Agents

It is apparent from the list of reagents in Table 2.4-2 that a number of potential reagents are available which pose minimal harm to the environment and could be readily handled, stored and deployed by Coast Guard personnel. The important criteria remaining are the amount of reagents required to neutralize a given spill and the consequences of using excess reagent or of misapplication of reagent if the spill cannot be accurately located.

2.4.3.1 Amounts of Neutralization Agent Required

In general a "strong" neutralizing agent (acid or base) will provide the minimum amount of agent to ameliorate the spill and restore an acceptable pH level. Figure 2.4-1 shows that the amount of base required to neutralize acids of different strengths (pKa values) remains fairly constant down to pKa $\approx$ 5-6 and then diminishes rapidly. It is interesting to note that the efficiency of sodium carbonate as a neutralizing agent closely parallels that of a saturated lime solution. Figure 2.4-2 shows a similar picture for the neutralization of a base; sulfuric acid is obviously more efficient than the other neutralizing agents for neutralization of bases where pKb<5.

To provide representative examples, the amounts of different neutralizing agents required to neutralize four different acids have been calculated in Table 2.4-3. It is assumed that the spilled acid occupies one cubic meter and is already diluted to a 0.1 molar solution. The neutralizing agent is a 1 molar solution* and the amount required is that which will give a pH = 6 if completely mixed with the spill. It becomes obvious from this table that urea is unacceptable as a neutralizing agent because of the large quantities which would have to be deployed. Sodium bicarbonate is probably acceptable although it is significantly less efficient than the other agents listed.

A similar comparison can be made for agents to neutralize bases. As is shown in Table 2.4-4, sodium bicarbonate is unacceptable for base neutralization because of the large quantity required. These tables also

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*A 1.0 M Solution is defined as a gram molecular weight of the solute dissolved in one liter of water.

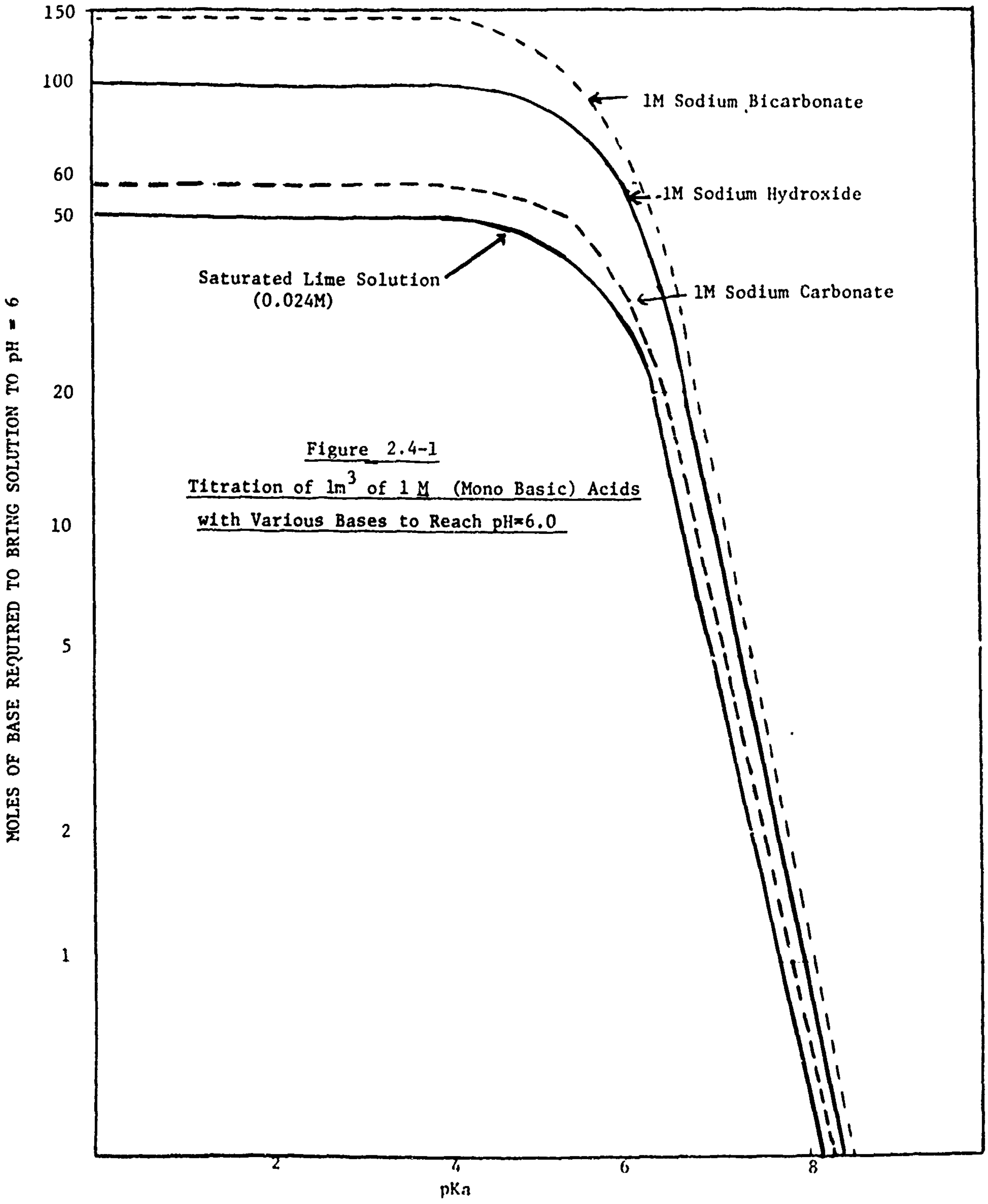

Figure 2.4-1

Titration of $1 m^3$ of 1 M (Mono Basic) Acids with Various Bases to Reach pH=6.0

FIGURE 2.4-2

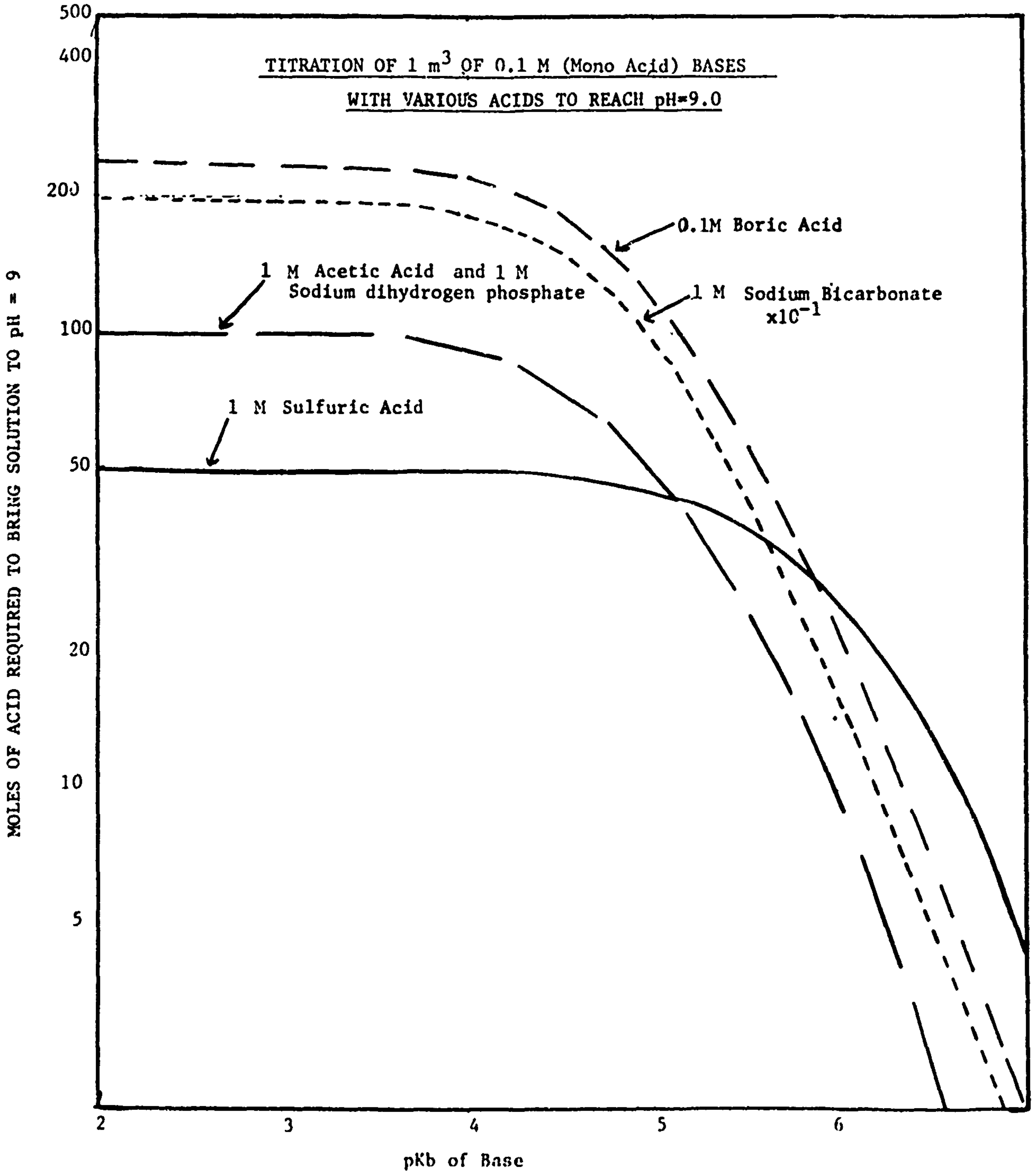
TITRATION OF 1 m^3 OF 0.1 M (Mono Acid) BASES
WITH VARIOUS ACIDS TO REACH pH=9.0
0.1M Boric Acid
1 M Acetic Acid and 1 M
Sodium dihydrogen phosphate
1 M Sodium Bicarbonate
x10^{-1}
1 M Sulfuric Acid
500
400
200
100
50
20
10
5
2
3
4
5
6
pKb of Base
MOLES OF ACID REQUIRED TO BRING SOLUTION TO pH = 9

TABLE 2.4-3

APPROXIMATE AMOUNTS OF NEUTRALIZING AGENT REQUIRED TO TREAT ACID SPILLS

Representative Spill Size: 1 cubic meter, 0.1 molar concentration
Neutralizing Agent: 1 molar concentration (except for lime, which is a saturated solution 0.024M)
pH = 6 after neutralization

Acid Solution to be Neutralized	Hydrochloric Acid Amount of Base Required			Sulfuric Acid Amount of Base Required			Maleic Acid Amount of Base Required			Acetic Acid Amount of Base Required		
Basic Neutralization Agent	Vol.of Sol. (M^3)	No. of gm-moles	Wt.of Base (kg)	Vol.of Sol. (m^3)	No.of gm-moles	Wt.of Base (kg)	Vol.of Sol. (m^3)	No.of gm-moles	Wt.of Base (kg)	Vol.of Sol. (m^3)	No.of gm-moles	Wt.of Base (kg)
Sodium Hydroxide	.1	100	4.0	.2	200	8.0	.146	146	5.83	.0947	94.7	3.79
Lime	2.08	50	2.80	4.16	100	5.6	3.04	72.9	4.09	1.97	47.3	2.65
Sodium Carbonate	.06	58.8	6.23	.118	118	12.4	.0858	85.8	9.10	.0557	55.7	5.90
Urea	39,800	4.0×10^7	2.4×10^6	79,700	8×10^7	4.8×10^6	58,200	5.8×10^7	3.5×10^6	37,700	3.8×10^7	2.3×10^6
Sodium Bicarbonate	.143	143	15.2	.286	286	30.4	.209	209	22.2	.135	135	14.4

TABLE 2.4-4

APPROXIMATE AMOUNTS OF NEUTRALIZING AGENT REQUIRED TO TREAT BASE SPILLS

Representative Spill Size: 1 cubic meter, 0.1 molar solution
Neutralizing Agent: 1 molar concentration (except for boric acid 0.1M)
pH = 9 after neutralization

Base Solution to be Neutralized	Potassium Hydroxide			Ammonium Hydroxide			Triethanolamine		
	Amount of Acid Required			Amount of Acid Required			Amount of Acid Required		
Acid Neutralizing Agent	Vol.of Sol. (m^3)	No.of gm-moles	Wt.of Acid (kg)	Vol.of Sol. (m^3)	No.of gm-moles	Wt.of Acid (kg)	Vol.of Sol. (m^3)	No.of gm-moles	Wt.of Acid (kg)
Sulfuric Acid	.05	50	4.90	.047	47	4.66	.021	21	2.06
Acetic Acid	.1	100	6.0	.064	64	3.84	.0068	6.8	.41
Sodium Dihydrogen Phosphate	.102	102	Anhydrous 12.2	.065	65	7.8	.0069	6.9	0.83
Boric Acid	2.38	238	14.7	1.53	153	9.46	.16	16	.99
Sodium Bicarbonate	1.88	1,880	158	1.21	1,210	102	.13	130	10.6

show clearly that quite different amounts of any given neutralizing agent may be required to neutralize various spills. The actual amounts needed can seldom be estimated on the basis of one mole of base to one mole of acid. Exact calculations are generally possible for solutes in pure water; these calculations usually involve solving a polynomial equation with three to six terms. Boric acid suffers from a low solubility which requires that a large volume of neutralizing solution be used. Note again that quite different amounts of any given neutralizing agent may be required to neutralize various spills.

2.4.3.2 Addition of Excess Neutralizing Agent

In many instances the exact amount of acid or base spilled will not be known; also the concentration in different parts of a water body will vary due to dispersion. This is particularly true where actual conditions may differ considerably from those predicted by a simple model. Under some circumstances it may be desirable to add an excess of reagent to ensure that the spill has been effectively neutralized. However, it is also important that the excess reagent does not cause the pH to move out of the range pH 6-9 in the opposite direction.

Calculations showing the pH obtained after the addition of 20% excess neutralizing agent are given in Table 2.4-5 for different neutralizing agents. Strong acids and bases (e.g., sulfuric acid, sodium hydroxide) are definitely unacceptable because excess neutralizing agent will produce extreme changes in pH. Even acetic acid is only marginally acceptable since the final pH would be well below pH 6. For neutralization of bases, the best choice appears to be sodium dihydrogen phosphate (boric acid and sodium bicarbonate are unacceptable because of the large quantity of neutralizing agent required).

Similarly, the most promising agents for neutralization of acids are sodium carbonate and sodium bicarbonate.

2.4.3.3 Misapplication of Neutralizing Agent

If it is necessary to keep the pH in the range pH 6-9 when the neutralizing agent is accidently applied in the wrong place, then the choice becomes more restricted. Table 2.4-5 shows that sodium dihydrogen phosphate is still the best reagent for bases; in the event of misapplication the pH could reach pH 4-5. Sodium bicarbonate is still acceptable for neutralization of acids, but misapplication of sodium carbonate could result in a pH of about 12.

TABLE 2.4-5 CONSEQUENCES OF OVERSHOOT OR MISAPPLICATION

EXAMPLE: NEUTRALIZATION OF 0.1M SODIUM HYDROXIDE

Neutralizing Agent	pH After Adding 20% excess past pH=9	pH for miss, i.e., of the neutralizing agent
1.0M Sulfuric Acid	0.85	0.3
1.0M Acetic Acid	5.46	2.4
1.0M Sodium Dihydrogen Phosphate	7.87	4.5
0.1M Boric Acid	8.87	5.2
1.0M Sodium Bicarbonate	9.0	8.3

EXAMPLE: NEUTRALIZATION OF 0.1M HYDROCHLORIC ACID

Neutralizing Agent	pH After Adding 20% excess past pH=6	pH for miss, i.e., of the neutralizing agent
1.0M Sodium Hydroxide	12.2	14.0
0.024M Lime (Sat. Soln.)	11.8	12.4
1.0M Sodium Carbonate	7.1	12.1
1.0M Sodium Bicarbonate	6.2	8.3
1.0M Urea	6.1	7.1
1.5×10^{-4}M Limestone (Sat.Soln.)		9.4
0.1M Borax		9.2

2.4.4 Categorization of Spill Chemicals Subject to Neutralization

The full list of chemicals considered for amelioration by neutralization techniques can be subdivided into the following four categories:

1. Acids
2. Compounds that react with water to form acids
3. Bases
4. Compounds that react with water to form bases

One chemical, acetophenone, cannot be classi either as an acid or a base; therefore, it has been deleted from the because it is not subject to neutralization. Chemicals falling into the first two categories are listed in Table 2.4-6 and into the second two categories in Table 2.4-7. A tabulation was made of the following chemical and physical properties:

Physical Form (gas, liquid, solid)
Chemical Formula
Molecular Weight
Solubility in water (gm/100ml)
Negative log of dissociation constant (pKa) at 25°C
Specific gravity of aqueous solutions at 20°C
Approximate concentration (Moles/ℓ) when pH = 6.0 for acids
Approximate concentration (Moles/ℓ) when pH = 9.0 for bases

The tabulation for acids is given in Table 2.4-8 and for bases in Table 2.4-9.

2.4.4.1 Spill Chemicals Which Should Not Be Neutralized

For a number of the chemicals listed, neutralization should be approached carefully because of the hazards to personnel from toxic or irritant vapors which may be present in the vicinity of a spill (e.g., hydrogen chloride, ammonium hydroxide). However, if the reaction with water is complete these chemicals can be treated by neutralization.

It is undesirable to treat the following compounds by neutralization for the reasons given.

Acids

Hydrogen Cyanide - High toxicity, vapor and liquid

Bases

Aniline
Dimethyl Formamide
Hexamethylene Tetramine
Methyl Ethyl Pyridine — Very weak bases which will not violate pH criteria
Pyridine
Urea

TABLE 2.4-6

CHEMICALS CLASSIFIED AS ACIDS (Total of 14)

Acetic acid
Acrylic acid
Formic acid
Hydrochloric acid
Hydrofluoric acid
Hydrogen chloride
Hydrogen cyanide
Hydrogen fluoride
Nitric acid
Oxalic acid
Phosphoric acid
Propionic acid
Sulfuric acid
Sulfuric acid (spent)

CHEMICALS THAT REACT IN WATER TO GIVE ACIDS (Total of 16)

Acetic anhydride → Acetic acid
Aluminum chloride → Hydrogen chloride (+ aluminum hydroxide)*
Benzoyl chloride → Hydrogen chloride + Benzoic acid
Bromine → Hypobromous acid
Chlorosulfonic acid → Hydrogen chloride + Sulfuric acid
Maleic anhydride → Maleic acid
Nitrogen tetroxide → Nitric acid (+ Nitric oxide)*
Nitrosyl chloride → Hydrogen chloride + Nitrous acid
Oleum → Sulfuric acid (+ Sulfur trioxide)*
Phosphorus oxychloride → Hydrogen chloride + Phosphoric acid
Phosphorus pentasulfide → Hydrogen sulfide + Phosphoric acid
Phosphorus trichloride → Hydrogen chloride + Phosphorous acid
Polyphosphoric acid → Phosphoric acid
Sulfur monochloride → Hydrogen chloride + Sulfuric acid (+ others)*
Sulfuryl chloride → Hydrogen chloride + Sulfuric acid
Titanium tetrachloride → Hydrogen chloride (+ Ti-hydroxyhalides)*

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*Reaction products listed in parentheses are not acids

TABLE 2.4-7

CHEMICALS CLASSIFIED AS BASES (Total of 28)

Aminoethanolamine
Ammonium hydroxide
Aniline
Caustic Potash solution
Caustic Soda solution
Cyclohexylamine
Diethanolamine
Diethylamine
Diethylenetriamine
Diisopropanolamine
Dimethylformamide
1,1-Dimethylhydrazine
Ethylenediamine
Hexamethylenediamine
Hexamethylenetetramine
Hydrazine
Methylethylpyridine
Monoethanolamine
Monoisopropanolamine
Morpholine
Potassium hydroxide
Pyridine
Sodium hydroxide
Triethanolamine
Triethylamine
Triethylenetetramine
Trimethylamine
Urea

CHEMICALS THAT REACT WITH WATER TO GIVE BASES (Total of 6)

Anhydrous ammonia → Ammonium hydroxide
Ethylene imine → Monoethanolamine
Lithium aluminum hydride → Lithium hydroxide (+ Hydrogen + Aluminum hydroxide) *
Sodium → Sodium hydroxide (+ Hydrogen)*
Sodium amide → Ammonia + Sodium hydroxide
Sodium hydride → Sodium hydroxide (+ hydrogen)*

* reaction products listed in parentheses are not bases.

TABLE 2.4-8

PROPERTIES OF THE ACIDS

CHEMICAL	FORMULA	MOLECULAR WEIGHT	SOLUBILITY IN WATER (g/100mℓ)	pKa(25°C)*	SPECIFIC GRAVITY OF AQUEOUS SOLUTIONS (20°C)	APPROX. CONC. FOR WHICH pH = 6.0 (moles/liter)
Hydrochloric	$HC\ell$	36.47	$82.3^{25^\circ C}$	< -8	40%: 1.198 20%: 1.098	$1\text{x}10^{-6}$
Sulfuric	H_2SO_4	98.08	∞	(1) very low (2) 1.92	100%: 1.830 50%: 1.395	$5\text{x}10^{-7}$
Nitric	HNO_3	63.02	∞	- 1.64	100%: 1.513 50%: 1.310	$1\text{x}10^{-6}$
Oxalic	$HOOCCOOH \cdot {}_2H_2O$	126.07	$9.15^{15^\circ C}$	(1) 1.23 (2) 4.19	Pure Solid:1.653 9.28%:1.050 5.00%:1.024	$5\text{x}10^{-7}$
Maleic	HOOCCH:CH-COOH	116.07	$78.8^{25^\circ C}$	(1) 1.83 (2) 6.07	Pure Solid: 1.590	$7\text{x}10^{-7}$
Phosphorous (ortho)	$H_2(HPO_3)$	82.00	$309^{0^\circ C}$	(1) 2.00 (2) 6.59(18°C)	Pure Solid: 1.651 50%: ∿ 1.25	$7\text{x}10^{-7}$
Phosphoric (ortho)	H_3PO_4	98.00	548	(1) 2.12 (2) 7.21(18°C) (3)12.67	100%: 1.870 50%: 1.335	$7\text{x}10^{-7}$
Nitrous	HNO_2	47.02	---	3.37(12.5°C)		$1\text{x}10^{-6}$
Hydrofluoric	HF	20.01	∞	3.45	50%: 1.155 25%: 1.086	$1\text{x}10^{-6}$
Formic	HCOOH	46.03	∞	3.75(20°C)	100%: 1.221 50%: 1.121	$1\text{x}10^{-6}$

TABLE 2.4-8 (cont'd)

CHEMICAL	FORMULA	MOLECULAR WEIGHT	SOLUBILITY IN WATER (g/100mℓ)	pKa (25°C)	SPEC.GRAVITY OF AQUEOUS SOLUTIONS (20°C)	APPROX. CONC. FOR WHICH pH =6.0 (moles/liter)
Benzoic	C_6H_5COOH	122.12	$0.27^{18°C}$	4.19	Pure Solid: 1.266 15°C	$1x10^{-6}$
Acrylic	CH_2:CHCOOH	72.06	∞	4.25	100%: $1.062^{16°C}$	$1x10^{-6}$
Acetic	CH_3COOH	60.05	∞	4.75	100%: 1.050 50%: 1.058	$1x10^{-6}$
Propionic	CH_3CH_2COOH	74.08	∞	4.87	100%: .992	$1x10^{-6}$
Hydrogen Sulfide	H_2S	34.08	$.64^{0°C}$ $.27^{40°C}$	7.20		$1.6x10^{-5}$
Hypochlorous (Hypochlorite)	$HOC\ell$	52.47		7.53		$3.4x10^{-5}$
Hypobromous	H BrO	96 .92	$221^{0°C}$	8.69	60%: 1.679 30%: 1.258	$4.9x10^{-4}$
Hydrocyanic	HCN	27.03	∞	9.31	100%: .691 80%: .759	$2.0x10^{-3}$

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* When more than one dissociation constant is involved, the pKa for each dissociation step is given, when known; in such cases the first dissociation constant is listed first (preceeded by "(1)").

TABLE 2.4.9 PROPERTIES OF THE BASES

CHEMICAL	FORMULA	MOLECULAR WEIGHT	ULTIMATE SOLUBILITY IN WATER (g/100ml)	pKa (25°C)**	SPEC.GRAVITY OF AQUEOUS SOLUTION (20°C)	APPROX.CONC. FOR WHICH pH = 9.0 (moles/liter)
Potassium Hydroxide	KOH	56.11	$107.^{15°C}$	very large	50%: 1.514 25%: $1.239^{15°C}$	$1x10^{-5}$
Sodium Hydroxide	NaoH	40.00	$42.^{°C}$	very large	50%: 1.525 24%: 1.263	$1x10^{-5}$
Lithium Hydroxide	L OH	23.95	$12.7^{0°C}$	13.9	Pure Solid: 1.43	$1.3x10^{-5}$
Hexamethylene-Diamine	$NH_2(CH_2)_6NH_2$	116.21	∞	11.10	anhyd.liq.:$.799^{60°C}$ 70%: .933	$< 1x10^{-5}$
Diethylamine	$(CH_3CH_2)_2NH$	73.14	∞	10.98	100%: .708	$1x10^{-5}$
Triethylamine	$(CH_3CH_2)_3N$	101.19	$5.5\%^{20°C}$	10.76	100%: .729	$1x10^{-5}$
Cyclohexylamine	$\underline{(CH_2)_5CH}\ NH_2$	99.18	∞	10.64	100%: .865	$1x10^{-5}$
Diethylene-Triamine	$NH_2(CH_2)_2NH-$ $(CH_2)_2NH_2$	103.17	∞	(1) 9.94 (2) 8.88 (3) 3.70	100%: .954	$7x15^{-6}$
Ethylene-Diamine	$NH_2CH_2CH_2NH_2$	60.10	∞	9.93	100%: .909	$\lesssim 1x10^{-5}$
Triethylene-Tetramine	$NH_2(CH_2)NH(CH_2)_2-$ $NH(CH_2)_2NH_2$	146.24	∞	(1) 9.92 (2) 9.20	100%: .982	$7x10^{-6}$
Trimethylamine	$(CH_3)_3N$	59.11	∞	9.74	100%: .633	$1.2x10^{-5}$

TABLE 2.4-9 (cont'd)

PROPERTIES OF THE BASES

CHEMICAL	FORMULA	MOLECULAR WEIGHT	ULTIMATE SOLUBILITY IN WATER (g/100ml)	pKa (25°C)**	SPEC. GRAVITY IN AQUEOUS SOLUTIONS (20°C)	APPROX. CONC. FOR WHICH pH = 9.0 (moles/liter)
Monoisopropanol-amine	$CH_3CH(OH)-CH_2NH_2$	75.11	∞	9.57 (20°C)	100%: .961	$1.3x10^{-5}$
Aminoethanol-amine	$HOCH_2CH_2NH-CH_2CH_2NH_2$	104.15	∞	(1) 9.56 (2) 6.34	100%: 1.028$^{(25°C)}$	$\sim 1x10^{-5}$
Monoethanol-amine	$HOCH_2CH_2NH_2$	61.08	∞	9.51	100%: 1.016	$1.4x10^{-5}$
Ammonium Hydroxide	NH_4OH	35.05	very soluble	9.25	100% NH_3: .618* 50% NH_3: .832* 20% NH_3: .923	$1.6x10^{-5}$
Diisopropanol-amine	$(CH_3CH(OH)CH_2)_2NH$	133.19	∞	EST. 8.97(20°C)	100%(Liq.):.99 (42°C)	$2.1x10^{-5}$
Diethanol-amine	$(HOCH_2CH_2)_2NH$	105.14	∞	8.92	100%: 1.095(28°C)	$2.2x10^{-5}$
1,1-Dimethyl-Hydrazine	$(CH_3)_2N \cdot NH_2$	60.11	very soluble	EST. ~ 8 to 9	100%: .791	$\sim 4.3x10^{-5}$
Hydrazine	NH_2NH_2	32.05	∞	8.48	80%: 1.040 40%: 1.038	$4.3x10^{-5}$

TABLE 2.4-9 (cont'd)

PROPERTIES OF THE BASES

CHEMICAL	FORMULA	MOLECULAR WEIGHT	ULTIMATE SOLUBILITY IN WATER (g/100ml)	pKa (25°C)	SPEC.GRAVITY OF AQUEOUS SOLUTIONS (20°C)	APPROX.CONC. FOR WHICH pH = 9.0 (moles/liter)
Morpholine	$OCH_2CH_2NHCH_2CH_2$	87.12	∞	8.33	100%: 1.00	$5.7x10^{-5}$
Triethanol-amine	$(HOCH_2CH_2)_3N$	149.19	∞	7.86	100%: 1.13	$1.4x10^{-4}$
Hexamethylene-tetramine	$C_6H_{12}N_4$ *	140.19	$150.^{20°C}$	6.30	Pure Solid: 1.35	$\sim 5x10^{-3}$
Methylethyl-Pyridine	$CH_3\ CH_2CH_3$ $NCHCHCHCH$	121.18	$1.2\%^{20°C}$	EST. ~5 to 6	100%: .922	$\sim 3x10^{-2}$
Pyridine	$N(CH)_4CH$	79.10	∞	$5.23^{(20°C)}$	100%: .983	$5.9x10^{-2}$
Aniline	$CH(CH)_4CH\ NH_2$	93.13	$3.4^{20°C}$	4.58	100%: 1.022	0.26
Dimethylform-amide	$HCON(CH_3)\ 2$	73.09	∞	EST. ~1 to 4	100%: .950	1 - 1000
Urea	NH_2CONH_2	60.06	$119.^{25°C}$	0.18	Pure Solid: 1.34	Past Saturation (> 6000)

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* Values determined in sealed tube, at 15°C

** When more than one dissociation constant is involved, the pKa for each dissociation step is given, when known; in such cases the first dissociation constant is listed first (preceeded by "(1)").

2.5 DEPLOYMENT METHODS

2.5.1 Dispersion and Neutralization Analysis

An accidental discharge of an acid or base (A/B) into a river or other body of water creates a relatively small hazardous zone initially. With time, however, dispersion both dilutes the A/B and increases the volume of water which is considered hazardous. In a few instances, one can treat the A/B with a neutralizing agent before significant dispersion has occurred. This might be the case for a spill into a small drainage ditch or a stagnant lake. Only approximate analytical methods are available to indicate pH profiles down-stream in rivers as a function of time for various cross sections, stream velocities, and type and magnitude of the spill. Spills into estuaries or harbors are even more complex to analyze, so we will concentrate on the easier problem of treating spills into rivers and bays.

To obtain some indication of the feasibility of treating spills in various water bodies, we employed the simplified dispersion models developed under the CHRIS[15] program. In Appendix C, the CHRIS models used for analyzing treatment feasibility are described along with a modification that gives an indication of the progress and extent of effectiveness of a neutralization response action after its initiation. These models, after further refinement, would constitute an important real-time response tool. Such analyses could provide a preliminary estimate of location and extent of contaminated zones when response is initiated and optimize the application of the treatment agent. Appropriate monitoring instruments would also be required as an interactive input in a real response situation.

The dispersion and neutralization models were employed in evaluating the feasibility of potential deployment methods for neutralization treatment. The objective was to identify, at least qualitatively, what neutralization treatment amelioration might be achieved for a range of spill sizes and response time intervals following postulated acidic or basic spills. Three response time intervals were chosen: 1, 6 and 48 hours. Practical response times are likely to be in the 6-8 hour range, but we wished to identify how critical response time might be in determining whether neutralization treatment was feasible. Five spill scenarios were considered: a confined spill (e.g., a drainage ditch which could be diked), a narrow river, a wide river, a lake, and an estuary. Typical conditions were assumed for the various water bodies.

- Confined System - a chemical spill into a confined water body can be held for treatment for indefinite times if the retaining material is not very porous.
- Narrow River - (See Appendix Section C.2: assume typical dimensions of 50m width by 5m depth with a 1 m/s flow velocity) - for a point spill at the center of the river, the chemical will take about 40 minutes to reach the banks. After 1 hour, the spilled chemical is dispersed quite uniformly across the stream cross-section and forms a plug in the axial direction about 70m long. The plug center would have moved about 3600m downstream in the interim. After 6 hours, and especially after 48 hours, the material continues to progress downstream and spread axially into a still larger diffuse band. However, for example, a spill of more than 15 lbs. of HCℓ or 150 lbs. of NaOH could still be treated after 50 hours to reduce environmental damage. For these chemicals, the volume of river contamination by the spill continues to grow for about 40% of the time required for complete dispersion by dilution. The maximum contaminated volume occurs when the pH values are within 0.2 of safe limits. For narrow rivers, rapid response with broad area spraying would seem to be the best deployment method to minimize the extent of environmental damage.
- Wide River - (See Appendix Section C.1: assume typical dimensions of 3200m width by 20m depth with a 1 m/s flow velocity) - for a point spill near mid-river, the chemical is distributed in a roughly cylindrical zone (i.e., vertical concentration gradients soon become negligible in comparison to radial gradients). After 1 hour, 98% of the spilled chemical is still located within a zone of 20m radius reaching to the full river depth. After six hours, the 98% mass zone

has grown radially to form a cylinder with about a 50m radius. Even after 50 hours, a spill of more than about 250 lbs of HCℓ or about 3000 lbs. of NaOH could be treated to reduce environmental upset. In a typical wide river, for these chemicals the maximum contaminated volume of water occurs in about 25% of the time required for complete dispersal by dilution. At the time the maximum occurs, pH values are within 0.4 of safe levels.

For an idealized wide river, the contaminated zone remains fairly localized as it moves downstream with the current. An accurate location of the affected zone and a localized application of treating agent, even six or more hours after the spill would be useful.

- Lake - the appropriate model for spill dispersion in a lake is similar to that for a wide river without the effects of stream flow velocity and perhaps with a different value for the turbulent diffusion rate parameter (or eddy diffusivity). Thus, we may assume that the best deployment methods for a lake will be similar to those for a wide river. Location of the application point should, however, be easier in a lake than in a river, although local currents in any particular lake may complicate the treatment procedure.
- Estuary - (assume fresh water flow velocity = 1 m/s; tidal peak flow velocity = 1 m/s; rapid lateral and vertical dispersion) - for a spill occurring at slack water with the tide about to come in, we estimate that the contaminated water zone would constitute about a 130m long axial band after a 1 hour period. After 6 hours, the material would have been carried to sea.

Depending on the time of spill relative to the tidal flow period, response may or may not be practical. Once tidal flow carries the contaminated water to sea, it may be impractical to attempt to locate the treatment application point. Only when tidal actions will keep the contaminated zone in the estuary long enough for treatment, does a response action seem practical. Area application then would appear to be the preferred deployment technique.

2.5.2. Methods of Application

Viable methods to apply a neutralizing chemical must recognize that the hazard zones cannot be well-defined a priori. Thus application cannot be planned on the basis of calculations: disregard of this fact can easily lead to situations where the spilled A/B is followed (or preceded) by a zone containing the ameliorating chemical. Therefore, we feel that the spill must be tracked with surface craft to allow one to delineate the extent of the hazardous zone before any neutralizing chemical is applied. We assume this vital information is available in the discussion to follow.

Neutralizing chemicals (sodium bicarbonate for acid spills and sodium dihydrogen phosphate for alkaline spills) are assumed to be available in the immediate vicinity of a spill from cooperating chemical companies. Normally such neutralizing chemicals are stored as dry powder (or granules) in 50-100 pound bags. This assumption is important because no special power equipment is needed to move the material from storage to the waterfront. If storage is in bulk or large barrels, then it is unlikely that men could carry out the transfer without prior planning and ready availability of bulk carriers, power loaders, etc. Not only must the neutralizing chemical be packaged in sizes convenient for one (or two) men, but there must be a sufficient amount stored in hazardous areas to be useful for the largest credible accident. For example, for each ton of 100% hydrochloric acid spilled, 3.3 tons of sodium bicarbonate are required to neutralize the spill. Thus for multi-ton spills, it is apparent that a large quantity of neutralizing chemical must be available.

Assuming that a sufficient supply of the desired neutralizing chemical is available and can be transported to the spill site and that means are available to track the spill downstream, techniques must be found to apply the neutralizing chemical to the hazardous area at the appropriate location and in the proper amount.

A simple analysis indicates that application can be made in three ways:

A. from a mobile marine ship
B. from an aircraft
C. from a convenient shore or bridge location.

Further, application can be made:

I. with the dry powder (as received)
II. with a slurry of powder in water
III. with a solution of the powder in water

Combination of these two lists yields nine application methods. Within each main class, there are other sub-classes which are discussed below.

First, let us consider A, B, C. In case A, appropriate ship(s) must be available and have the ability to load and store sufficient quantities of the neutralizing chemicals on deck or in an accessible hold with protection from the weather. The crews must have had some prior training in simulated spill scenarios in order to exercise good judgment and to cooperate with the local Coast Guard officer in charge of the application. Communications with other ships involved in the operation must be available, especially with those craft which are responsible for monitoring the local pH values. Strict adherence to orders relating to the quantity of neutralizing chemical applied and the time of application is necessary.

For case B, appropriate fixed-wing aircraft or helicopters must be available. An advantage such craft have over mobile marine units is that they can be moved rapidly to the scene of the spill. Also, it is possible that with helicopters, the transportation of the chemical for storage to the waterside may be avoided. Aircraft have, however, the serious disadvantage that they have a low carrying capacity relative to marine units and multiple trips would probably be required. Also, precise dumping in hazardous areas is obviously much more difficult from an aircraft.

In case C, there would appear to be few advantages. At a fixed position on the shore or on a bridge, there is only one opportunity to apply the appropriate amount of neutralizing chemical as the hazardous zone passes by. From shore locations, it is difficult to achieve any more than local neutralization of the water near the shore line. Our calculations have indicated that, even with dispersion, the downstream hazardous zone is still very localized and moves as a wave with approximate stream velocity. To neutralize this wave, even for a convenient bridge crossing, would require detailed planning and cooperation between monitoring ships and those on the bridge. The critical time period to add the neutralizing chemical is short. Except in very special situations, we do not feel that case C represents a practical method and it will not be discussed further.

Of cases I, II, and III, the first is obviously the simplest. One could visualize the operation as follows:

- The monitoring craft locates an area of pH imbalance.
- Free-floating buoys are set to indicate this zone.
- The cooperating marine unit or aircraft are alerted and are told how much neutralizing chemical to disperse in the marked zone.
- After application, the monitoring craft measures the pH (surface and lower layers) and indicates if more chemical is desired.

Note that excellent communications are required between the monitoring and application craft - although it is possible both could be in the same vessel.

If the dry powder is simply dumped overboard, little mixing will take place and the bulk (dense) powder will sink. There are several ways this application method can be improved, although each requires more equipment.

- A device can be used to distribute the powder over a wider area. Mechanical "slingers" are a possibility as are compressed air-powder sprays. By breaking up the bulk powder, there is less tendency for it to "clump" and sink and solution is achieved more rapidly.

- The powder can be mixed with water to form either a slurry (case II) or a true solution (case III). For either of these cases, mixing and pumping equipment must be available. The more neutralizing chemical dissolved in water, the more rapid is the effect in the hazardous area. Also, there is little tendency for sinking if a well-dispersed slurry or a true solution is distributed over a wide area.
- The powder may be added carefully in the region of maximum propeller turbulence. This should promote more rapid solution and neutralization.

It is difficult to visualize an aircraft carrying any equipment to prepare or dispense slurries or solutions. Even the concept of mechanical slingers is not reasonable because of wind drift problems. Thus, for aircraft, simple powder dumps are the only feasible alternative. Some dispersion in the wind or propeller (rotor) wash will occur but not in a very controlled manner and this will increase the difficulties of accurate placement of powder.

Therefore, our preliminary analysis indicated that only the following application methods are candidates for further study:

- Apply powdered chemical with mechanical slinger or air jet from a mobile marine unit
- Prepare slurries or solutions in mixing tanks on board and spray on the lee side of a mobile marine unit
- Possibly, use aircraft with powder dumps for localized spills when the time element is critical.

A preliminary design was carried out for four potential methods:

1. Manual dump of powdered agents into prop wash of marine craft.
2. Mechanical slinger dispensing powder over side of marine craft.
3. Water pumped into mixing tank where powdered agent is added. Mixed solution or slurry overflows overboard into spill area.
4. Water pumped, powder injected from hopper, slurry passed through static mixer and discharged overboard.

2.5.3. Preliminary Design of Application Equipment

In order to compare these alternatives, we selected a spill size of 10,000 gallons as representative of the largest size spill that might occur and still be amenable to full treatment over practical response periods of six hours to 24 hours. Smaller spills could be treated more quickly with this same equipment. Should a larger spill occur, partial treatment would still allow some amelioration of the hazard. Since extremely large spills occur so infrequently, it seems economically and logistically unreasonable to design response equipment for these situations, especially since the response equipment would then be cumbersome to transport and there might be less flexibility as to the type of deployment craft that might be used.

As a preliminary design basis, we assumed treatment of a 10,000 gallon spill of 37% hydrochloric acid. Six hours after a sudden release of this quantity of acid into a wide river, for example, the zone of unacceptable acidity would cover about 20,000 ft^2 of river surface (and would extend from the water surface to the river bottom) according to the assessment models described in Appendix C. The affected zone would be roughly circular, with a diameter of about 160 ft. It is evident that finding a hazardous zone of this size after a several hour transit downstream will require detection equipment in addition to the basic treating equipment considered in this study.

For the assumed spill, we estimate that a minimum of 90 tons of sodium bicarbonate would be needed to bring the affected zone back within acceptable pH limits. Since both treating agents for neutralization are fairly common chemicals, available in powder form in 100 lb bags, the required amounts of treating agent probably could be obtained and transported to the vicinity of the spill location using C130 aircraft. Although the bags could be handled manually, for a spill of this magnitude some 1800 bags would be required. Several C130 aircraft or a shuttle operation would be needed for the transport of 90 tons of treating agent.

Controlling design requirements are the air transport gross dimension and weight limits. (These are defined in a COMDT (FSP) letter dated 15 October 1971, file DOT-CG-14,057A.) These requirements establish maximum dimensions of a 7-ft 10-in. width, 9-ft height, and 40-ft length, and a weight limit of 25,000 lb.

In the basic response scheme, treating chemical would be supplied to marine craft which would search, locate and follow the hazard zone. The types of marine craft that are likely to be available for a response effort at a random site probably will be able to carry loads of 1-10 tons at a time so several craft and/or a shuttling of treatment chemical to the hazard zone will be required. The weight of chemical involved for treating a spill of this size mitigates against deployment from a helicopter (in addition to wind drift problems).

Coast Guard seagoing cutters in the buoy tender class(WLBs) and the medium- and high-endurance classes are candidates for the warer transport task, as are other public vessels and those commercial vessels certificated for offshore operations. The principle water-carrier design parameters are the cargo boom handling capacity, the deck space available, the habitability of the deck space during transit, and the on-scene cargo-handling capability. Typical buoy tenders have adequate deck space, normal load capacities in the 2 - 10 ton range and hydraulic hoists capable of lifting 1 - 2 ton weights.

At the contaminated zone, the powdered neutralizing agent must be introduced into the water. If the bags of chemical were dropped overboard intact, they would sink to the bottom before much chemical could dissolve and the spill in moving water would pass by. Therefore, as a minimum, the bags would have to be slit open and the contents dumped. Again, depending on water depth and turbulence, the treating agent may not fully dissolve. Some advantage might be taken of the extra mixing available in the vessel's wake.

- Manual dumping of hundreds of bags of powder, while not impossible, involves much heavy labor and is not a very good method for distributing the treatment powder throughout the water. Some skid-mounted equipment could greatly facilitate the operation.

To treat the assumed design spill in a sixteen hour period, sodium bicarbonate would have to be applied at a rate just under six tons per hour. If the powder were dissolved in water, the solution would have to be applied at a rate of about 325 gpm. If the powder were applied in slurry form, lower water pumping rates could be used.

For the three equipment alternatives listed earlier, a mechanical slinger system to dispense powder at a rate of 185 lbs/min would weigh about 1/2 ton and would cost about $2000. The pump and mixing tank system and the pump - powder injection system both would weigh about 1 ton and would cost about $7000. The latter concept is the more attractive since the rate of powder injection is controlled mechanically (Figure 2.5-1). It might be desirable to add another system for conveying and dumping powder into the supply hopper to reduce the manual labor requirements.

The skid-mounted treatment equipment is light enough to be transported by helicopter to the spill location and could be conveniently used on boats of the 45 ft. buoy boat type which usually have load capacities of 5-10 boats and deck space for equipment and chemicals.

A more sophisticated system incorporates a metered slurry mixture with a convenient automatic bag opening device (see Figure 2.5-2). This concept provides for the proper percentage of slurry mix by prior adjustment of the auger screw feed into the eductor. Furthermore, with the addition of the bag opener not only is the manual labor reduced but the dust level is also controlled by the enclosure. A bag disposer may also be added.

The entire unit cost including skid mounting pump and drive would range from 13,000 to 15,000 dollars. The total weight would be around 3000 pounds.

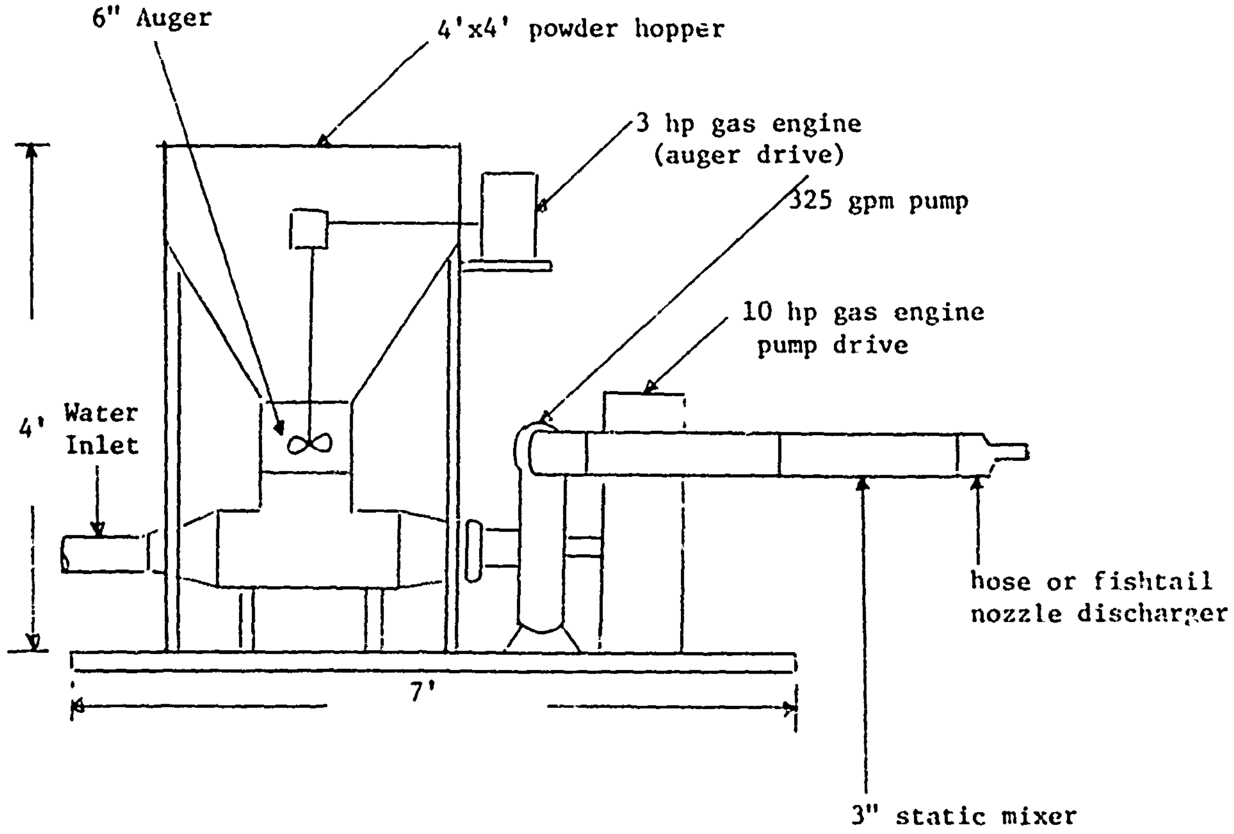
2.6 PREFERRED TECHNIQUES

For response to spills subject to neutralization, the evaluation of potential treating agents identified two preferred agents: sodium bicarbonate for treatment of acidic spills and sodium dihydrogen phosphate for treatment of basic spills. The choice of these agents was based on several criteria including considerations of availability, cost, efficacy, and safety. The primary consideration in selecting these two preferred agents, however, was that excessive application or misapplication would have a minimal effect on the water quality. If the preferred agents are not available, second choice alternatives are probably sodium carbonate (for acidic spills) and boric acid (for basic spills). Both these agents will produce more severe pH excursions in the water body if misapplied than will the preferred agents.

For practical purposes, spills in excess of about 10,000 gallons are rare and also will require tremendous quantities of treating agent. For this reason, we have recommended that response equipment be designed to cope with spills smaller than about 10,000 gallons. The equipment still would be useful for partial treatment of very large spills.

FIGURE 2.5-1

SIMPLE POWER MIXING
AND SLURRY DEPLOYMENT SKID

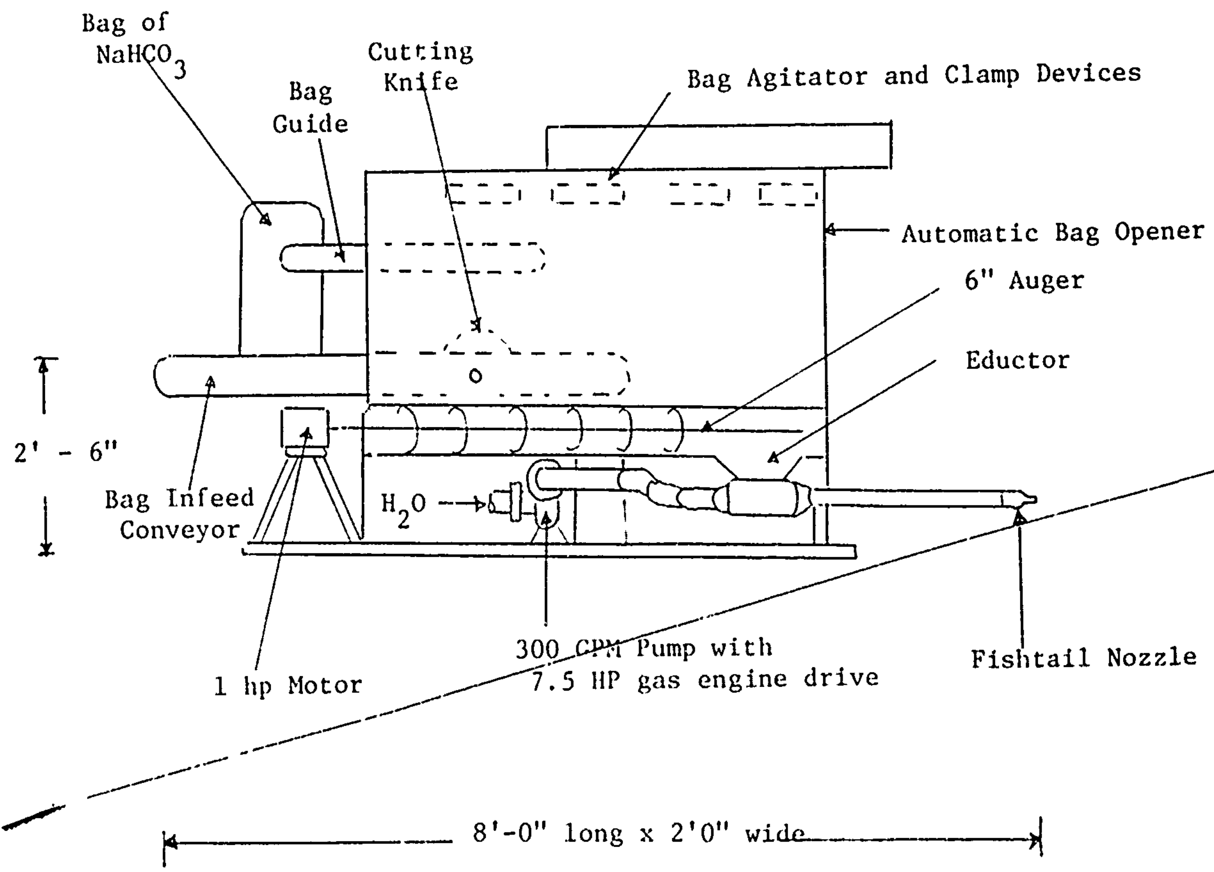


Skid mounted unit for treating
10,000 gallon spill in 16 hour period

Cost: $7000 (approx.)
Weight: 1 ton (approx.)

FIGURE 2.5-2

Neutralizing Agent Deployment Skid
with Automatic Bag Opener



Skid mounted unit for treating
10,000 gallon spill in 16 hour period

Cost: \$13-15,000 (approx.)
Weight: 3,000 lbs. (approx.)

In the preferred response scheme, treatment skids would be constructed and stored at Coast Guard spill response depots. Each skid would contain the following equipment:

- A conveyor and bag opener for the treating agent
- A feed bin
- A positive mixer for adding treating agent to water in the desired proportion
- A pump
- A fish tail nozzle for dispersing neutralizing solution over the spill zone.

A sketch of the equipment is shown in Figure 2.5-2. The skid weight is estimated at about 3000 pounds and the unit cost at about $15,000.

In marshalling a response effort the skid could be carried by helicopter to the response location. Simultaneously, treating chemical would be obtained from the nearest source and trucked or air lifted to the scene. The response strike team would be at the spill scene to oversee the installation of the treatment skid on a boat of the buoy tender class. (For spills into confined areas such as drainage ditches, the skid could be truck mounted and hauled to the proper location). Treatment chemical, available in 50 or 100 lb. bags, would be shuttled to the skid for application by the strike team.

This response technique appears feasible for neutralization of hazardous water-soluble chemicals which result in unacceptable water pH levels. In stagnant water, long response times are acceptable; in flowing water, response within six to twelve hours appears to have considerable potential for spill hazard amelioration. In estuaries or tidal waters, response becomes less likely to be effective unless accomplished before the next tidal reversal.

An important factor in the overall feasibility is, obviously, the ability to locate the contaminated zone during the response period. This facet was not a part of the present study. Nevertheless, overall feasibility of the treatment by neutralization will depend on the ability to locate the contaminated region; also equipment for marking the spill and for monitoring in situ pH before and during treatment will be required in addition to the response skid equipment.

Also, since we considered neutralization as a general technique, some special properties of individual chemicals were not considered. For example, a dense soluble chemical might tend to sink before entering the water column and dispersing. Such factors would have to ultimately be worked into the response strategy data base available to the response team.

2.7 FATE AND CONSEQUENCES OF TREATMENT BY NEUTRALIZATION

2.7.1 Fate and Consequences of the Spilled Chemical

2.7.1.1 Physio-Chemical Consequences

The major physio-chemical consequences of a spill of an acid or base into water is, of course, a significant change in the pH (assuming a relatively strong acid or base and a relatively large spill). Physio-chemical consequences expected to be relatively minor are associated with:

- An increase in the ionic strength of the water;
- A slight increase in water temperatures - for most, but not all, spills - due to the heat of solution (See 2.7.2 for a more detailed discussion of this point);
- A possible increase in the Chemical Oxygen Demand (COD) resulting in lower levels of dissolved oxygen;
- The resolubilization of heavy metals from a lowering of pH; and,
- Other changes in water chemistry.

2.7.1.2 Biological Consequences

The severity of the biological consequences will, as mentioned in the Introduction, depend on several factors, e.g.:

- Amount of spill; resulting rate and extent of pH change;
- Duration of spill effects (before neutralization);
- Identity of the chemical; its specific toxicity, BOD, COD, etc.;
- The nature of the affected water; fresh versus salt, naturally high or low pH, buffering capacity, rate of mixing;
- The season; this will be a determining factor in the number and types of aquatic organisms present.

2.7.1.3 Two Case Histories [4]

2.7.1.3.1 Fly Ash Pond Spill into the Clinch River (Virginia)

In 1967, the contents of a fly ash pond - roughly 130 million gallons - spilled into the Clinch River. The spill contained significant amounts of $Ca(OH)_2$ and had a pH of 12.0 to 12.7. This caustic spill equalled 40% of the daily flow of the Clinch River at the time and resulted in blocking the normal flow for several minutes; some spill was forced upstream. The alkaline slug traveled downstream at a rate of approximately 0.85 miles an hour killing essentially all the fish in its path for about four and one-half days. Fish kills - totaling over 200,000 fish - were reported for a 90 mile segment of the Clinch River. The lethal agent was primarily a high pH; a secondary, contributing effect, was a depression in dissolved oxygen caused by the decaying organic matter.

A survey of aquatic life 10 days after the spill showed a complete elimination of fish food organisms for 3 to 4 miles downstream of the spill and a drastic reduction in the number and kinds of bottom dwelling fish food organisms for 77 miles below the spill. Another survey two years later indicated the Clinch River had not fully recovered.

2.7.1.3.2 Sulfuric Acid Spill into the Clinch River (Virginia)

In 1970, an undetermined amount of sulfuric acid was spilled into the Clinch River resulting in a kill of about 5,300 fish. Stream damage was estimated to extend approximately 13.5 miles downstream from the spill site. Aquatic communities of mayfly and mollusk species were completely eliminated by the low pH shock for a distance of 11.7 river miles; other species were significantly reduced in number. Significant recovery of aquatic life was noted six weeks after the spill. Sixty days after the spill, the river had recovered to the point that representative species of aquatic insects found before the spill were present at all affected locations. Mollusk species were slower to reappear and had still not recovered a few months after the spill.

2.7.1.4 Ultimate Fate of the Spilled Chemicals

In all cases, dilution will eventually reduce the concentration of the spilled chemical to essentially harmless levels. If the spill is into a water body (or stream) of adequate size, then dilution will be the primary factor in the natural amelioriation of the spill. Various other factors will also be involved depending on the chemical and the affected waters:

- Adsorption onto colloidal particles and sediments may be significant, especially for the weaker electrolytes;
- Cation exchange may take place;
- Hydrolysis - this may be important for some organic species;
- Biochemical Oxidation - this may be important for some chemicals;
- Evaporation - this may only be a factor for chemicals such as NH_3 and HCl.

2.7.2 Potential for Thermal Pollution From Neutralization

All chemical reactions involve some heat effects causing either absorption of heat (cooling the local environment) or evolution of heat (heating the local environment). The reaction may consist of dissolution, dilution, neutralization, or other processes.

The effects of a short term temperature change on the aquatic biota in, or downstream of, a spill site are very complex and thus difficult to evaluate. The effects, both beneficial and detrimental, will depend on the normal temperature for the season, the deviation from this normal caused by the spill and ensuing neutralization (which in turn depends on several factors), and the species present.

The initial spill will itself cause some heat effects. Some of the chemicals react violently with water giving off large amounts of heat; this will create a local hot spot which will dissipate with time. Even when there is no actual reaction with water, there are heat effects associated with the dissolution of the chemical in water. The dissolution of the acids and bases being considered here will almost always result in the evolution of heat, with the stronger acids and bases evolving more heat than the weaker agents (see Table 2.7-1). One exception to this rule is acetic acid; it will absorb a small amount of heat upon dissolution.

The dissolution of the neutralizing agent will also involve heat effects. Heat may either be absorbed or evolved depending not only on the chemical involved, but also on the degree of hydration of a particular chemical (see Table 2.7-1).

TABLE 2.7-1[14]

HEATS OF SOLUTION* FOR SOME CHEMICALS IN WATER (∿18°c)

	Kcal/gram formula wt.
Sodium carbonate, Na_2CO_3	+5.69
Sodium carbonate, $Na_2CO_3 \cdot H_2O$	+2.15
Sodium carbonate, $Na_2CO_3 \cdot 10H_2O$	-16.15
Sodium bicarbonate, $NaHCO_3$	-4.30
Sodium dihydrogen phosphate, $NaH_2PO_4 \cdot H_2O$	(no information)
Trisodium phosphate, $Na_3PO_4 \cdot 12H_2O$	-14.6
Sodium acid phosphite, NaH_2PO_3	+7.41
Disodium hydrogen phosphate, Na_2HPO_4	+5.64
Disodium hydrogen phosphate, $Na_2HPO_4 \cdot 2H_2O$	- .382
Disodium hydrogen phosphate, $Na_2HPO_4 \cdot 7H_2O$	-11.5
Phosphoric acid, H_3PO_4	+2.70
Sulfuric acid, H_2SO_4	+17.75
Hydrochloric acid, $HC\ell$	+17.44
Nitric acid, HNO_3	+7.17
Acetic Acid, CH_2COOH	-2.15
Ammonia, NH_3	+8.46
Sodium hydroxide, NaOH	+10.30
Potassium hydroxide, KOH	+12.95

* Negative sign implies absorption of heat.

The neutralization reaction will most always involve the evolution of heat. When strong bases and strong acids are mixed, the heat of neutralization is always very close to 13.7 Kcal/mole when equivalent amounts are mixed. This value is the heat of neutralization for the following reaction:

$$H_3O^+ + OH^- \longrightarrow 2H_2O + 13.7 \text{ Kcal} \qquad 2.7\text{-}(1)$$

If either the acid or the base is not completely ionized, the heat of neutralization may be more or less than the value given above. Some examples follow:

$$CH_3COOH + Na^+OH^- \longrightarrow H_2O + CH_3COO^-Na^+ + 13.4 \text{ Kcal} \qquad 2.7\text{-}(2)$$

$$NH_3 + H_3O^+Cl^- \longrightarrow H_2O + NH_4^+Cl^- + 12.3 \text{ Kcal} \qquad 2.7\text{-}(3)$$

$$HF + Na^+OH^- \longrightarrow H_2O + Na^+F^- + 16.3 \text{ Kcal} \qquad 2.7\text{-}(4)$$

Thus, the heat evolved in neutralization reactions is seen to be the same order as the heat evolved in the dissolution of a very strong acid or base.

The temperature rise that would be associated with this evolution of heat would depend on the details of the spill, spill site, concentrations of both acid and base, mixing, etc. When relatively dilute concentrations, large volumes, and good mixing are involved, the temperature rise should not be significant. The temperature rise could be offset somewhat if a highly hydrated form of the neutralizing agent were used since the dissolution of the agent involves the absorption of heat. It seems very unlikely that the temperature rise would reach a critical range in any significant volume of water. For example, the 24-hour median lethal temperature limit for several species of common fish is in the range of 25°C - 38°C (77°F - 100°F) ;[24] neutralization would not be expected to cause more than a few degrees rise from normal when large volumes are considered.

As a sample calculation of the temperature rise following a neutralization reaction, consider the reaction of 100 moles of a strong acid with 100 moles of a strong base in 1 cubic meter of water. The amount of heat liberated would be approximately 100 x 13.7 Kcal or 1.37×10^6 calories. If this amount of heat is applied to 1 cubic meter of water (10^6 ml) initially at 15° C, the temperature rise would be just over 1°C (the specific heat of water is 1 cal/°C at this temperature).

2.7.3 Fate and Consequences of the Neutralizing Agent and the Reaction Products

2.7.3.1 Consequences of Optimum Treatment

Optimum treatment, i.e., the attainment of a safe pH of 6-9 in the spill site with no overshoots or misses, will essentially eliminate the worst aspect of the initial spill, the excessively high or low pH.

This major benefit will be slightly offset by:

1. A further increase in the ionic strength of the water, to which aquatic organisms will be variously sensitive;
2. A slight increase in temperature, probably no more than 1°C, due to the heat of reaction. (See 2.7.2 for a more detailed discussion of this point);
3. An increase in nutrient concentration - primarily in the case of neutralization with NaH_2PO_4 - which could lead to algal growth (and, thus, an increase in the oxygen demand), and a temporary increase in the rate of eutrophication in confined waters.

None of the offsetting factors mentioned are expected to pose a serious problem. The increase in ionic strength due to the addition of the neutralizing agent is not likely to make matters much worse, compared to the damage done initially by the spill. The temperature increase due to the heat of reaction is unlikely to exceed 1°C and, thus, should not result in any adverse effects. The addition of a nutrient, phosphate in the case of NaH_2PO_4, may or may not lead to temporary increase in algal growth. Phosphate is sometimes the biomass-determining nutrient, but it is expected that in a majority of cases the limiting nutrient will be some other compound or element (e.g., N, S, Ca, Mg, K, Fe, Mn, Zn, Mo, or B). Carbonate, like phosphate, is a nutrient, but it is rarely the limiting nutrient in water bodies.

The other components of the neutralizing agents (Na^+ for both acid and base neutralization and HCO_3^- for acid neutralization) should not have any significant adverse effects on natural waters aside from the ionic strength aspect mentioned above. Both components may be considered essentially non-toxic; both are constituents of unpolluted waters at modest levels.

2.7.3.2 Consequences of Sub-Optimum Treatment

2.7.3.2.1 Addition in the Wrong Place

If a recommended neutralizing agent were added in the wrong location the consequences (to aquatic life) would be negligible to moderate depending on the conditions.

A misapplication of $NaHCO_3$ to neutral, unbuffered waters could, at most, raise the pH to about 8.3, which is technically within the designated safe range. This pH is achieved only for $NaHCO_3$ concentrations near the ultimate solubility of about 1.0 M. The abrupt, but temporary, increase in ionic strength associated with a misapplication could affect aquatic life; ionic strength affects transport across biomembranes and their osmotic properties, and a sufficiently abrupt change in ionic strength may even result in cell rupture. This effect would be expected to be local and temporary.

A misapplication of NaH_2PO_4 to neutral, unbuffered waters could, at most, lower the pH to about 4.1. This pH is achieved by NaH_2PO_4 at a concentration of 1.0 M; the ultimate solubility is about 10 M. This pH lowering could have moderate, local impact on the aquatic life. The problem of ionic strength change would be present as would any problems relating to nutrient addition (where phosphate was the limiting nutrient).

2.7.3.2.2 Addition of Too Little or Too Much

Addition of an inadequate amount of neutralizing agent, such that the pH is not returned to the range of 6-9, will improve the situation. Partial neutralization is better than no neutralization since it will reduce the extent of damage due to the original spill.

Addition of too much neutralizing agent should, generally, have a negligible adverse effect. The recommended agents, $NaHCO_3$ and NaH_2PO_4, were chosen (in part) because they would not result in a serious overshoot problem. If neutralization is stopped at the limits of the safe pH range (e.g., at 6 when neutralizing acids and at 9 when neutralizing bases), then a significant excess can be added without having the pH leave the safe range. This has been demonstrated both with sample calculations and with laboratory experiments carried out in this study. A description of the laboratory experiments is presented in Appendix B; calculations analyzing underaddition of agent are described in Appendix C.

2.7.3.3 Ultimate Fate of the Neutralizing Agents and/or Reaction Products

If the neutralization is carried out in a water body of adequate size, then dilution will be the primary factor in reducing the chemical concentrations to harmless levels. Various other factors will be involved, such as adsorption, cation exchange, hydrolysis and biochemical oxidation (see Section 2.7.2.4 above), depending on the chemicals involved.

3.0 SOLVENT EXTRACTION

3.1 PRINCIPLES OF SOLVENT EXTRACTION

3.1.1 Definition

For the purposes of this report, solvent extraction can be defined as mixing water containing a hazardous chemical with a liquid which is immiscible with water and then allowing the two liquids to separate again. At this point, the hazardous chemical is distributed between the two phases; its concentration in the water has been reduced.

3.1.2 Thermodynamic Equilibria

A two-phase ternary mixture of water, solvent and one other component may have a wide range of properties. The theoretical background can be obtained from a number of standard reference works.[15,18,27,31,32] However, we are not concerned with all possible combinations of three components - only with the extraction of one relatively dilute component from water into a solvent. Water will either be in excess or at about the same volume as the solvent. For this simple case, the equilibrium properties of the system can be described in terms of the partition coefficient. This parameter describes the way in which the third component (the hazardous chemical to be extracted) distributes itself between the solvent and water after the two phases are mixed and then allowed to separate. Mathematically, the partition coefficient equals the weight fraction of C in solvent/the weight fraction of C in water, where C is the hazardous chemical.

3.1.3 Kinetics

In the approach to thermodynamic equilibrium, the rate of transfer of the material from the water to the solvent must be considered. This mass transfer process is generally limited by the extent of interfacial contact of the two phases. Therefore, equipment for solvent extraction is generally designed to maximize the area and rate of contact of the water and solvent phases to achieve a rapid extraction. Although thermodynamic equilibrium might be closely approached after the two phases are mixed and separated, the partition coefficient is rarely large enough that one such operation suffices to remove most of the hazardous chemical. Therefore, the aqueous layer must be mixed with fresh solvent and the process repeated. Because the concentration of hazardous chemical in the aqueous layer has decreased, a second extraction with a given volume of solvent will remove less of the solute. Each extraction removes a smaller quantity and it is theoretically impossible to remove all the hazardous chemical from the aqueous layer by this means. However, by carefully prescribing the solvent and the type and number of extraction stages, it may be possible to reduce the concentration of hazardous chemical in the aqueous layer to below the toxic limit.

3.2 PRACTICAL LIMITATIONS OF SOLVENT EXTRACTION

3.2.1 Physical Properties

It is difficult to define theoretical limits to solvent extraction other than those mentioned above. However, for purposes of ameliorating spills of hazardous chemicals in water, practical limitations restrict the types of systems considered. Constraints are imposed by the chemical components of the system, particularly solvent and spill chemical, which determine whether adequate extraction and separation of the two phases can occur. Contacting equipment must be selected to insure that the procedure can be carried out on site in a reasonable period of time and in a manner consistent with Coast Guard clean-up operations.

3.2.1.1 Phase Separation

The ease with which the two phases, solvent and water, separate after an appropriate mixing interval is an important criteria for successful solvent extraction. The two critical physical properties are the difference in densities between the two phases and the difference in interfacial tension between them. The ease of separation is a compound function of these two properties. For example: if the density difference between the two phases is 10-20%, then a relatively low interfacial tension of 5-10 dynes per sq. cm. can be tolerated; conversely, if the density difference between the two phases is only 1-5%, then a high interfacial tension, 40-50 dynes per sq. cm., will be essential to achieve an adequate separation. The interfacial tension may, in practice, be a critical property because the presence of small amounts of impurities, particularly those with detergent properties, can modify the surface film severely and prevent efficient separation.

3.2.2 Solubility of Solvent in Water

Although any useful solvent must be essentially insoluble in water, all solvents will have a finite solubility (in addition to possible losses by entrainment of droplets). This loss of solvent will occur after every contacting operation and should be as low as possible - certainly less than 1% by weight of the solvent. If the solvent solubility were higher than this figure, then a second extraction (with another solvent) would be required to remove the first solvent from the water. We believe that the complexities and disadvantages of such a two-step extraction process outweigh the potential limitations of a single-step extraction (where the solvent may be less efficient in extracting the spill chemical but is not lost by solution in water). An equally important criteria is that the equilibrium concentration of solvent in water at the solubility limit must be lower than the toxicity limit for that material. Otherwise the addition of solvent compounds the problem by introducing a second material at a toxic level.

3.2.1.3 Solvent Recovery

Recovery and reuse of solvent during the clean-up operation is an essential part of the solvent extraction system; without solvent recovery any multistage operation would require such large volumes of solvent as to be impractical for any but the smallest spills. To simplify this portion of the equipment, the relative volatility of the spilled chemical solvent system should significantly exceed unity so that the chemical can be removed overhead without the necessity of evaporating and condensing the solvent. In addition, solvents which might form azeotropes (i.e., mixtures which have a unique boiling point like a separate compound) with the spill chemical or with water should be avoided.

3.2.1.4 Partition Coefficient

The partition coefficient of the spill chemical defined earlier should be greater than or equal to one. This means that a single extraction (using equal volumes) would remove 50% of the spill chemical; 5 separate extractions would give 97% recovery, assuming 100% theoretical efficiency in each extraction stage. Appropriate equipment is limited to about 5 extraction stages in a single operation; this assuming that there are no kinetic constraints on the extraction so that the amount extracted is close to that implied by the value of the partition coefficient.

3.2.2 Selection of Equipment

3.2.2.1 Introduction

There are two major types of equipment for solvent extraction:

1. Single-stage equipment: the fluids are mixed, extraction occurs, and the immiscible liquids are allowed to settle and separate. A cascade of such stages may be arranged. A single stage must provide facilities for mixing the liquids and for settling and decanting the emulsion or dispersion which results. In batch operation, mixing, settling and decanting may take place in the same or in separate vessels. In continuous operation, different vessels are required.
2. Multi-stage equipment: the equivalent of many stages may be incorporated into a single device or apparatus. When the liquids flow countercurrently through a single piece of equipment, the contacting may be equivalent to as many stages as desired. In such devices, countercurrent flow is induced by virtue of the different densities of the liquids; with few exceptions, the equipment takes the form of a vertical tower which may or may not contain internal devices to influence the flow pattern. Other forms include centrifuges, rotating discs, and rotating buckets. Depending upon the nature of the internal structure, the contact may be either stagewise or continuous.

Examples of various types of contacting are given in Table 3.2-1 below:

TABLE 3.2-1 [18]

CLASSIFICATION OF CONTACTING EQUIPMENT

Type of Agitation	Discrete Stage Contact	Continuous Contact
None		Spray column Baffle plate column Packed column Sieve-tray column
Rotary devices	Holley-Mott Simple mixer-settler Pump-mix mixer-settler Individual stage centrifuges Stacked-stage mixer settler	Schiebel column Oldshue-Rushton column Rotating disc contactor Multistage mixer column Podbielniak extractor DeLeval extractor Luwesta Graesser Westfalia

TABLE 3.2 -1 (Continued)

CLASSIFICATION OF CONTACTING EQUIPMENT

Type of Agitation	Discrete Stage Contact	Continuous Contact
Pulsed	Pulsed mixer-settler	Pulsed packed column Pulsed sieve-plate column

3.2.2.2 Important Parameters

The choice of a contactor involves consideration of several factors. Some of these are discussed by Lagsdail and Lowes[18] as follows:

Number of Stages Required - All types of extractor can be used satisfactorily when few (two or three) theoretical stages are required. When more are needed, the choice becomes limited; the columns required would be very tall and mixer-settlers would occupy a large area. Centrifugal extractors are limited to about 10 stages.

Capacity - For low and moderate throughputs a spray or packed column can be used; for intermediate and high throughputs a rotating disc contactor (RDC), pulsed plate column or mixer-settler can be used. Centrifugal extractors have the highest throughput per unit volume of contactor.

Drop Size - The drop size in differential extractors is a function of the parameter ($\sigma/\Delta\rho$), where σ is the interfacial tension and $\Delta\rho$ the density difference between phases; large values of this parameter correspond to large drops and hence to a low interfacial area which is commensurate with poor mass transfer performance. With mechanically agitated contactors, the drawbacks of a system having a high interfacial tension (hence high ($\sigma/\Delta\rho$) value) can be overcome by increasing the power input to the system. Thus, a certain degree of flexibility is available for matching the mass transfer efficiency and capacity to give the required performance.

Phase Dispersion and Hold-up - To obtain the greatest interfacial area over which to affect mass transfer, the phase having the highest throughput should be dispersed. However, it may prove difficult to disperse the aqueous [illegible] in column contractors, since many packings and construction materials [illegible] preferentially wetted by an aqueous phase. If this happens, the dispersed [illegible] move through the column in streams, films and large irregularly [illegible] rather than as discrete drops, giving rise to a poor performance. [illegible] are available and can be used so long as they withstand [illegible] If contamination of the extract phase is likely to occur due to the collection of particular impurities at the interface in a column contactor, then the phase dispersion should be such that the interface is at the raffinate end of the column. If a low hold-up of one of the phases is desired, for instance when handling unstable solutes or high-cost solvents, minimum contact time and contactor volume are required. These requirements are best met with one of the centrifuge contactors.

Presence of Solids - When solids are present in one or both of the feeds, many types of extractions have to be shut down periodically to remove solid deposits. An exception is the pulsed plate column, which to a large extent is self-cleaning, and the Luwesta centrifugal extractor, which has provisions for solids removal. It is also claimed that the Graesser contactor can handle solids in suspension.

For the amelioration of chemical spills, the most important considerations are (1) the number of stages required (about five for the singly substituted hydrocarbons); (2) the need for a high throughput per unit volume of contactor (so that a small portable unit can be used); and, (3) the need to separate two liquid phases having small density differences. (See Section 3.3.)

3.2.2.3 Centrifugal Extractors

Information on three of the best known centrifugal extractors (DeLaval, Podbielniak, Westfalia) was obtained from the literature and from the manufacturers or distributors.

Some specifications on the models of interest from these three companies are given in Table 3.2-2. The DeLaval and Podbielniak centrifuges are of a continuous or differential type whereby the internal arrangement of baffles provides the equivalent of several stages within a single bowl or cylinder. The Westfalia centrifuges are discrete stage contactors with the two (and three) stage units incorporating a second (and third) bowl above the first. In addition, the Westfalia line includes a nozzle bowl separator (single stage only) which can remove suspended solids (which are heavier than either of the two liquid phases) while the unit is in operation; the other models of all three companies do not have such a feature and would have to be periodically taken apart for the removal of accumulated solids. Most units are designed for quick disassembly and reassembly to keep downtime to a minimum.

TABLE 3.2-2

SPECIFICATIONS FOR SOME CENTRIFUGAL EXTRACTORS

Make	Model	Maximum Capacity (gal/min)	Number of Stages	Maximum Rotation Speed of Bowl (ppm)	Power for Main Motor (HP)	Material of Construction	Approximate Weight of Basic Unit (lbs)	Dimensions of Basic Unit (in) (l x w x h)	Estimated Cost (000$)
DeLaval	ABE 210	22.8	(2- 7)	4,000	15- 25	SS**	4,620	132 x 51 x 53	?
DeLaval	ABE 216	90.	4-15	6,000	40	SS	5,950	142 x 71 x 75	150 - 200
Podbielniak	A-1	3	3-10	10,000	3	SS	385	43 x 27 x 16	13
Podbielniak	B-10	75	3-10	3,200	7.5	SS	2,700	68 x 56 x 33	40
Podbielniak	D-18	225	3-10	2,100	15	SS	8,600	85 x 76 x 45	75
Podbielniak	D-36	450	3-10	2,100	25	SS	10,250	85 x 94 x 45	100
Podbielniak	E-48	800	3-10	1,600	40	SS	21,500	107 x 113 x 59	180
Westfalia*	Nozzle Bowl	700-1000	1	?	(~150)	SS	(~22,000)	(~6' x 3' x 6')	180
Westfalia*	Liq-Liq Separator	500	1	?	(~100)	SS	(~12,000)	(~6' x 3' x 6')	120 - 140
Westfalia*	Liq-Liq Separator	500	2	?	(~100-150)	SS	(~14,000)	(~6' x 3' x 7')	-
Westfalia*	Liq-Liq Separator	500	3	?	(~150-200)	SS	(~16,000)	(~6' x 3' x 8')	-

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* Specific model information not obtained.

** Stainless steel.

3.3 SELECTION OF SOLVENT

3.3.1 Criteria

All organic chemicals which have a low solubility in water are potential solvents in an extraction process. Therefore, it is necessary to develop criteria which will rapidly eliminate less desirable solvents from consideration, in order to concentrate on those which show the best properties with respect to clean-up of the listed spill chemicals. We have developed the criteria in Table 3.3-1; 1 is considered most important, 2, 3, and 4 about equally important, and 5 and 6 less important.

3.3.2 Toxicity Limitations

The 22 solvents shown in Table 3.3-2 were selected on the basis of availability of data (for NAS hazard rating, solubility in water and partition coefficients, etc) and also to represent the various classes of solvents. The key to the NAS toxicity rating is provided as a footnote to the table. These solvents were first evaluated to decide whether their solubilities in water were less than their acceptable toxic limits according to the NAS rating. On this basis, only three solvents were clearly acceptable: heptane, vegetable oils, and oleyl alcohol. Octanol is of borderline acceptability because of its appreciable solubility and its moderate toxicity. Further data on these four most promising solvents are shown in Table 3.3-3. Heptane was eliminated from further consideration because of its relatively low boiling point and appreciable fire hazard and because of the low partition coefficients for the chemicals of interest in this solvent.

The literature search (see list in Appendix D) revealed that partition coefficients between these solvents and the spill chemicals reached 1 only in the most favorable cases; for many spill chemicals, they were much less than 1. Octanol shows the most favorable range of partition coefficients, with values as high as 250, although some compounds still had coefficients much less than one. In addition to potential toxicity, 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 is much more limited.

Vegetable oils appear to be the most attractive compounds as solvents because of their low toxicity. The density difference between vegetable oil and water is only about 10%, but this should be acceptable because of the high interfacial tension. The partition coefficients are acceptably high for

TABLE 3.3-1

CRITERIA FOR CHOICE OF SOLVENT

1. SOLUBILITY IN WATER LESS THAN TOXIC LIMIT
2. LOW SOLVENT LOSSES
3. HIGH PARTITION COEFFICIENT (≥ 1)
4. EASY SEPARATION OF SOLVENT AND WATER
5. EASE OF HANDLING
6. AVAILABILITY AND COST

TABLE 3.3-2

TOXICITY CRITERIA FOR SOLVENTS

Solvent	NAS Hazard Rating		Maximum Concentration		Acceptable According to Toxicity Criteria
	Human Toxicity	Aquatic Toxicity	Water In Solvent (Wt.%)	Solvent In Water (Wt.%)	
n-Amyl Alcohol	2	3	9.0	2.6	No
Benzene	1	3	.041	.08	No
n-Butanol	2	2	20.	7.9	No
2-Butanone	2	1	12.	35.	No
Carbon Tetrachloride	2	2	.018	.08	No
Chloroform	1	2	.12	1.0	No
Cyclohexane	1	2	.0045	.015	No
Cyclohexanol	1	3	11.	4.3	No
Cyclohexanone	1	3	8.1	5.0	No
Diethyl Ether	0	1	1.2	7.5	No
Ethyl Acetate	1	2	3.4	8.7	No
Heptane	1	1	.0059	.005	Yes
Isobutanol	2	1	15.	9.5	No
Isopentylacetate	ND	3	.82	1.	No
Methyl Isobutyl Ketone	2	1	2.4	2.	No
Nitrobenzene	3	3	.32	.19	No
Octanol	1	2	4.1	0.6	Questionable
Oils (Vegetable)	0	0	.13	Very Small	Yes
Oleyl Alcohol	ND	0-1	1.3	Very Small	Yes
2-Pentanol	ND	2	9.6	5.3	No
Toluene	1	3	.046	.05	No
Xylene	1	3	.034	Very Small	Questionable

NAS TOXICITY RATING	MAXIMUM SAFE PPM	SOLUBILITY WT.%
0	10,000	1.0
1	1,000	0.1
2	100	0.01
3	10	0.001
4	1	0.0001

TABLE 3.3-3

DATA ON FROMISING SOLVENTS

	DENSITY gms/cc(20°C)	INTERFACIAL TENSION DYNES/CM (20°C)	BOILING POINT °C	RANGE OF PARTITION COEFFICIENT	FIRE HAZARD
HEPTANE	0.68	40	98.4	0.001 - 1	Flash point below 38°C
VEGETABLE OIL	0.92	50	high	0.0004 - 80	Flash point above 60°C
OCTANOL	0.83	8.5	195	0.01 - 250	Flash point above 60°C
OLEYL ALCOHOL	0.83	35	300	0.02 - 200	Flash point above 60°C

CHARACTERISTICS OF VEGETABLE (SOYBEAN) OIL

1. Non Toxic
2. Stable to heat
3. Flash point above 280°C
4. Produced in high volume (> 7.5 million pounds annually)
5. Acceptable cost (20-40¢/lb)

many of the spill chemicals; however, some on the list would not be readily extractable with vegetable oils.

Soybean oil is a typical vegetable oil which is produced in high volume (greater than 7.5 billion lbs annually) and is widely available. The cost is acceptable, 20-40¢/lb. Vegetable oil is readily stored in closed containers (to prevent oxidation and bacterial attack) and is stable to heat, with a flashpoint above 280°C.

3.4 EXTRACTABILITY OF SPILL CHEMICALS

3.4.1 Effect of Hydrophilic Groups

The range of partition coefficients encountered with all of the promising solvents suggest that some spill chemicals may be difficult to extract with any solvent. In addition, data are not available for many compounds and a method of estimation is desirable. Therefore, an examination was made of the different chemical classes of compounds to evaluate the potential for solvent extraction with vegetable oil. Data for some of the chemical classes were restricted to one compound but the results in Table 3.4-1 show that it is clearly possible to separate the list into two types of compounds, i.e., those with only one hydrophilic group (monosubstituted hydrocarbons) and those with more than one hydrophilic group (polysubstituted hydrocarbons). Available data for the polysubstituted hydrocarbons indicate that these compounds in general have a very low partition coefficient for vegetable oils (and for other promising solvents); they therefore are not readily extractable because they have such a great affinity for water compared to any organic solvent. The data for monosubstituted hydrocarbons are more promising for many of the chemical classes. All the monosubstituted classes except acids show some partition coefficients of one or higher; acids run an order of magnitude lower and therefore would not be readily extractable with vegetable oils.

3.4.2 Effect of Carbon Chain Length

Data from the literature were also evaluated for different chemical classes to see the effect of carbon chain lengths on the partition coefficient with the results shown in Figure 3.4-1. The partition coefficient increases with increasing carbon chain length in each chemical class; the large molecules are more extractable than small molecules. Even the acids, normally the most difficult class to extract, have sufficiently large partition coefficients [illegible] compounds with more than about 6 carbon atoms.

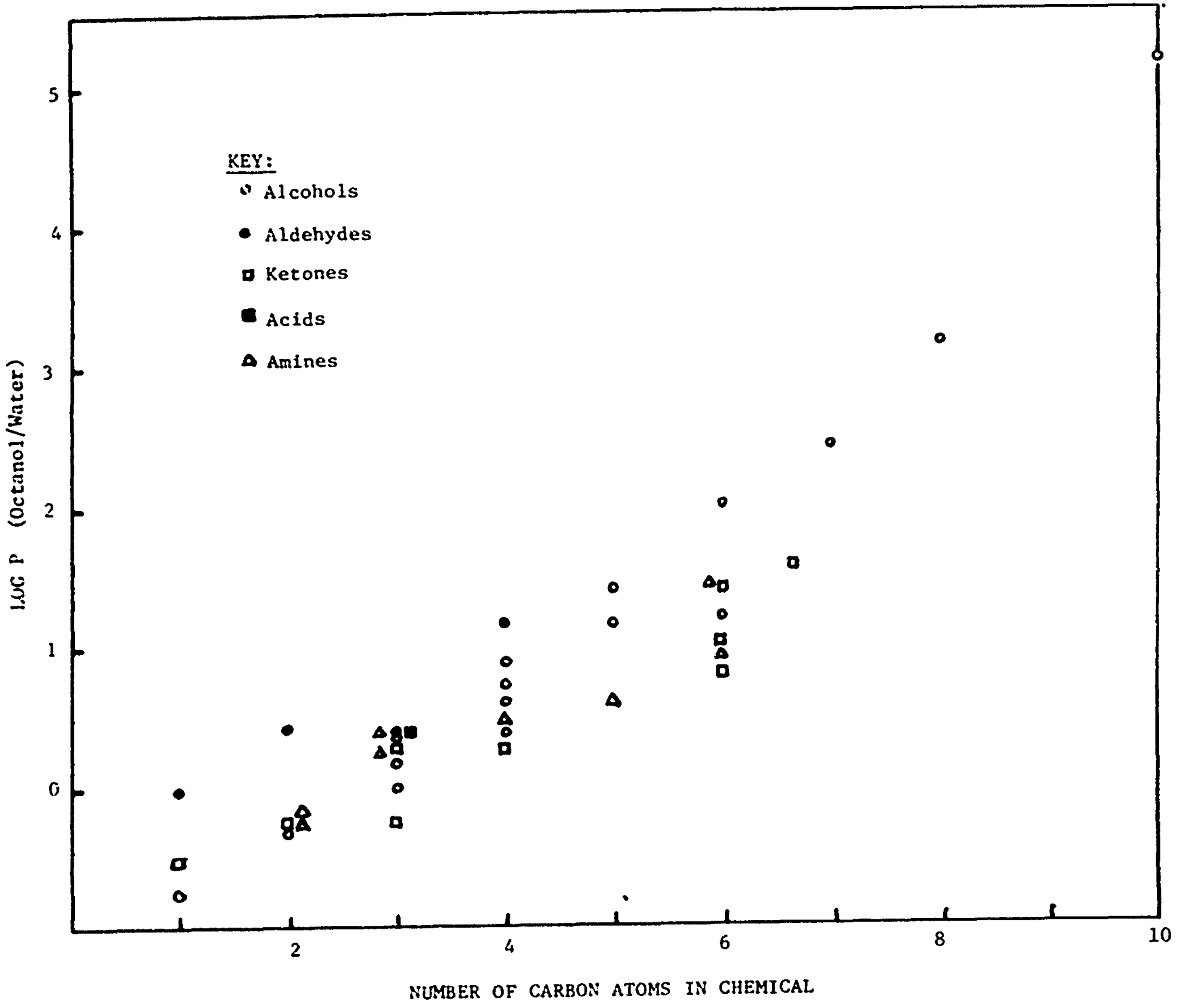
TABLE 3.4-1

PARTITION COEFFICIENT RANGES ASSOCIATED WITH THE PARTITION OF CHEMICALS BETWEEN VEGETABLE OILS AND WATER

Chemical Class	Range In Partition Coefficients	Number of Data Points	Number of Carbon Atoms Associated With Range Min.	Max.	Comments
I MONO SUBSTITUTED HYDROCARBONS					
Alcohols	.01 → 20	12	1	7	
Ketones	5.	1*	3		*Acetone
Ethers	.50 → 5.8	4	2	4	
Acids	.016 → .16	3	1	3	
Esters	3.2	1*	4		*Ethyl Acetate
Amines	.96	1*	5		*Pyridine
Nitro Compounds	.48	1*	1		*Nitromethane
Sulfides	79.	1*	1		*Carbon Disulfide
Chlorinated Hydrocarbons	25. → 500.	3*	1	2	*May have > 1 Cl on Molecule
II POLY SUBSTITUTED HYDROCARBONS					
Diols & Polyols	.0001 → .025	6	2	6	
Alcohol-Ethers	.0005 → .063	7	4	6	
Poly-Amines	.0002	1*	6		*Hexamethylene-Tetramine

* See comment column

FIGURE 3.4-1 CHANGE IN PARTITION COEFFICIENT AS A FUNCTION OF CHAIN LENGTH



3.4.3 Final Analysis

Each compound on the list of 75 provided in the RFP has been evaluated in terms of aquatic toxicity and extractability and classified in one of four groups, as shown in Table 3.4-2.

1.	Extractable with vegetable oil (T)	18 chemicals
2.	not extractable with vegetable oil (NX)	23 chemicals
3.	no treatment required (NT)	26 chemicals
4.	no data available (ND)	8 chemicals

Thirty eight other compounds which we have identified have also been included in the final classification (an alphabetical listing with the suggested grouping is provided in Appendix D.) Those compounds classifed as extractable have partition coefficients $\geq$ 1 (log P $\geq$ 0). Those compounds classified as not extractable have partition coefficients < 1. "No treatment required" indicates low toxicity (aquatic toxicity rating of 1 or 0). "No data available" means both insufficient data available to estimate the partition coefficient and appreciable toxicity (aquatic toxicity 2 or 3).

To summarize, only about 20% of the chemicals listed are extractable with vegetable oil; an additional 30% require no treatment because the spill chemicals have a relatively low toxicity.

3.5 PREFERRED METHODS OF SOLVENT EXTRACTION

The use of vegetable oil as the solvent would seem to allow a relatively simple system design. It would consist of the following basic components:

- initial settling tank and filter
- differential centrifugal extractor
- boiler tank with propane heater
- condenser
- temporary storage for extracted hazardous chemicals
- surge storage for the solvent
- possibly a heat exchanger
- pumps, valves, flow meters and associated piping
- motor-generator

The whole system, except for the motor-generator is shown schematically in Figure 3.5-1. The actual size of the system would depend on the limitations of the components (principally the centrifugal extractor), the availability of funds, and the size and weight limitations for a mobile unit.

TABLE 3.4-2 CHEMICALS SUBJECT TO SOLVENT EXTRACTION

Chemical	Aquatic Toxicity Code[1]	Log of Oil/Water Partition Coefficient[2]	Comments[3]
Acetone Cyanohydrin	3*	(-2)	NX
Allyl Alcohol	3	(-1)	NX
Aminoethanolamine	1*	ND	NT
n-Amyl Alcohol	2	0.36	T
1,4-Butanediol	2***	-2.68	NX
1,4-Butenediol	2**	-2	NX
n-Butyl Acetate	2 NRC 3 CHRIS	(1.0)	T
n-Butyl Alcohol	2	-0.24	T
sec-Butyl Alcohol	1	-0.51	NT
tert-Butyl Alcohol	1	-0.65	NT
1,4-Butynediol	2**	-2	NX
Carbon Bisulfide	2 NRC 3 CHRIS	1.89	T
Chloroform	2	1.86	T
Chlorohydrins (Crude)	2*	ND	NX
Corn Syrup	0	(-3)	NT
Dextrose Solution	0**	(-3)	NT
Diacetone Alcohol	2***	ND	NT
Dichloromethane	2**	(1)	T
Diethanolamine	1	(-1)	NT
Diethylene Glycol	1 NRC 0 CHRIS	(-1)	NT
Diethylene Glycol Dimethyl Ether	3**	(-2)	NX
Diethylene Glycol Monoethyl Ether	3	-2.22	NX
Diethylene Glycol Monomethyl Ether	3	-2.38	NX
Diisopropanolamine	2*	(-1)	NX
Dimethylsulfate	3*	ND	ND
Dimethylsulfoxide	0	(-2)	NT
1,4-Dioxane	2*	(-1)	NX
Dipropylene Glycol	1	ND	ND
Epichlorohydrin	3	ND	ND
Ethoxytriglycol	1*	(-2)	NT
Ethoxylated Dodecanol	ND	(-2)	NT
Ethoxylated Pentadecanol	ND	(-2)	NT
Ethoxylated Tetradecanol	ND	(-2)	NT
Ethoxylated Tridecanol	ND	(-2)	NT
Ethyl Acetate	2	0.5	T
Ethyl Acrylate	2	ND	ND
Ethyl Alcohol	1 NRC 2 CHRIS	-1.4	NT
Ethylene Cyanohydrin	2*	(-1)	NX
Ethylene Glycol	1 NRC 2 CHRIS	-3.31	NT
Ethylene Glycol Monobutyl Ether	2	(-2)	NX
Ethylene Glycol Monoethyl Ether	2	-1.43	NX

TABLE 3.4-2 CHEMICALS SUBJECT TO SOLVENT EXTRACTION - continued

Chemical	Aquatic Toxicity Code[1]	Log of Oil/Water Partition Coefficient[2]	Comments[3]
Ethylene Glycol Monomethyl Ether Acetate	2**	(-2)	NX
Ethylene Glycol Monomethyl Ether	2	-2.25	NX
Ethyleneimine (Monoethanolamine)	3*	(-2)	NX
Formaldehyde Solution	3	(0)	T
Glycerine	0	-4.15	NT
Hexylene Glycol	2	(-2)	NX
Isoamyl Alcohol	2	0.3	T
Isobutyl Alcohol	1	-0.3	NT
Isopropyl Acetate	1	1	NT
Isopropyl Alcohol	2	-1.18	NX
Methanearsonic acid, sodium salts	1	ND	ND
Methyl Acrylate	2	0	T
Methyl Alcohol	1 NRC 2 CHRIS	-2	NT
Methyl Amyl Alcohol	2	0.88	T
Methyl Isobutyl Carbinol	2**	0.88	T
Methyl Methacrylate	2	0.5	T
Monoethanolamine	1	(-3)	NT
Monoisopropanolamine	1*	-1	NT
Morpholine	2*	ND	ND
Paraformaldehyde	3	0	T
Polypropylene Glycol Methyl Ether	2**	(-2)	NX
n-Propyl Acetate	2*	1.0	T
n-Propyl Alcohol	2	-.85	NX
Propylene Glycol	1	-2.77	NT
Propylene Glycol Methyl Ether	2**	(-1)	NX
Propylene Oxide	1*	ND	NT
Sodium Alkylbenzene Sulfonates	3	(1)	T
Sodium Alkyl Sulfates	3	(1)	T
Sorbitol	0-1***	(-3)	NT
Sulfolane	3*	ND	ND
Tetrahydrofuran	2***	NND	ND
Triethanolamine	1 NRC 2 CHRIS	(-2)	NX
Triethylene Glycol	1	(-3)	NT
Vinyl Acetate	1 NRC 3 CHRIS	0	T

1. Codes with asterisk(s) were estimated either by the National Research Council (*) or ADL (**)
2. Values in parentheses are rough estimates by ADL. Data otherwise from Leo et al[19]
3. See text for explanation of codes

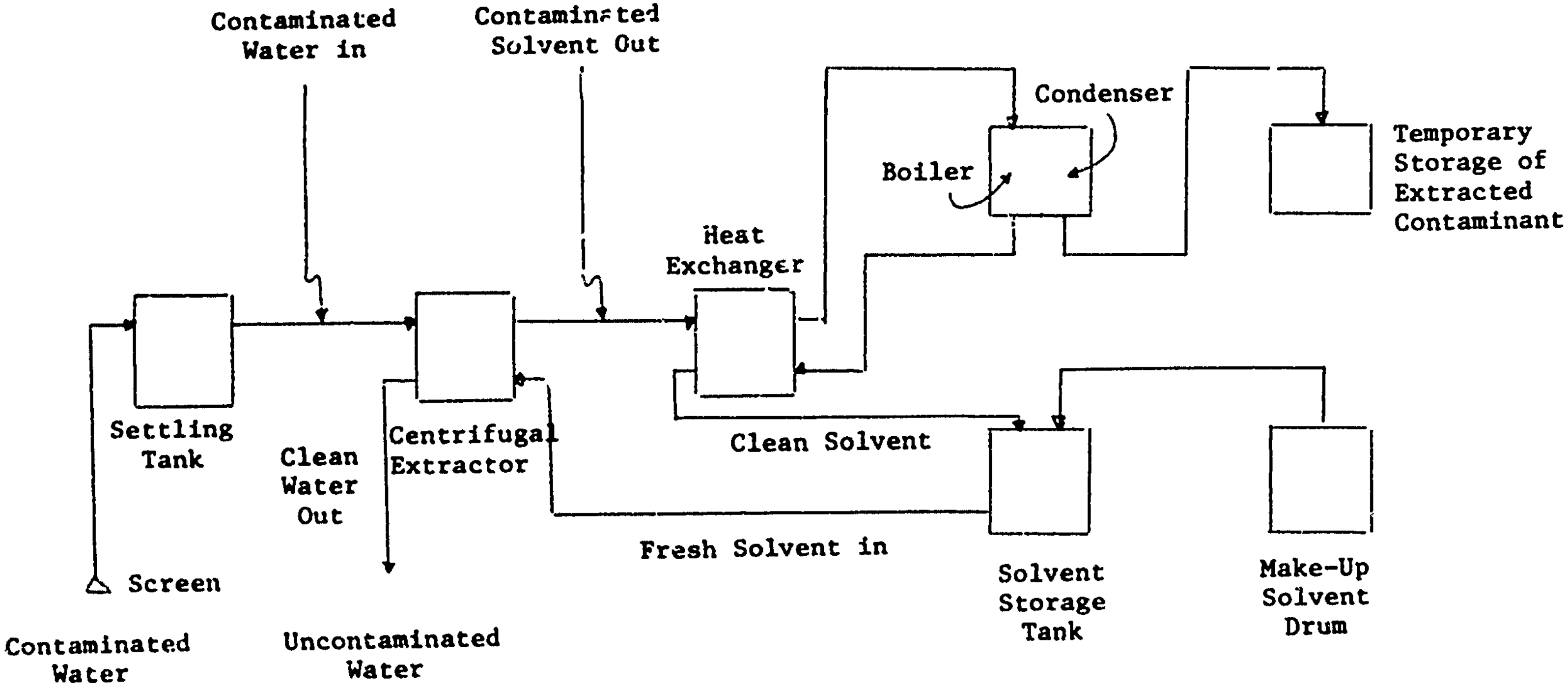


FIGURE 3.5-1

SCHEMATIC DIAGRAM OF EXTRACTION SYSTEM

(motor-generator not shown)

Some aspects of the major components are discussed below.

Initial Settling Tank

An initial settling tank and/or filter would be required any time the waters to be treated contain moderate to high levels of suspended solids. Otherwise. the centrifugal extractor would require frequent stops for cleaning.

Centrifugal Extractor (discussed in Section 3.2)

Boiler Tank with Propane Heater

It would seem likely that a simple boiler tank, heated underneath by a propane burner, would be adequate to heat the vegetable oil to 200°F to 300°F in order to separate the spill chemical after extraction.

Condenser

The condenser could use water from any source on a once-through basis.

Heat Exchanger

In order to reduce propane fuel requirements, a heat exchanger on the oil line to and from the boiler would be desirable.

The data in this report show a number of chemicals are theoretically amenable to solvent extraction treatment. However, except for contained spills or spills into small stagnant water bodies, many practical problems are encountered. First, the equipment is more complex, costly and cumbersome than that typically required for neutralization. The treatment skid is estimated to weigh about ten to twenty tons and would probably cost around $400,000. Because of its weight, these skids would have to be designed for transport by truck or C130 aircraft. For marine application, the skids would be moved onto a barge using a construction crane or a dockside marine loading crane. It will be more difficult to follow a spill in moving water with a barge.

Another problem is that treated water must be discharged beyond the contaminated zone. Otherwise, dilution of contaminated intake water would make the extraction process much less effective.

An interesting possibility seems to be the development of a multi-skid system. One skid, with an inlet pump, settling tank and filter would be designed to accomplish a precipitation response in addition to its use as part of the solvent extraction scheme. Another skid with the solvent extraction portion of the system may also provide a means for recovery of certain chelating agents.

At present, the usefulness of a solvent extraction spill response concept seems limited. However, this method may be the only way of coping with some particularly severe spill hazard, it is possible to design a system which will allow a solvent extraction process response to be implemented. There also will be requirements for spill detection and monitoring equipment in addition to the basic treatment equipment.

3.6 FATE AND CONSEQUENCES OF SOLVENT EXTRACTION

3.6.1 Introduction

There is relatively little available information on spills of water-soluble organic chemicals, their frequency, typical size, and environmental impact. Some limited data on spills of water-soluble hazardous substances (liquids only) reported to the USCG (during 1970-1972) indicate roughly 30 "discharges" per year, and a median discharge volume of about 400 gal.[16] However, since many of the subject chemicals are transported in tank cars, barges, or freighters, much larger spills may be expected from time to time. For example, a derailment of a tank car near Dearborn, Michigan in 1973 resulted in the spill of 19,000 gal. of butyl alcohol and formaldehyde. An unknown, (but presumably large), quantity of vinyl acetate was spilled following the sinking of a barge in Corpus Christi, Texas in 1973.[21]

A compilation of the NRC aquatic toxicity codes for each of the 75 subject chemicals indicated that none of the chemicals had an extremely high level of acute toxicity (code 4 on a 0 to 4 scale), and that a significant number, about 20, had a relatively low level of acute toxicity (codes 0 and 1). Roughly 50 chemicals had assigned codes of 2 or 3 which relate to a threshold range for acute toxicity of 1 to 1,000 ppm.

The data on which these codes are based are usually TL_m values* for a test period of 12 to 96 hours. There is no way to predict from these data

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* TL_m is the concentration of a substance which will, within the specified time period, kill 50% of the exposed test organisms. The bioassay may be conducted under static or continuous flow conditions.

what the mortality would be for different exposure periods or different concentrations. Shorter exposure periods might be expected, for example, (1) in the case of a spill plume moving down a river, or (2) in large open bodies of water where many aquatic species (especially fish) would be able to avoid areas of high concentration.

We are not aware of any instance in which the environmental impact (species kills, repopulation rates, etc.) of a spill of one of the subject chemicals has been documented. Because of this, and the other uncertainties mentioned above, the fate and consequences of an untreated spill can only be roughly estimated.

3.6.2 Fate and Consequences of an Untreated Spill

Because of the high water solubility of the subject chemicals, dilution--at a rate depending on the natural mixing rate of the waters-- will be the primary factor in the natural amelioriation of the spill. Other factors which will be involved, depending on the chemical and the affected waters, are:

- Vaporization - Some of the more volatile chemicals (e.g., butyl alcohol, ethyl acetate, ethyl alcohol, etc.) will tend to vaporize, but the amounts lost to the air will not be large.
- Adsorption onto suspended particles and sediments - Some minor adsorption may take place onto both inorganic and (primarily) organic particulates.
- Chemical degradation - Chemical degradation via hydrolysis, photo-oxidation, etc., will contribute to the breakdown of the organic chemicals.
- Biochemical oxidation - Biochemical oxidation will also contribute to the breakdown of these organic chemicals.

Once a spill of one of the subject chemicals has taken place and the chemical has dissolved in the water, the adverse impacts or hazards will be associated with the following:

- Direct toxic action on aquatic life - Large kills of most species can be expected when concentrations and exposure times are large.

Depending on several factors, the hazards may be low enough to allow repopulation on the order of days to months after the spill.

- Reduction in Levels of Dissolved Oxygen - Most of the subject chemicals are biodegradable and some lowering in dissolved oxygen may be anticipated as a result of biochemical oxidation. The rate of biochemical oxidation will be slow and thus dissolved oxygen levels may not fall to critical levels.
- The threat to water supplies - Water supplies using the affected waters (or riverbeds associated with them) may be threatened. Those water supply systems regularly using activated carbon treatment will be afforded some measure of protection.
- Tainting of Flavor - Chemicals ingested by fish or other edible aquatic life may cause a tainting of the flavor. It seems unlikely that any of the subject chemicals would accumulate to levels which would prove toxic to humans.

3.6.3 Fate and Consequences of a Treated Spill

3.6.3.1 Estimate of Amount Discharged

The vegetable oil that would be discharged under optimum operating conditions from an on-board (or on-shore) solvent extraction unit would consist of dissolved oil only. The precise solubility of vegetable oil in water will depend on its composition, but the material is generally considered insoluble. Solubility in pure water may be roughly estimated from data for other long-chain hydrocarbons as shown in Table 3.6-1:

TABLE 3.6-1[20]

SOLUBILITY OF HYDROCARBONS IN WATER

Chemical	Solubility (mg/l)	Temp.
Tridecane (nC_{13} saturated hydrocarbon)	.013	77°F
n-Octadecane (nC_{18} saturated hydrocarbon)	.007	77°F
n_{36} saturated hydrocarbon	.003	77°F

In natural waters, other factors, such as adsorption on colloidal particles, might increase the apparent solubility. Thus, for practical purposes, we can use a conservative estimate of 0.1 g/l for the solubility of vegetable oils in natural waters. Excluding the possibility of a spill, the amount of vegetable oil that would be discharged from a solvent extraction process is simply the volume of water processed (liters) multiplied by the effective solubility of 0.1 g/l. Dilution of the treated water by the receiving waters will subsequently reduce the effective concentration in a predictable manner.

3.6.3.2 Environmental Transformations of Discharged Oil

We have not found any data from which quantitative estimates of various transformations can be made. Several processes can, however, be discussed qualitatively.

- Adsorption - A significant fraction of the discharged oil may be expected to associate with suspended matter in the receiving waters. Adsorption onto organic matter is especially favored because of the strong lipophylic nature of the oil.
- Formation of Surface Film - A surface film, perhaps no more than a monolayer thick, can be expected if the oil is discharged in excess of its effective solubility.
- Hydrolysis - Some of the oil will react with water to form free fatty acids which have the chemical formula $CH_3 (CH_2)_n COOH$ (n is generally 16 or 18). (Some degree of unsaturation is also present.)
- Chemical Oxidation - Direct oxidation of the dissolved fraction of the vegetable oil is probably not a major means of degradation. Oxidation via reaction with intermediate radicals may be more likely. Oxidation-polymerization may be expected on any surface film or shore accumulation of the vegetable oil.
- Biochemical Oxidation - Degradation via biochemical oxidation will likely be one of the more important methods of degradation in natural waters.[9] The BOD_5 for Soybean oil has been given as 0.39 lbs O_2/lb oil; since the theoretical BOD is about 2.0 lbs/lb, the implication is that about 20% of the ultimate BOD is used up in the first 5 days. Thus one might assume that the half-life for degradation via biochemical oxidation is on the order of a few weeks for relatively warm waters.

3.6.3.3 Environmental Effects

Several environmental effects may result from the discharge of vegetable oils.

- Formation of a Surface Film - This is likely only if the vegetable oil is discharged in excess of its effective solubility. Such a surface film could (i) interfere with the natural processes of reaeration and photosynthesis, (ii) adversely affect waterfowl in a manner similar to that of petroleum oils, and (iii) create adverse aesthetic effects such as the fouling of shorelines and beaches.
- Reduction in Level of Dissolved Oxygen - The relatively high BOD of vegetable oils could lead to a serious depletion in dissolved oxygen if the discharged (i.e., treated) waters were not sufficiently diluted by the receiving waters. Assuming a discharge with 0.1 g oil/liter and a BOD_5 of .39 g 0_2/ g oil, the resulting 5-day oxygen demand is .039 g 0_2/liter. Since the receiving waters may have around 4-8 ppm dissolved oxygen (.001 - .002 g 0_2/liter), a dilution factor of at least 50 would seem to be desirable in waters where the level of dissolved oxygen was low and the rate of reaeration was small. Without such dilution or reaeration, the level of dissolved oxygen could temporarily fall below a point necessary for the survival of many species of aquatic life.
- Direct Toxic Action - Vegetable oils may be considered non-toxic to humans. The FDA stipulates that vegetable oils used in human food contain less than 2% free fatty acids. There do not appear to be any data relating to the aquatic toxicity of vegetable oils. One recent EPA paper indicates that the aquatic toxicity of vegetable oils depends upon the content of fatty acids, and that solubility calculations indicate that fatty acids are sufficiently soluble to exceed the toxicity threshold for fish.[11] The oil does not, of course, have to be in a dissolved state in order to be ingested by aquatic organisms. In spite of the lack of any real data, the level of aquatic toxicity may be considered quite low.

- Indirect Toxic Action - Free oil and emulsions, if present in sufficiently high concentrations, could accumulate on sensitive portions of aquatic organisms (e.g., gills) in such a manner as to seriously affect them.
- Tainting of Flavor - Oil ingested by fish or other aquatic life may cause a tainting of the flavor, though the effect would be expected to be small.

4.0 PRECIPITATION

4.1 PRINCIPLE OF PRECIPITATION

Chemical precipitation occurs when two reagents which are soluble in water react and form an insoluble compound. This compound then precipitates as a solid in the water column. 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 process of coagulation can be assisted by reagents which are different from the primary reactants. Precipitation followed by coagulation and separation is widely practiced in industrial and waste treatment processes.

In the case of a spill in a water body, it is envisioned that the addition of an appropriate amount of reagent will:

- React with the contaminant,
- Form an insoluble compound which precipitates,
- Reduce the level of contaminant in the water to within acceptable limits, and
- Not produce any additional harmful effects on aquatic life.

4.2 THEORY OF PRECIPITATION

Precipitation is a physicochemical process by which the concentration of a chemical species in solution is decreased through the formation of a solid phase. 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 $MA = M^+ + A^-$. If S_o is the solubility of MA in moles/liter, then

$$S_o = [M^+] = [A^-] \qquad 4.2\text{-}(1)$$

Hence, for the solubility product K_s*:

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

For insoluble compounds this solubility product is obviously a very small number. For example, the solubility product of silver chloride is 1.2 x 10^{-10} $[\text{moles/liter}]^2$. This tells us that, at thermodynamic equilibrium, with both silver and chloride ions present in the solution, the product of their concentration cannot exceed this very low value and additional silver chloride will form an insoluble precipitate. Thus, the stoichiometric addition of sodium chloride to a solution of silver nitrate will form a precipitate of silver chloride and reduce the concentration of silver ion in the water body to very low values.

When two reagents are mixed together complete precipitation is not instantaneous although many precipitation reactions are very fast. Therefore, for a time the concentration of ions in solution exceeds the solubility product and the solution is said to be supersaturated. Supersaturation is an unstable state, and a minor disturbance in the solution is normally sufficient to result in precipitation. We do not anticipate that a supersaturated solution would be maintained during a typical spill situation.

Precipitation of a species in solution can be brought about by the addition of a salt containing an anion capable of forming an "insoluble" compound, e.g., copper can be precipitated from a solution of copper sulfate $CuSO_4$ by the addition of a stoichiometric amount of sodium sulfide:

$$CuSO_4 + Na_2S \rightarrow Na_2SO_4 + CuS \text{ (precipitated)}. \qquad 4.2\text{-}(3)$$

(Note that another ion, sodium, is introduced into the solution.)

$$K_s = [Cu^{2+}][S^{2-}] \qquad 4.2\text{-}(4)$$

Since the solubility product must hold under all conditions the addition of excess reagent, e.g., excess sulfide (S^{2-}) ions will further reduce the

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*The general formula for a solid M_mA_n is $K_s = [M^{+n}]^m \times [A^{-m}]^n$

concentration of copper ions in solution. This is known as the common ion effect. This principle may serve to further reduce the toxic ion in solution if the excess reagent can be tolerated.

Precipitation has an inverse phenomenon, dissolution, which must also be considered. If the concentration of toxic ions in solution decreases, the solubility product is no longer satisfied, and the precipitate may redissolve to restore the equilibrium. This might occur in the case of a precipitate deposited in a moving water body. Solubility is also affected by temperature; generally an increase in temperature produces an increase in solubility, which may induce the dissolution of precipitated solids. The addition of an electrolyte with no ion common to the precipitate can increase the solubility of that precipitate (salt effect). This is a direct result of an increase in the ionic strength, which is a complex function of species valence states and concentrations. An increase in ionic strength tends to increase the concentration of the sparingly soluble salt at saturation. This might occur for example, in a water body with a very high total dissolved solids (TDS) level. In this case, the amount of reagent necessary to attain a safe metal ion concentration would be greater than the simple calculations indicate.

Dissolved solids in a water body can also participate in the precipitation reaction, in two ways. First, natural ions in the water might be precipitated by the reagent, e.g., calcium can form an insoluble salt with phosphate reagents. And second, co-precipitation might occur, in which a species precipitates although a solubility product has not been exceeded. This phenomenon is the result of either surface adsorption on a particle, or occlusion during crystal growth. These secondary effects cannot be predicted without a detailed knowledge of the water body in question.

4.3 SPILLS TREATABLE BY PRECIPITATION

4.3.1. Categorization of Chemicals

Table 4.3-1 gives the list of spill chemicals which are being considered for treatment by reactions; recommended allowable limits for each

TABLE 4.3-1. CHEMICALS SUBJECT TO PRECIPITATION

Chemical	Formula	Toxic Species	Class*	Recommended Allowable Limit** (mg/l)	(molarity)
Cadmium Chloride	$CdC\ell_2$	Cd^{+2}	1	0.0002	$1.79x10^{-9}$
Copper Sulfate	$CuSO_4 \cdot 5H_2O$	Cu^{+2}	1	0.01	$1.57x10^{-7}$
Ferrous Sulfate	$FeSO_4 \cdot 7H_2O$	Fe^{+2}	1	0.05	$8.96x10^{-7}$
Nickel Sulfate	$NiSO_4$	Ni^{+2}	1	0.002	$3.41x10^{-8}$
Zinc Chloride	$ZnC\ell_2$	Zn^{+2}	1	0.02	$3.06x10^{-7}$
Antimony Trifluoride	SbF_3	Sb^{+3}	2	0.2	$1.64x10^{-6}$
Silver Nitrate	$AgNO_3$	Ag^{+}	2	0.001	$9.27x10^{-9}$
Titanium Tetrachloride	$TiC\ell_4$	Ti^{+4}	2	N/D	--
Potassium Dichromate	$K_2Cr_2O_7$	$Cr_2O_7^{=}$	3	0.05 Cr	$9.62x10^{-7}Cr$
Potassium Permanganate	$KMnO_4$	MnO_4^{-}	3	0.02 Mn	$3.64x10^{-7}$ Mn
Chromic Anhydride	CrO_3	$CrO_4^{=}, Cr_2O_7^{=}$	3,4	0.05 Cr	$9.62x10^{-7}Cr$
Latex, Liquid Synthetic	Various Polymers	--	4	N/D	--
Sodium Ferrocyanide	$Na_4Fe(CN)_6$	$Fe(CN)_6^{-4}$	4	N/D	--

* See text for explanation of codes

** Based on 1972 Water Quality Criteria (NAS) --level for minimal risk of deterious effects upon marine aquatic life.

N/D = No data available

toxic species (from water quality criteria) are also included. The chemicals have been separated into four classes:

(1) divalent metals forming insoluble products with a variety of anions,

(2) metals with other valence states which might form insoluble compounds similar to the divalent metals,

(3) oxyanions subject to oxidation-reduction reactions and subsequent precipitation, and

(4) compounds which require individual treatment.

All the Class 1 metals can generally be precipitated by the same anionic species, although the solubility product varies throughout the group. In an aerobic water body, it is likely that oxidation of the ferrous ion (in ferrous sulfate) to ferric ion will occur. However, since ferric hydroxide begins to precipitate at low pH levels (pH 4-5), it is unlikely that the higher valence species will pose a problem. Thus in carrying out the analysis with respect to ferrous ions alone, a "worst case" situation is anticipated. Class 2 has three members: antimony trifluoride, silver nitrate and titanium tetrachloride. The latter decomposes rapidly in water to hydrogen chloride and insoluble titanium dioxide. Thus, treatment of this compound by precipitation is considered unnecessary, but neutralization of the hydrochloric acid formed will be required.

The Class 3 anions, permanganate and dichromate, contain manganese and chromium with valence states +7 and +6, respectively. Precipitation of these metals can be affected by reduction to a lower valence state. Chromic anhydride in solution is a mixture of chromic and dichromic acids (H_2CrO_4 and $H_2Cr_2O_7$, respectively).

In Class 4, synthetic latex is discussed separately in section 4.6, with the final recommendation that no action be taken in the event of a spill. Sodium ferrocyanide is not subject to the precipitation reactions of Classes 1 and 2, nor will it undergo the redox schemes of Class 3. However, the anionic species is subject to precipitation by substitution of another metal for the sodium; such treatment would be specific for this chemical.

4.3.2. Water Quality Criteria for Toxic Chemicals

Table 4.3-1 presents upper limits for metal concentrations to minimize the toxic action of these species on aquatic life. Typically the value will vary with the biological species under examination and is subject to some degree of interpretation. We have generally been conservative in selecting the most sensitive species for which data are available. For most of the metals, meaningful data are available only for marine aquatic life. Date for freshwater aquatic life are generally presented as a function of LC_{50} values (concentration at which a material is lethal to 50% of a population sample); such values are difficult to interpret in terms of allowable limits for aquatic life.

The data presented for dichromate and permanganate are based on the toxicity of the metal (Cr and Mn), not the oxyanion. This may not be realistic but unfortunately, the toxicity of the anions has not been documented. The ferrocyanide ion is similarly undocumented. It is quite stable and certainly less toxic than cyanide ion.

4.4 INITIAL SCREENING OF PRECIPITANTS

In the selection of a suitable treatment agent there are several criteria which must be met.

- The reagent must reduce the concentration of toxic species in solution to within acceptable limits.
- The reagent should be soluble in water to the extent that application to a spill is necessary.
- Any agent remaining in solution after treatment must be at a non-harmful level, and should not produce adverse environmental effects, e.g., large pH changes.
- Misapplication of the treatment chemical should not cause toxic effects by violating the water quality criteria.
- It should be low cost, readily available, and easily handled.

For the metals in Class 1, the carbonate, hydroxide, phosphate, and sulfide salts of these metals are all insoluble in water. In addition an organic acid capable of forming insoluble metal salts, oxalic acid, was included for study. The solubility products of the various metal salts obtained from the literature [28,35,10] are tabulated in Table 4.4-1. The accurate determination of solubility product is difficult in practice, depending on temperature, ionic strength, degree of supersaturation, and other parameters. Differing values for the same solubility product were frequently found but these differences were not sufficient to affect the conclusions. The results (Table 4.4-2) give the concentration of metal ion remaining in solution after precipitation with a stoichiometric quantity of reagent. In the case of hydroxide, the concentration of the anion (hydroxyl ion) is directly related to pH.

Table 4.4-2 also indicates where the calculated values of toxic ion concentration are greater than (GT) or lower than (LT) the recommended allowable limits of Table 4.3-1, from application of a stoichiometric amount of reagent. In light of the uncertainties in solubility products and toxicity data, a metal concentration that is reasonably close to the allowable limits is considered admissible.

It is evident from Table 4.4-2 that the metal ion concentration is lowest in a saturated solution containing sulfide. For each of the Class 1 metals, the concentration is several orders of magnitude below the recommended allowable limits. Solubility product calculations for the Class 2 metals, silver and antimony, produce similar results.

A stoichiometric amount of phosphate ion does not reduce concentrations as much as sulfide, but is acceptable for four of the five Class 1 metals. The remaining anions decrease in effectiveness in the following order: hydroxide > carbonate > oxalate. Thus, on the basis of the initial screening in Table 4.4-2, sulfide and phosphate reagents appear to be strong potential candidates.

The second step in the screening sequence involves a determination of the excess reagent required to reach the allowable limits (by the common ion effect), if stoichiometric addition of a reagent is not

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TABLE 4.4-1.SOLUBILITY PRODUCTS OF METAL SALTS

Chemical Compound	Metal Species	Sulfide	Hydroxide	Carbonate	Oxalate	Phosphate
Cadmium Chloride	Cd^{+2}	$3.6x10^{-29}$	$2.0x10^{-14}$	$5.2x10^{-12}$	$1.5x10^{-8}$	$2.7x10^{-33}$
Copper Sulfate	Cu^{+2}	$8.5x10^{-45}$	$1.6x10^{-19}$	$2.5x10^{-5}$	$2.9x10^{-8}$	$1.3x10^{-37}$
Ferrous Sulfate	Fe^{+2}	$3.7x10^{-19}$	$1.6x10^{-14}$	$2.0x10^{-11}$	$2.1x10^{-7}$	$1.3x10^{-30}$
Nickel Sulfate	Ni^{+2}	$1.4x10^{-24}$	$1.6x10^{-16}$	$1.4x10^{-7}$	N/D	$5.3x10^{-31}$
Zinc Chloride	Zn^{+2}	$1.2x10^{-23}$	$1.8x10^{-14}$	$2.0x10^{-10}$	$1.4x10^{-9}$	$1.0x10^{-32}$
Antimony Trifluoride	Sb^{+3}	$3.0x10^{-53}$	N/D	N/D	N/D	N/D
Silver Nitrate	Ag^{+}	$2.0x10^{-50}$	$1.5x10^{-8}$	$6.2x10^{-12}$	$1.6x10^{-49}$	$1.2x10^{-18}$

N/D = No data available

The units assigned to each solubility product are different and depend on the formula of the precipitated compound. See the Theory of Precipitation (P.91)

TABLE 4.4-2. METAL CONCENTRATIONS IN SATURATED SOLUTIONS OF DIFFERENT ANIONS

Metal Species	Sulfide		Hydroxide			Carbonate		Oxalate		Phosphate	
	mg/ℓ		mg/ℓ	pH		mg/ℓ		mg/ℓ		mg/ℓ	
Class 1											
Cd^{+2}	$7x10^{-10}$	LT	2	9.5	GT	0.3	GT	14	GT	0.04	GT
Cu^{+2}	$6x10^{-18}$	LT	0.02	7.8	LT	318	GT	11	GT	$3x10^{-3}$	LT
Fe^{+2}	$3x10^{-5}$	LT	0.9	9.5	LT	0.25	GT	26	GT	0.07	LT
Ni^{+2}	$7x10^{-8}$	LT	0.2	8.8	GT	22	GT	N/D	--	0.06	LT
Zn^{+2}	$2x10^{-7}$	LT	1	9.5	GT	1	GT	2	GT	0.03	LT
Class 2											
Sb^{+3}	$3x10^{-6}$	LT	N/D	--	--	N/D	--	N/D	--	N/D	--
Ag^{+}	$4x10^{-12}$	LT	13.2	10.1	GT	25	GT	$7x10^{-12}$	LT	4.71	GT

GT = greater than recommended allowable limits
LT = less than recommended allowable limits (or close enough to be acceptable)
N/D= no data available

sufficient. This can be calculated from a knowledge of the solubility product and the desired final metal concentration. For example, for nickel carbonate

$$K_{SP} = [Ni^{+2}]\ [CO_3^{-2}] = 1.4 \times 10^{-7}\ (mole/\ell)^2;$$

to achieve the recommended allowable limit of $Ni^{+2} = 3.41 \times 10^{-8}$ $\underline{M}$, the carbonate concentration must be

$$[CO_3^{-2}] = 1.4 \times 10^{-7}/3.41 \times 10^{-8} = 4.1\ \underline{M}.$$

This is clearly an unattainable level of carbonate ion and implies that the nickel level cannot be brought down to an acceptable level by addition of excess carbonate reagent. For the salts under consideration, these calculations are summarized in Table 4.4-3. In the cases where a stoichiometric amount of the anion reduces the metal concentration sufficiently (all of the sulfide salts), the saturated solution concentration is reported instead. The table shows that a small excess of phosphate ion will reduce cadmium ions to an acceptable concentration but not silver ions.

The remaining three anions show less success. Hydroxide can effectively reduce the level of the five transition metals but the pH is unacceptably high. Carbonate would be applicable for only three of the transition metals; cadmium, iron and zinc. Oxalate shows some potential for the treatment of silver.

4.5 SELECTION OF A PRECIPITANT

4.5.1 Sulfide

Sulfide ions could be introduced into a water body in gaseous, solution or solid form. The gaseous form (hydrogen sulfide) is acidic and H_2S or HS^- ions are quite toxic.[34] Few solid sulfides are soluble in water; one exception is sodium sulfide, Na_2S. The pH of a solution of Na_2S is very close to that of sodium hydroxide, due to hydrolysis of the sulfide. Thus, a 0.1N solution of sodium sulfide would have a pH of about 13, whereas a pH of 6-9 is the acceptable range. Misapplication of either of these reagents could produce adverse effects in the water body. Therefore, although a very effective precipitant, sulfide is not the first choice.

TABLE 4.4-3 ANION CONCENTRATIONS REQUIRED TO MEET WATER QUALITY CRITERIA FOR THE METALS

METAL SPECIES	SULFIDE	HYDROXIDE		CARBONATE	OXALATE	PHOSPHATE
	M	M	pH	M	M	M
Class 1						
Cd^{+2}	$6.0x10^{-15}$*	$3.0x10^{-3}$	11.5	$2.9x10^{-3}$	> 1	$6.9x10^{-4}$
Cu^{+2}	$9.2x10^{-23}$*	$1.0x10^{-6}$	8.0	> 1	0.18	$3.3x10^{-8}$*
Fe^{+2}	$6.1x10^{-10}$*	$1.0x10^{-4}$	10.1	$2.2x10^{-5}$	0.23	$1.3x10^{-6}$
Ni^{+2}	$1.2x10^{-12}$*	$7.0x10^{-5}$	9.8	> 1	N/D	$1.2x10^{-4}$
Zn^{+2}	$3.5x10^{-12}$*	$2.0x10^{-4}$	10.4	$6.5x10^{-4}$	$4.6x10^{-3}$	$5.9x10^{-7}$
Class 2						
Sb^{+3}	$3.7x10^{-11}$*	N/D	--	N/D	N/D	N/D
Ag^{+}	$1.7x10^{-17}$*	1.6	> 14	> 1	$6.84x10^{-17}$*	> 1

*Solution concentration after stoichiometric addition of anion.
N/D = No data available

4.5.2 Hydroxide

Table 4.4-3 shows that for most of the metals precipitation of hydroxides requires pH's above 9 to reduce metal concentrations to within acceptable limits. Also, because many fresh water bodies are neutral or acidic, not alkaline, there would be distinct possibility of the dissolution of a hydroxide precipitate.

4.5.3 Carbonate

Sodium bicarbonate is applicable for the treatment of cadmium, iron and zinc but not for the other chemicals.

4.5.4 Oxalate

Sodium oxalate or oxalic acid are applicable reagents for the treatment of silver and possibly zinc. However, the oxalate ion is toxic and therefore, misapplication of the reagent could produce adverse effects.

4.5.5 Phosphate

The phosphate ion by itself is not considered toxic, although it is a plant nutrient and under appropriate environments can lead to algae growth. This is only a minor disadvantage to its use in an emergency spill situation. The three forms of sodium phosphate deserve primary consideration.

- Sodium dihydrogen phosphate, NaH_2PO_4, is acidic in solution and precludes the formation of insoluble metal compounds.
- Dibasic sodium phosphate, Na_2HPO_4, is slightly alkaline with a 0.1N solution pH of about 9.7. Small quantities of the monobasic phosphate can be added to reduce the pH further if desired; such mixed systems are usually effective buffers.
- Tribasic sodium phosphate, Na_3PO_4, is quite alkaline and might present some environmental hazard.

The dibasic sodium phosphate (also called disodium phosphate) is recommended as the most appropriate precipitating agent for the Class 1 metals.

4.6 COST AND AVAILABILITY OF PHOSPHATE REAGENTS

Dibasic sodium phosphate is widely used as a water treatment chemical, a softener for boiler water, and as a buffer for pH control. It is also used extensively in the food industry to decrease the cooking time of cereals and in the processing of certain starches.

Major U.S. producers include FMC Corp., Monsanto Co., Olin Corp., and Stauffer Chemical Co. [3] It is sold as a solid (technical and food grade), usually in 100 lb. bags. Two chemical forms are commonly produced: anhydrous (Na_2HPO_4) and dihydrate ($Na_2HPO_4 \cdot 2H_2O$). In 1973 an estimated 42 million lbs were produced.[3] The current cost for technical grade (anhydrous) is 48¢/kg.[8]

4.6.1 Required Quantities

The quantities of disodium phosphate required to stoichiometrically precipitate the Class 1 metals have been calculated and are given below in Table 4.6-1. A 10% excess of phosphate would probably be advisable to ensure adequate treatment.

TABLE 4.6-1. QUANTITIES OF PRECIPITATING AGENT

Spill Chemical	Na_2HPO_4 (kg/kg spill chemical)
$CdC\ell_2$	0.52
$CuSO_4 \cdot 5H_2O$	0.38
$FeSO_4 \cdot 7H_2O$	0.34
$NiSO_4$	0.61
$ZnC\ell_2$	0.70

The requirements for the five spill chemicals range from 0.34-0.70 kg/kg spill chemical. To provide some indication of the relative cost of treating a spill, one kg of cadmium chloride would require about 25¢ worth of Na_2HPO_4.

4.7 TREATING AGENTS FOR PRECIPITATION OF OTHER SPILL CHEMICALS

For the remaining six spill chemicals, data on the solubility of potential reaction products were not available. A study of the pertinent literature produced several possible reagents for each chemical, but very little quantitative information. Therefore, test tube-scale laboratory experiments were performed to verify the efficacy of several proposed precipitating agents.

4.7.1 Antimony Trifluoride

Two common insoluble antimony salts were identified--carbonate and phosphate. In separate tests, the addition of sodium bicarbonate and dibasic sodium phosphate both produced precipitation from a solution of antimony trifluoride. The latter would be the preferred reagent because of the known insolubility of other phosphate salts, as well as the recommendation for use with Class 1 metals.

4.7.2. Silver Nitrate

The most common technique for precipitating silver is as silver chloride; sodium chloride is an ideal reagent for this purpose. It is not toxic, inexpensive, and readily available. To reach the allowable limit for silver in Table 4.3-1, a chloride concentration of about 0.017 M is required ($K_{SP} = 1.2 \times 10^{-10}$). The concentration of chloride ion in sea water is about 0.5 M, therefore no treatment is necessary under these conditions.

4.7.3 Potassium Dichromate

There are two approaches to the precipitation of chromium. First, in alkaline solution the various chromium oxyanions (Cr^{+6}) are all converted to chromate (still Cr^{+6}). The addition of barium hydroxide will produce insoluble barium chromate. However, the chromium is still in a very toxic form. An alternative method for treatment of the dichromate ion requires reduction of the chromium (VI) in dichromate to chromium (III) with subsequent precipitation as insoluble chromic oxide, Cr_2O_3. The sulfite ion in the form of sodium sulfite or sodium bisulfite, is a suitable reducing agent. In the laboratory experiments it was found that the reaction occurred only in slightly acidic solutions ($pH > 5$).

(Sodium bisulfite is somewhat acidic.) Ferrous sulfate was also found to be a satisfactory precipitating agent.

4.7.4 Potassium Permanganate

The preferred treatment of permanganate ion is reduction with sodium sulfite to yield an insoluble manganese dioxide (MnO_2) precipitate.

4.7.5 Chromic Anhydride

Chromic anhydride can be reduced to precipitate insoluble chromium oxide (Cr_2O_3). The reduction was tested in the laboratory using sodium sulfite, ferrous chloride, and ferrous sulfate; only the latter compound gave a precipitate (also, the reaction was slow).

4.7.6 Sodium Ferrocyanide

The most common insoluble ferrocyanide salts are the ferrous and ferric ferrocyanide compounds (different forms of the Prussian Blue dyes). The former is precipitated as a colloidal material, which does not settle as rapidly as the ferric salt. Ferric chloride is the most effective reagent for precipitating the anion.

4.8. COAGULATION AND PRECIPITATION OF SYNTHETIC LATEX

4.8.1 Types of Latexes Produced

Synthetic latex is, by definition, any emulsion in water of finely divided particles of synthetic rubber or plastic. The individual particles— which range from about 700 Å to over 3,000 Å in size— are not actually dissolved in the water. Most commercial latexes contain about 45-55% (by weight) solids, though some may reach 68%[17].

The most common plastics used for synthetic latexes include (1) various copolymers of styrene and butadiene, including terpolymers with vinyl pyridine, (2) various copolymers of butadiene and acrylonitrile, and (3) neoprene (polychloroprene)[6]. Various formulations of these, and other polymers, are produced resulting in hundreds, if not thousands, of different formulations.

The formulations produced usually contain several additives including (1) emulsifiers (e.g., fatty acid or rosin acid soaps), (2) catalysts (e.g., potassium persulfate), (3) modifiers (e.g., dodecyl mercaptan), (4) antioxidants (e.g., phenyl-beta-naphthalene), (5) pigments (e.g., titanium dioxide), (6) solvents, (7) fungicides or bactericides, and (8) anti-foam agents.[6,22] There are hundreds of such additives currently in use. Trace levels of the original monomers may also be present.

4.8.2 Physio-Chemical and Toxic Properties

The dispersion of latex in water is usually milky-white in color (unless colored pigments have been added) and non-flammable (unless coagulated). A spill of latex will "mix" with the water body and some of the additives, but not the plastic components, will dissolve in the water.

The specific gravity of the liquid latex-- 0.96 to 1.08 at 20°C[9]-- and of the solids present is very close to that of water. It is likely that the particles would remain in suspension for some time (hours or days) following a spill. Latex is relatively resistant to biochemical oxidation; the five-day BOD is only 1%[9], i.e., only one pound of oxygen is consumed for every 100 pounds of latex in the specified time period.

No information on the human, aquatic or waterfowl toxicity of synthetic latexes has been found; no hazard classifications have been assigned by the Code of Federal Regulations, the National Academy of Sciences, or the National Fire Protection Association.[9] We anticipate that the toxicity of the polymeric material in latex will not be high since (1) it will not pass through cell membranes, and (2) it is relatively inert. The additives present may, in fact, be the determining factors in the chemical toxicity of latexes. Latex may adversely affect aquatic life by the plugging of gills, the coating of surfaces or some similar action.

4.8.3 Coagulation and Precipitation of Latex

Coagulation of latex is carried out in some latex manufacturing operations, and in some wastewater treatment operations.* The most common

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*e.g., wastewater from textile plants that apply a foam rubber backing to carpets.

method of coagulation is by acidification, to about pH 5-6, by the addition of alum (aluminum sulfate). Sulfuric acid, caustic or salts (e.g., calcium chloride) are also used.

There is no simple way to predict a priori whether a given latex formulation will or will not coagulate following chemical addition. Some latexes will coagulate spontaneously after a spill into water (especially salt water) while others will be quite resistant to coagulation even after chemical addition. The attainment of a good floc in any coagulation operation usually requires careful control over (1) the amounts of chemical added, (2) the mixing rate (usually slow), and (3) the mixing time (often 10 to 40 minutes in waste treatment operations). The resulting floc may float, remain as a dispersion, or sink, depending on the resulting specific gravity. Excessive turbulence in the water body will hinder phase separation.

4.9 METHODS OF APPLICATION

Two approaches for application of precipitating agents can be considered. First, the agent can be applied in situ. In this case, depending on the characteristics of the precipitant, the solids may settle to the bottom or else remain suspended. If the spilled chemical, after precipitation, is in an environmentally inert form, then in situ treatment may be feasible. A precipitate that settles out has potential for eventual removal from the bottom by dredging. However, not enough information is yet available on the character of in situ precipitates in the water column. Some experimental work will be needed before the feasibility of in situ precipitation can be evaluated.

A second possibility is to treat the contaminated water by flow through a treatment apparatus. The basic unit might include an inlet pump, a mixing tank, a separator or filter unit and a storage bin for precipitate. In Section 3.5 we noted that this basic equipment might be identical to the first skid section used in a solvent extraction response apparatus. The cost and weight of such a skid would be reasonable (around 1-2 tons and $10,000), but weights of treating agent and precipitate will tend to be large if spills of several thousand gallons are treated.

4.10 FATE AND CONSEQUENCES (PRECIPITATION)

4.10.1 Introduction

It is difficult to generalize on the fate and consequences of untreated (and treated) spills of the inorganic hazardous chemicals listed in Table 4.10-1. Toxicity information is limited and an overall assessment of the toxic properties not available. For example, the toxicity of most heavy metals in fresh water is affected by (1) other chemicals or physical parameters (e.g., pH, temperature); (2) the relative sensitivity of various aquatic organisms present; (3) the probable exposure time; and, (4) the possibilities for bioconcentration.

Another important factor to consider is the natural background levels of various metals in surface waters. Table 4.10-1 gives some typical values for the metals of interest; calcium, magnesium, potassium and sodium are also included for comparison. Concentrations in lakes and ponds will generally be ∿ 10 to 50% of the river water concentrations for the more insoluble metals.

Of specific note in Table 4.10-1 is the fact that the heavy metals are more concentrated in river sediments. This occurs by precipitation via hydroxides, chlorides, carbonates and sulfides, and cation exchange onto clay particles. The last column in Table 4.10-1 gives some data on the amounts of heavy metals transported (to the ocean) each year by a large river, mostly as suspended solids.

The available information on spills of heavy metal compounds is quite limited. One compilation of spill reports, shown in Table 4.10-2 indicates that many spills are quite small in size, often just a few pounds and perhaps up to the equivalent of the contents of a 55-gallon drum. If, in fact, most spills of heavy metal compounds are this small, then the environmental impact of an untreated spill will be quite local, and any treatment must be undertaken very soon after the spill since it will (at least in flowing waters) tend to dissipate to non-toxic levels rapidly.

A final uncertainty is the lack of any information on the environmental consequences following a heavy metal spill; such tests have been carried out following acid and base spills (see section 2.7) and, of course, oil spills.

TABLE 4.10-1

CONCENTRATIONS OF CERTAIN METALS IN SURFACE WATERS

	Conc. in Sea Water (ug/1)[1]	Conc. in U.S. Rivers: Typical Range (ug/1)[2]	Conc. in Potomac River Estuary Sediments (ug/1)[3]	Trace Element Transport by the Susquehanna River (tons/yr)[4]
Antimony	0.5	0-40[5]	-	-
Cadmium	0.1	0-20[5]	0-600	-
Chromium	0.05	0-8	5,000-70,000	870
Copper	3.	5-30	8,000-60,000	-
Iron	10.	200-4,000	0.7-4.2%	-
Manganese	2.	50-300	70,000-3,200,000	120,000
Nickel	2.	0-15	4,000-50,000	3,000
Silver	0.3	0-.5	0-6,000	45
Titanium	1.	.5-35	-	-
Zinc	10.	20-100	50,000-350,000	-
Calcium	400,000.	2,000-100,000	40,000-2,000,000	-
Magnesium	1,350,000.	100-30,000	2,500,000-5,000,000	-
Potassium	380,000.	300-8,000	20,000-200,000	-
Sodium	10,500,000	2,000-130,000	-	-

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1. Hem, J.D., "Study and Interpretation of the Chemical Characteristics of Natural Water", 2nd Edition (1970), Geological Survey Water Supply Paper 1473.

2. a. National Water Quality Inventory, 1975 Report to Congress, U.S. EPA (EPA 440/9-75-014); and
   b. Handbook of Environmental Control, Vol III; CRC Press, Cleveland, Ohio, 1973. (p. 22)

3. N.A. Jaworski, et al., Water Resource-Water Supply Study of the Potomac Estuary, Technical Report to EPA, Water Quality Office, April, 1971.

4. Same as Ref. 2b (p. 53).

5. Conc. in selected drinking water supplies; Water Quality Criteria Data Book, Vol 2., USEPA, Water Pollution Control Research Series, 18010 DPV 07/71 (1971).

TABLE 4.1C-2

HEAVY METAL SPILLS DURING 1971 AND EARLY 1972

MATERIAL	CONTAINER	CAUSE	QTY. SPILLED	SPILLED INTO
CHROMIC ACID	STORAGE TANK	RUPTURE	140 lbs	CREEK, TENN. RIVER
CHROMIUM IN ACID	STORAGE TANK	OVERFLOW	?	MILL CREEK
MERCURY	TREATMENT PLANT	LEAK	?	DETROIT RIVER
NICKEL SOL. & GROUND LIMESTONE	PILE	AVALANCHE	?	ILLINOIS RIVER
POTASSIUM PERMANGANATE	PLANT	EQUIPMENT FAILURE	11 lbs	OHIO RIVER
TETRAETHYL LEAD	RR TANK CAR	DERAILMENT	?	LAND
ZINC SULFATE	PLANT	EQUIPMENT FAILURE	7-1/2 lbs	?

Source: "Methods to Treat, Control and Monitor Spilled Hazardous Materials", Environmental Protection Technology Series, EPA-670/2-75-042, June 1975 (p.60)

4.10.2 Fate and Consequences of a Treated Spill

Optimum treatment, i.e., the addition of the proper amount of reagent in the proper location, will essentially eliminate the worst aspect of the initial spill, the excessively high concentration of toxic heavy metals (or toxic anions). In addition, some readjustment (increase) of pH may result offsetting the initial low pH created by some spills.

These beneficial effects will be slightly offset by:

- A further increase in the ionic strength of the water, to which aquatic organisms may be sensitive;
- An increase in suspended solids concentration (and turbidity); if the precipitate formed settles slowly it may have some minor adverse effect on aquatic life due to direct toxic action, fouling of gills and membranes, or decreased light penetration.
- Abnormally high concentrations of the metal in the sediments wherever the precipitate settles (in slow moving or still waters) which may have a local effect on benthic organisms; and
- An increase in nutrient concentration (when Na_2HPO_4 is used) which might trigger increased algae growth (and, thus, an increase in the oxygen demand), and a temporary increase in the rate of eutrophication in confined waters.

It should be clear that precipitation in situ does not remove the hazardous material (e.g., heavy metal) from the water body-- it only reduces the concentration of the dissolved fraction to low levels. Further, some of the material that initially precipitates may later redissolve.

The adverse effects of adding the recommended reagents in the wrong location (or in excess) should not be serious and will primarily be associated with (1) pH changes, (2) increased ionic strength, (3) increased nutrient concentrations (with Na_2HPO_4).

4.10.3 Fate and Consequences of an Untreated Spill

The physio-chemical consequences of a spill of one of the subject inorganic chemicals would include the following:

- Initially, a locally high concentration of the dissolved chemical, followed by dispersion at a rate depending on the natural mixing rate in the water body;
- An increase in the ionic strength of the water and a decrease in the pH (minor contributing toxic effects);
- Heavy metal cations will be involved in several chemical processes which will tend to remove them from solution:
  1. precipitation after reaction with naturally occurring oxides, hydroxides, carbonates, sulfides, etc.
  2. chelation by naturally occurring organic molecules;
  3. cation exchange (e.g., by replacement of H^+) resulting in adsorption on clay (or other) particles.

These processes will take place most rapidly in water bodies that (1) are well mixed, (2) have high concentrations of total organic carbon, (3) have high levels of suspended solids, and (4) have high concentrations of anions which can precipitate the metals.

- Eventually the heavy metal will be converted to the least soluble species for which anions are available; in reducing environments this generally is the sulfide form and in oxidizing environments the oxide or hydroxide (possibly the sulfate).
- There may be some tendency for the heavy metals to resolubilize when they reach the ocean; silver which precipitates easily as silver chloride is an exception.
- The biological consequences of a spill of one of the subject chemicals could be highly variable. To the extent that toxicity thresholds are exceeded, kills of and/or sub-lethal effects on, most aquatic life may be expected locally. Biological uptake followed by bioaccumulation

(above natural levels) may temporarily make some species of fish, etc., unfit for human consumption. Water supplies in the area could be threatened.

4.10.3 Synthetic Latex

A spill of synthetic latex, if untreated, may be expected to have a minor to moderate short-term impact (days) on aquatic life and a minor impact on aesthetic values (water color, surface fouling). The long-term impact (months to years) would probably be minor or negligible. The polymeric material in the latex would eventually be incorporated into the sediments (or collected along the shore lines) where it would undergo slow degradation via biochemical oxidation, chemical oxidation, and/or photo-oxidation.

Any attempt to treat the spill, e.g., by coagulation with alum, may create significant adverse effects. A misapplication or excess reagent would result in a local acid pH. The precipitate created could blanket the bottom of the water body (or the shore line) and have adverse impacts on benthic organisms.

5.0 CHELATION

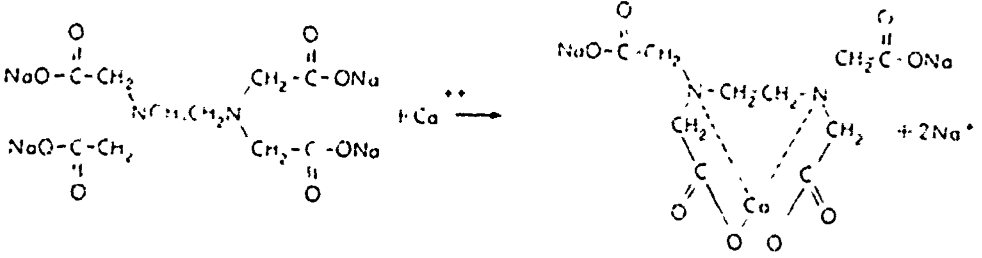
5.1 Principles of Chelation

Chelating agents are compounds or ligands (generally organic) that coordinate, or bind, a metal ion in more than one position. The metal becomes the central ion in a heterocyclic ring, after reaction with two or more functional groups of the same ligand (ion or molecule of the chelating agent). This binding of the metal ion, in most cases, results in its deactivation. The metal is no longer able to react chemically, and is therefore made less toxic.

The phenomenon of chelation can best be described by a sample illustration. The figure (5.1-1) below is a representation of the chelation of a calcium ion by the tetrasodium salt of EDTA, ethylenediaminetetraacetic acid. Calcium displaces two of the sodium ions from the ligand and bonds the carboxyl groups-- at the same time coordinating with the amino nitrogens.

FIGURE 5.1-1

CHELATION OF A CALCIUM ION BY THE TETRASODIUM SALT OF EDTA



The classification of ligands is usually with respect to the number of coordinating groups-- bidentate (two), terdentate (three), quadridentate (four), etc. A unidentate ligand, which only coordinates with metals in one position, forms a chelate often called a "complex" and is frequently an inorganic compound, e.g., NH_3. Chelating agents can be synthetic or natural in origin, and may react either selectively with only one or two metals or with a number of different metals.

No chelating agent is suitable for treatment of all spill chemicals listed. For the purpose of this study, reagents capable of treating at least <u>several</u> metals on the spill chemical list are most useful. The most important chelating agents for these metals involve coordination through either a nitrogen or oxygen atom, or both. Since several of the metals considered for chelation are transition metals, the relative order of affinities is presented here:

$$-NH_2 > -N= > N(\text{aromatic}) > -COO^- > -O- >> C{=}O$$ [38]

Thus, the chelates between a metal and a compound with an amine group, NH_2, should be quite stable. The relative stabilities of metal complexes have been determined for elements in the first transition series; e.g., Mn < Fe < Co < Ni < Cu >Zn. This increase in stability with increasing atomic number shows a maximum at copper. The stability of zinc is usually below that of nickel. Although the interaction between a metal and a chelating agent is complex, the relationships described above do permit qualitative predictions of behavior.

5.2 THEORY OF CHELATION

The formation of a metal-ligand chelate is a step-wise process.[12] In the first step, a metal ion, M, combines with a ligand, L, to form a simple complex, ML, with a stability constant K_1:

$$M + L \rightleftharpoons ML, \quad K_1 = \frac{[ML]}{[M][L]}$$

If there are excess ligands (chelating agent), this complex then combines with another ligand and so on until the coordination number of the metal, i.e., the maximum number of molecules with which it can chemically combine, is satisfied. Chelate ligands usually have more than one site to react with a metal. The stepwise scheme of complex formation is represented by:

$$ML + L \rightleftharpoons ML_2 \qquad K_2 = \frac{[ML_2]}{[ML][L]}$$

$$ML_{n-1} + L \rightleftharpoons ML_n \qquad K_n = \frac{[ML_n]}{[ML_{n-1}][L]}$$

Thus the magnitude of the stability constant, K_n, is a measure of chelate stability in solution. Frequently the stability of multi-ligand chelates is substantially less than for a 1:1 ligand to metal complex. This implies that addition of further ligand (over a 1:1 ratio) decreases the free metal concentration, but not necessarily in a proportional manner.

Stability is affected by the metal ions in solution, the particular coordinating groups of the ligand, and by the ring size of the ligand, the number of rings, and the basic strength of the chelating agent. The latter effect is important since, in a solution with the acid form of the ligand, there is competition between hydrogen and metal ions. A stepwise equilibrium between hydrogen ions and ligands may be found to produce changes in the metal-ligand equilibria. Competition from hydrogen usually occurs at low pH levels and a decrease in pH always produces a shift towards dissociation of the complex (an increase in free metal concentration). The converse is also true; the addition of a chelating agent to a solution containing metal ions results in the displacement of hydrogen ions from the ligands and a corresponding decrease in pH. Certain chelating agents may act as buffers over a specific pH range and thus restrict changes in pH accompanying the application of the agent.

5.3 Spills Treatable by Chelation

The chemicals containing metals subject to chelation are listed in Table 5.2-1, along with the recommended allowable limits for the respective metals defined by the Water Quality Criteria.[34] One would predict that effective chelation of the divalent transition metals-- iron, nickel, copper, cadmium and zinc-- could be accomplished by the same reagent. In an aerobic water body it is likely that oxidation of the ferrous ion in ferrous sulfate to ferric ion will occur. However, since ferric hydroxide begins to precipitate at low pH levels (around 4-5), it is unlikely that the higher valence species will pose a problem. In addition, chelating agents which complex ferrous ion will also chelate ferric ion (often forming an even more stable complex).

TABLE 5.2-1 CHEMICALS SUBJECT TO CHELATION

Chemical	Formula	Metal Ion	Recommended Allowable Limit		
			(mg/ℓ)(1)		(M)(1)
Antimony Trifluoride	SbF_3	Sb^{+3}	0.2		1.64×10^{-6}
Cadmium Chloride	$CdC\ell_2$	Cd^{+2}	0.0002	(0.0004(2))	1.79×10^{-9}
Copper Sulfate	$CuSO_4 \cdot 5H_2O$	Cu^{+2}	0.01		1.57×10^{-7}
Ferrous Sulfate	$FeSO_4 \cdot 7H_2O$	Fe^{+2}	0.05	(1.0(3))	8.96×10^{-7}
Nickel Sulfate	$NiSO_4$	Ni^{+2}	0.002		3.41×10^{-8}
Silver Nitrate	$AgNO_3$	Ag^{+}	0.001		9.27×10^{-9}
Titanium Tetrachloride	$TiC\ell_4$	Ti^{+4}	No Data		--
Zinc Chloride	$ZnC\ell_2$	Zn^{+2}	0.02	(0.07(3))	3.06×10^{-7}

(1) Based on 1972 Water Quality Criteria (NAS)[34]--level for minimal risk of deleterious effects upon marine aquatic life, unless otherwise noted.

(2) Limit for freshwater aquatic life.

(3) EPA proposed criteria (1975)[24]: Aquatic life support.

Additional comments concerning the other compounds suggested for chelating are given below.

- Antimony is an amphoteric* metalloid-- and although it can apparently be chelated, little information on the subject is available.
- Silver, a monovalent metal, can be complexed by a limited number of ligands.
- Titanium tetrachloride decomposes rapidly in water to hydrochloric acid and insoluble titanium dioxide. Therefore, treatment should be neutralization as for hydrochloric acid.
- Anions, such as dichromate ($Cr_2O_7^=$), permanganate (MnO_4^-), and ferrocyanide, ($Fe(CN)_6^{-4}$) cannot be chelated by common reagents.
- Chromic anhydride, CrO_3, is not directly treatable by chelation. If complex formation is desired, pretreatment with alkali to form chromate, CrO_4^-, and subsequent chelation of this anion would be necessary.

5.4 SELECTION OF CHELATING AGENTS

5.4.1 Sequestrants and Precipitants

Organic chelating agents may be divided into two classes, sequestrants and precipitants. In both cases the metal ion is firmly bound and not able to participate in the normal physical or chemical processes. Sequestrants form chelate complexes which are soluble in water; therefore, the compound still remains distributed throughout the water body although in a less toxic form.

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*Amphoteric-- having both acidic and basic properties.

5.4.2 Selection of Sequestrants

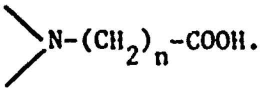
The criteria used to screen prospective sequestrants were as follows:

1. Any agent or complex remaining in solution after treatment must be at a non-harmful level and should not produce adverse environmental effects, e.g., large pH changes.
2. The removal of essential trace elements, such as calcium and magnesium, from the aquatic environment must be minimized.
3. Misapplication of the treatment chemical should not cause a violation of water quality criteria.
4. The reagent should be soluble in water to the extent that application to a spill is necessary.
5. It should be low cost and readily available.
6. The metal chelate should be stable in solution against degradation for a reasonable time.

Amino carboxylate and sulfonate are the coordinating groups most commonly found in sequestering agents. Frequently the hydroxyl group is present as an auxiliary coordinating group. The most widely studied include:

- Ethylenediaminetetraacetic acid (EDTA)
- 1, 2-Diaminocyclohexanetetraacetic acid (CDTA)
- Hydroxyethylethylenediaminetriacetic acid (HEDTA)
- Nitrilotriacetic acid (NTA)

Of these sequestrants, all are amino acids containing acid carboxyl groups, COOH, in addition to the nitrogen of the parent amine. EDTA, NTA, and CDTA are aminopolycarboxylic acids of the form: [5]



$$>N-(CH_2)_n-COOH.$$

HEDTA is a hydroxy-alkylamino acid of the general form: [5]

$$HO-(CH_2)_m-\overset{|}{N}-(CH_2)_nCOOH,$$

a hydroxyl ion being substituted for a carboxyl group. Natural amino acids such as glycine (H_2NCH_2COOH), and cysteine ($HSCH_2CH(NH_2)COOH$)[2] are also known to have the ability to bind metals to proteins in the body. The former chelates in a manner similar to EDTA by losing its acid hydrogen ion; cysteine, however, forms complexes with its sulfhydryl group (-SH).

Other ligands which have sequestering properties include α-hydroxy acids and the condensed phosphates. Citric and gluconic acids are hydroxy acids used industrially for sequestering. Since coordination occurs only through hydroxy groups, the stability of these acid chelates is considerably lower than the aminocarboxylic acid chelates. Polyphosphates are the only inorganic chelating agents in wide-spread use, the most common form being a sodium salt, such as sodium pyrophosphate. They are capable of sequestering alkaline earths, e.g., calcium and magnesium, but unfortunately are unable to chelate heavy metals effectively.

Evaluation of the various sequestering agents discussed above leads to several conclusions:

1. α-hydroxy acids exhibit stabilities of such a low order as to remove them from consideration.
2. Condensed polyphosphates are applicable to a limited number of metals, and these chelates have low stability constants.
3. The natural amino acids do not form sufficiently stable chelates. Substitution with the sulfhydryl group, as in cysteine, improves stability somewhat, but, the cost and availability of these compounds would prohibit their use for spill treatment.
4. Synthetic aminocarboxylic acids can form exceedingly stable compounds with a variety of metals.

Therefore, the final selection was limited to a sequestrant from this last group of compounds.

EDTA is an obvious candidate. Its proven applications include:

- metal cleaning-- EDTA is used to complex iron, copper and water-hardness metals in removing scale.
- fruits and vegetables-- EDTA is used to complex trace metals and prevent discoloration and improve flavor.
- leather tanning-- EDTA complexes calcium, chrome and iron in cleaning, stripping, and stain removal.

- medicinal uses-- EDTA complexes zinc, iron, nickel, lead, and mercury, used in cases of metal poisoning.

Because of the hydrophilic anionic groups, the EDTA molecule penetrates biological cell walls poorly and is, thus, of limited toxicity. Other aminopolycarboxylic similar to EDTA, but not as widely used, were also chosen for further investigation-- NTA, CDTA, and HEDTA (full chemical names given on page 118.)

The stability constants of chelates formed between these compounds and the heavy metals [5] have been compiled in Table 5.4-1. The values given are the $\log_{10}$ of the first stability constant,

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

M = metal
L = ligand

Using the Cu-EDTA chelate as an example, $\log K_1 = 18.8$ or $K_1 = 6.3 \times 10^{18}$. Thus, $[ML] = 6.3 \times 10^{18} [M][L]$, i.e., the concentration of metal chelate is over 10^{18} times the product of free metal and ligand concentrations in neutral solution. It should be remembered that pH has a strong influence on the final free metal concentration (as a result of the acid dissociation of the ligand). For example [17], EDTA is diprotonated at pH 4-6, monoprotonated from pH 7-9, and completely dissociated above pH 10. Table 5.4-1 shows that the order of stability of the metal chelates is

NTA < HEDTA < EDTA < CDTA.

The calculation of free metal concentrations as a function of pH has been carried out by Chaberek & Martell[5] for NTA and EDTA, assuming a total metal concentration of 0.01 M: NTA and EDTA concentrations of 0.022 M and 0.011 M, respectively, were selected to provide a 10% excess in ligand concentrations. (EDTA forms stable 1:1 ligand to metal complexes while NTA forms 2:1 complexes.) The results of the calculations are shown in Table 5.4-2. NTA can reduce free metal concentrations to within allowable limits at a pH of 8 or above. 'EDTA can reach safe metal levels at a pH of 6 or above. The efficiency of chelation increases for the metals in the following order:

Mg < Ca < Fe < Cd < Zn < Ni < Cu.

TABLE 5.4-1. STABILITY CONSTANTS OF METAL CHELATES
(Values are $\log_{10}$ of the first stability constant)

Chelating			Metals				
Agent	Copper	Nickel	Zinc	Cadmium	Iron	Calcium(2)	Magnesium(2)
NTA	12.7	11.3	10.5	9.8	8.8	6.4	5.4
HEDTA	17.4	17.0	14.5	13.0	12.2	8.0	5.2
EDTA	18.8	18.6	16.5	16.5	14.3	10.6	8.7
CDTA	21.3	--	18.7	19.2	--	12.5	10.3

Chaberek & Martell[5] - values are $\log_{10}$ of first stability constants

(2) Important trace elements in the aquatic environment.

TABLE 5.4-2. FREE METAL CONCENTRATION AS A FUNCTION OF pH

pH	Cu	Ni	Zn	Cd	Fe	Ca	Mg
				NTA			
2	4.4	3.0	2.4	2.1	2.0	2.0	2.0
4	7.0	5.6	4.8	4.1	2.8	2.0	2.0
6	9.1	7.6	6.7	6.4	4.1	2.8	2.2
8	11.5	10.5	8.7	9.4	6.1	3.7	3.3
10	13.1	12.2	10.0	11.5	7.7	5.2	4.2
				EDTA			
2	3.9	4.0	2.2	2.3	2.1	2.0	2.0
4	8.9	9.0	6.7	7.0	5.1	2.3	2.0
6	12.6	12.8	10.5	10.7	8.8	5.5	3.8
8	15.0	15.1	12.8	13.1	11.3	7.3	5.4
10	16.8	17.0	14.6	15.0	14.2	9.2	7.2

Note: Values listed in the table are $-\log_{10}[M]$.

HEDTA is only slightly less effective than EDTA, and CDTA is the most effective judging from the data in Table 5.4-1. EDTA appears to be the most promising agent for the following reasons:

1. The differences in stability from CDTA are not sufficiently great to be significant.
2. EDTA chelates effectively in a pH range within which most natural waters fall.
3. EDTA is a well-known, commonly used material, which has a demonstrated lack of toxic properties.
4. EDTA functions as an effective hydrogen ion buffer, preventing undesirable pH swings.

5.4.3 Chelation of EDTA with Other Metals

EDTA does form complexes with silver, antimony, and bismuth,[28] but there are serious limitations which must be recognized in these cases:

- Silver has a first stability constant which is less than those for calcium and magnesium. Therefore, EDTA will chelate silver ions after the more stable calcium and magnesium chelates have been formed. From a water quality standpoint, such an occurrence could be harmful to aquatic life.
- Antimony does not chelate directly with EDTA, but only through the hydrolyzed species, SbO^+. Such chelates are quite stable ($K_1 = 24.8$) but antimony trifluoride only hydrolyzes to a small extent. Thus chelation would be slow under spill conditions.
- Titanium, similarly, forms stable chelates only through TiO^{+2} ($K_1 = 17.5$). Chelation may occur upon hydrolysis of titanium tetrachloride; however, specific data are not available.

5.4.4 Cost and Availability of EDTA

EDTA is generally applied as a soluble sodium salt of the acid in one of the following forms:

- EDTA disodium salt-- the pH of a 0.1N solution is 5.
- EDTA tetrasodium salt-- the pH of a 0.15N solution is about 11.8.
- EDTA calcium disodium salt-- the pH of a 0.1M solution is about 7.

The order of increasing cost per unit of reagent is tetrasodium, disodium, then calcium disodium. The tetrasodium salt, while the least expensive, would produce an undesirable increase in pH in the case of misapplication to a spill. The disodium salt has a desirable solution pH and is somewhat more effective as a sequestrant than the calcium disodium salt.

The EDTA disodium salt is sold as a powder or crystal with several generic names, such as Edathamil Disodium and Disodium Edetate. Major producers in the U.S. include Dow Chemical, Eastman Kodak, and Geigy Chemical. Some of the more common trade names for the material are Questex, Sequestrene, and Versene.

The reagent can be purchased in small or large quantities and is readily available. Annual production in 1972 was 587,000 kg.[33] The cost is approximately $5.50/kg for bulk shipments.

The quantities of EDTA disodium salt required to form 1:1 ligand to metal complexes with the treatable metals of Table 5.4-1 have been calculated in Table 5.4-3. Requirements for the five spill chemicals are in the range of 1.2-2.5 kg. reagent/kg. chemical.

TABLE 5.4-3. QUANTITIES OF CHELATING AGENT

Species	Na_2 EDTA (kg/kg spill chemical)
$CdC\ell_2$	1.8
$CuSO_4 \cdot 5H_2O$	1.3
$FeSO_4 \cdot 7H_2O$	1.2
$NiSO_4$	2.2
$ZnC\ell_2$	2.5

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- EDTA calcium disodium salt-- the pH of a 0.1M solution is about 7.

The order of increasing cost per unit of reagent is tetrasodium, disodium, then calcium disodium. The tetrasodium salt, while the least expensive, would produce an undesirable increase in pH in the case of misapplication to a spill. The disodium salt has a desirable solution pH and is somewhat more effective as a sequestrant than the calcium disodium salt.

The EDTA disodium salt is sold as a powder or crystal with several generic names, such as Edathamil Disodium and Disodium Edetate. Major producers in the U.S. include Dow Chemical, Eastman Kodak, and Geigy Chemical. Some of the more common trade names for the material are Questex, Sequestrene, and Versene.

The reagent can be purchased in small or large quantities and is readily available. Annual production in 1972 was 587,000 kg.[33] The cost is approximately $5.50/kg for bulk shipments.

The quantities of EDTA disodium salt required to form 1:1 ligand to metal complexes with the treatable metals of Table 5.4-1 have been calculated in Table 5.4-3. Requirements for the five spill chemicals are in the range of 1.2-2.5 kg. reagent/kg. chemical.

TABLE 5.4-3. QUANTITIES OF CHELATING AGENT

Species	Na_2 EDTA (kg/kg spill chemical)
$CdC\ell_2$	1.8
$CuSO_4 \cdot 5H_2O$	1.3
$FeSO_4 \cdot 7H_2O$	1.2
$NiSO_4$	2.2
$ZnC\ell_2$	2.5

TABLE 5.4-4 STABILITY CONSTANTS OF METAL OXINATES

(Values quoted are $\log_{10}$ of the stability constant)

	Copper	Nickel	Zinc	Cadmium	Iron(III)	Magnesium	Silver
First Constant	12	10	8.5	8.2	8	4.5	5.2
Second Constant	23	18	16	--	15	--	--

TABLE 5.4-5. CONDITIONS FOR PRECIPITATION BY OXINE[2]

METAL	pH RANGE
Nickel	4.3-14.0
Zinc	6.0-13.4
Titanium	4.8- 8.6
Copper	5.4-14.0
Cadmium	5.6-14.0

of the same order as for EDTA. Thus oxine seems capable of reducing free metal concentrations to within accepted limits, particularly if 2:1 complexes are formed. Although stability data are not available, oxine may also be capable of chelating antimony and titanium. Data on the acceptable pH range for precipitation of the metals is presented in Table 5.4-5. (Solutions were buffered with ammonium acetate-acetic acid.) Thus all the chelate complexes are stable within the pH range 6-9.

Three natural polyelectrolytes also appear promising as metal complexing agents.[36,13] They are:

- Alginic acid-- a polysaccharide found abundantly in marine algae.
- Polygalacturonic acid-- a polysaccharide similar to alginic acid, a major component of plant tissue.
- Starch xanthates-- salt or ester of a thio acid, made from corn or wheat starch.

These materials have the advantage of being non-toxic natural substances and potentially capable of regeneration and reuse. The reagents are water insoluble and are applied as solids, in a manner similar to ion-exchange resins. Laboratory tests[36,13] have shown that these compounds are capable of effectively precipitating the divalent heavy metals: copper, cadmium, zinc and nickel. The two acids do produce decreases in pH (unspecified) while the xanthates produce increases in pH.

Two potential treatment agents for anionic species were also identified:

(1) α-Benzoinoxime (Cupron) is a powder, slightly soluble in water but fairly soluble in alcohol. It can partially precipitate chromate.

(2) Nitron (triazonium compound) is insoluble in water, but soluble in alcohol and acetic acid. It forms insoluble compounds with chromate and ferrocyanide.

These compounds may also form complexes with dichromate and permanganate, but further data are lacking.

Based on the discussion presented in this section, the most promising chelating agent for precipitation is oxine. It is of proven value in precipitating a wide range of metals to very low levels of concentration. The toxicity of the chelating agent by itself is not great, although some questions remain concerning the environmental impact of the required buffer and of the final metal-chelates.

5.4.6. Cost and Availability of Oxine

U.S. producers of oxine (sold as a solid) include American Hoechst Corp., Ashland Chemical Co., and Merck & Co., Inc. It is sold under a variety of generic and trade names, such as: 8-Quinolinol, Oxin, Oxychinolin, Quinophenol, Tumex, 8-OQ, and Bioquin. Annual production data is not available; however, since the material is quite widely used, the cost is expected to be approximately $13.60/kg.[7]

Oxine may form chelates containing more than one ligand. However, for comparison with EDTA, 1:1 ligand to metal complexes are assumed. Table 5.4-6. shows that the quantities of oxine required to treat the five spill chemicals range from 0.52 to 1.07 kg. reagent/kg. chemical.

TABLE 5.4-6. QUANTITIES OF CHELATING AGENT

Species	Oxine (kg/kg spill chemical)
$CdC\ell_2$	0.79
$CuSO_4 \cdot 5H_2O$	0.58
$FeSO_4 \cdot 7H_2O$	0.52
$NiSO_4$	0.93
$ZnC\ell_2$	1.07

Oxine is more economical than EDTA on a weight basis (due to its lower molecular weight), but the cost of treatment is comparable. For example, the cost of reagent to treat a one kg spill of cadmium chloride is $9.90 for EDTA and $10.90 for oxine.

5.4.7. Solvent Extraction of Chelate Compounds

Metal chelate complexes can be extracted from an aqueous phase into an organic solvent under suitable conditions and this process is used commercially. The organic phase is frequently a common solvent, such as kerosene, while the chelating agent may be a proprietary formulation. Some examples of chelating agents are:

- LIX 64N-- hydroxyoxime, a General Mills reagent to extract copper.
- Kelex 100-- alkylated 8-hydroxyquinoline, Ashland Chemical Co. reagent specific for copper.
- DEHPA calcium salt-- di-2-ethylhexyl phosphoric acid, preferential extraction of zinc.

For the amelioration of chemical spills a non-specific chelating agent is desirable, and for successful solvent extraction it must be preferentially soluble in the organic solvent. Data are available on the extraction of metals from aqueous solution into chloroform using oxine.[29] Effective extractions of silver, titanium, nickel, copper, zinc and cadmium were obtained. The oxine concentration in the chloroform was insensitive to pH. Zinc was extracted and formed an insoluble complex in the extracting solvent.

Clearly solvent extraction of metal-chelate compounds shows promise but insufficient data are available to make positive recommendations.

5.5 METHODS OF APPLICATION

Since there are a number of specific options involved in the use of chelation as a spill response method, the application methods are varied. In a few cases, in situ chelation may be acceptable since the chelation compound may be inert enough to be acceptable or at least preferable to the untreated species.

Since most of the chelating agents that form precipitates are insoluble in water, but soluble in solvents, the solvent extraction apparatus with its initial stage for precipitate removal seems to be adaptable to use with these agents.

Even with the sequestering agents which are water soluble, an extraction scheme may be desirable for recovery of the chelating agent.

5.6 FATE AND CONSEQUENCES

The fate and consequences of an untreated spill are the same as those discussed under precipitation (Section 4.10). Use of sequestrants and precipitants is discussed separately.

5.6.1 Treatment with a Sequestrant (EDTA)

Optimum treatment with a sequestrant should reduce the concentration of free metal cations to very low levels. All available metal cations will be chelated to some degree (i.e., those from the spill and those present naturally), though the most stable complexes will be favored. The resulting chelation complexes will tend to remain in solution since EDTA is fairly hydrophylic.

The beneficial effect of a reduction in the free toxic metal concentration will be offset by any toxic effect of the chelation complex. EDTA by itself, has a NAS aquatic toxicity rating of 2[9], indicating the toxic threshold limit is in the range of 100-1,000 ppm. The threshold limits for various metal ion complexes with EDTA are unknown but they are probably similar to EDTA. Thus, the treatment of spills requiring the addition of EDTA in concentrations above about 1,000 ppm should probably only be considered when human health considerations are predominant.

The extent to which EDTA will combine with heavy (toxic) metals from sediments or suspended particles in uncertain. This would result in a solubilization of additional toxic material. Transfer of metals from sediments to solution in this manner has been shown to correlate with the concentration of the chelating NTA agent present.

EDTA, and presumably its complexes with metals, have a finite lifetime in the aquatic environment. Both chemical (photo) oxidation and biochemical oxidation (a 5-day BOD of 1% has been reported[9]) will eventually break down the organic molecule and could result in the release of metal ion. The rate of release would be expected to be slow.

Chelation of metals will also tend to increase their residence time in solution by impeding the natural removal processes such as precipitation and/or cation exchange. A misapplication of EDTA (in the wrong location or in excess) will not present any additional environmental effects.

5.6.2. Treatment with a Precipitant (Oxine)

Optimum treatment with oxine will significantly reduce the concentration of free heavy metal(s); in addition, the oxine-metal complex will precipitate. The settling characteristics of such complexes are not known;* but we assume they would be poor. In that event, a colloidal suspension of the oxine-metal complex might be transported with the main flow of water in the affected water body.

The beneficial effect of a drastic lowering of the free metal cation concentration will be offset by any toxic effects of the chelation complex. No information on the aquatic toxicity of oxine or its complexes is available. Oxine, in the presence of Cu^{2+}, Fe^{2+}, or Fe^{3+}, is a powerful bactericide and fungicide-- and is used as such in pharmaceutical preparations and ointments for use on human skin surfaces-- which suggest that the level of toxicity to aquatic microorganisms would be quite high. Other adverse effects include:

- Mobilization of metals from sediments;
- Eventual release of the metal and BOD associated with the degradation of oxine; and
- Increase in the residence time (of the metal) in the water column.

A misapplication of oxine would result in similar environmental effects.

5.6.3. Solvent Extraction with Oxine

The use of oxine in a closed loop solvent extraction system would also be capable of chelating a significant amount of the free heavy metal

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*Quinoline itself is slightly denser than pure water; the specific gravity is 1.095.

cations following a spill. The extraction efficiency of such a system can only be postulated, but relatively high extraction efficiencies should be achieved in a multi-stage centrifugal extractor. High metal concentrations in the spill would probably require relatively high solvent-to-spill ratios.

The use of such a closed loop system would minimize the four major adverse side effects associated with in situ treatment:

1. There would be no mobilization from the sediments (since there would be no contact);
2. There would be no eventual release of the metal (which would be recovered in a concentrated solution);
3. There would be no increase in the residence time of the metals in the water; and
4. The potential hazards associated with adding large amounts of chelating agent to a water body would not be present.

The only adverse environmental effects from the use of such a system would be associated with small losses of the chelate and solvent in the discharged (treated) water. If a low solubility, low toxicity solvent such as vegetable oil is effective, solvent losses (and resulting harmful effects) would be small. Losses of oxine cannot be accurately estimated since the literature data do not give a quantitative value for its solubility.

6.0 CONCLUSIONS

6.1. NEUTRALIZATION

Chemicals subject to neutralization are either acids or bases, or react with water to form acids or bases. Acids are neutralized by the addition of a basic reagent and bases by the addition of an acidic reagent. Acidity or basicity is measured on a scale of pH from 1-14 where acids have a low pH and bases have a high pH. Neutrality is defined as pH 7.

All natural waters deviate to some extent from neutrality and may be acidic or basic (alkaline). Most organisms are sensitive to extremes of pH and to rapid fluctuation in pH which would be caused by a chemical spill. Water Quality Criteria[34] defines a pH range from 6-9 as acceptable to most forms of aquatic life.

Strong bases are the most economical reagents for the neutralization of strong acids and vice versa. However, if excess reagent is applied or if the reagent is applied in an area away from the spill, then the result is a large deviation in pH in the opposite direction, thus compounding the effects of the original spill. Therefore, the most promising reagents are weaker acids and bases which will not cause the pH to fall outside the range of 6-9 if excess reagent is used or if the reagents are applied in the wrong position. We have selected sodium bicarbonate as the most promising agent for treatment of acid spills, and sodium dihydrogen phosphate as the most promising agent for the treatment of alkaline spills. Both of these reagents are available in solid form, cost about 10 - 20 cents/lb in bulk, are readily soluble in water and pose no handling or storage problems.

A summary of the treatment recommendations for the list of spill chemicals subject to neutralization is given in Table 6.1-1. Some of the spill chemicals listed are very weak acids or bases which would not cause deviation of pH outside the range 6-9 if they were spilled into a water body. For these chemicals, we recommend no treatment.

TABLE 6.1-1. SPILL CHEMICALS SUBJECT TO NEUTRALIZATION

1. ACIDS - Recommend treatment with sodium bicarbonate

Acetic acid
Acrylic acid
Formic acid
Hydrochloric acid
Hydrofluoric acid
Hydrogen chloride
Sulfuric acid (spent)
Hydrogen fluoride
Nitric acid
Oxalic acid
Phosphoric acid
Propionic acid
Sulfuric acid

2. COMPOUNDS THAT REACT IN WATER TO GIVE ACIDS - Recommend treatment with sodium bicarbonate

Acetic anhydride
Aluminum chloride
Benzoyl chloride
Bromine
Chlorosulfonic acid
Maleic anhydride
Nitrogen tetroxide
Nitrosyl chloride
Oleum
Phosphorus oxychloride
Phosphorus pentasulfide
Phosphorus trichloride
Polyphosphoric acid
Sulfur monochloride
Sulfuryl chloride
Titanium tetrachloride

3. BASES - Recommend treatment with sodium dihydrogen phosphate

Aminoethylethanolamine
Ammonium hydroxide
Caustic potash solution
Caustic soda solution
Cyclohexylamine
Diethanolamine
Diethylamine
Diethylenetriamine
Diisopropanolamine
1,1-Dimethylhydrazine
Ethylenediamine
Hydrazine
Monoethanolamine
Monoisopropanolamine
Morpholine
Potassium hydroxide
Sodium hydroxide
Triethanolamine
Triethylamine
Triethylenetetramine
Trimethylamine
Hexamethylenediamine

4. COMPOUNDS THAT REACT IN WATER TO GIVE BASES - Recommend treatment with sodium dihydrogen phosphate

Anhydrous ammonia
Ethyleneimine
Lithium aluminum hydride
Sodium
Sodium amide
Sodium hydride

5. COMPOUNDS FOR WHICH NO NEUTRALIZATION TREATMENT IS RECOMMENDED

Acids - Hydrogen cyanide--high toxicity, vapor and liquid.

Bases - Aniline, dimethyl formamide, hexamethylene tetramine, methyl ethyl pyridine, pyridine, and urea--very weak bases, will not violate pH criteria, therefore treatment by neutralization is not necessary.

Most of the chemicals listed in Table 6.1.1 can be neutralized in situ; treatment appears to be worthwhile for spills of 50-100 gallons or more in confined areas, lakes, rivers and even estuaries if treatment can be done before a tide reversal. A treatment skid, costing about $7000 and weighing about 1 ton, consisting of a pump, a system for metering the powdered neutralizers into solution, and a spray discharge nozzle would be suitable for treatment of spills as large as 10,000 gallons and even for partial treatment of still larger spills.

The skid and the chemicals can be air transported to the spill site. Deployment using the skid equipment on a boat such as a buoy tender appears to be simple, although a fair amount of manual labor is needed in moving 50-100 lb bags of treatment chemical.

As a response technique, neutralization appears to be feasible, suitable for amelioration of a large group of soluble chemicals, and environmentally desirable. Misapplication of the selected agents has minimal adverse impact.

For successful implementation, improved data on in situ reactions and further development of analytical techniques for predicting dispersion through water columns are needed as well as development of techniques for following or locating contaminated zones prior to treatment initiation. Monitoring of pH during treatment and active interaction with on-line dispersion models is also desirable for most effective application of treating agent. Nevertheless, these are problems that are within the state of the art and it appears that the U.S. Coast Guard could develop effective response strategies for neutralizing acidic or basic spills of chemicals which dissolve in the water column.

6.2. SOLVENT EXTRACTION

If an organic compound is soluble in water, there then exist structural groups which are compatible with the highly polar nature of water. Typical of such groups are the -OH of alcohols and acids and the $-NH_2$ of amines. To transfer soluble organic compounds to a phase immiscible with water, one must consider the nonpolar or hydrophobic groups in the material. This also indicates that the solvent itself should be nonpolar.

Other criteria which are important in the choice of a solvent relate to its solubility in water and to its toxicity.

Many potential solvents were considered and vegetable oil (e.g., soybean oil) was finally selected. This material is inexpensive, readily available, non-toxic, and only slightly soluble in water. To limit the size and complexity of the extraction equipment, we examined the potential of soybean oil to extract soluble organic chemicals and equipment with five equilibrium stages assuming equal volume flows of fresh solvent and contaminated water in each stage. For some chemicals, such treatment would be sufficient to reduce the concentration of a chemical in water to a level below the toxic limits; in other cases, the extraction was less effective. Of the 75 chemicals considered, only 18 appear to be promising for removal by extraction. Another 27 soluble chemicals have such low toxicity limits that no treatment is necessary. Twenty-two compounds were found to be so polar that no extractive solvent appears reasonable. Finally, for 8 materials, insufficient data were located to allow one to determine the applicability of solvent extraction.

A listing of the compounds in the various groups is presented in Table 6.2-1.

Although there are 18 chemicals suitable for solvent extraction treatment with vegetable oil, the equipment for treating large spills of these chemicals is cumbersome and complicated both to operate and maintain. For 10,000 gallon spills, an apparatus weighing 10-20 tons and costing about $400,000 appears necessary. The equipment could be air lifted in a C130, but its size and weight would require deployment from a barge (for spills in a lake or river) or a heavy truck (confined spills). The contaminated portion of the water would be pumped on-board, treated by the apparatus, and returned to the water at a point far enough away from the contaminated zone to prevent dilution of the water remaining to be treated.

This equipment is sufficiently specialized so that the practical implementation of a solvent extraction treatment technique presents many problems, except perhaps for small, confined spills where a much smaller apparatus could be used for gradual amelioration treatment.

TABLE 6.2-1. SPILL CHEMICALS SUBJECT TO SOLVENT EXTRACTION

TREATMENT WITH VEGETABLE OIL IS SUGGESTED

n-Amyl alcohol
n-Butyl alcohol
Chloroform
Ethyl acetate
Isoamyl alcohol
Methyl amyl alcohol
Methyl methacrylate
n-Propyl acetate
Sodium alkyl sulfates
n-Butyl acetate
Carbon bisulfide
Dichloromethane
Formaldehyde solution
Methyl acrylate
Methyl isobutyl carbinol
Paraformaldehyde
Sodium alkylbenzene sulfonates
Vinyl acetate

NO EFFECTIVE SOLVENT

Acetone cyanohydrin
1,4-Butanediol
1,4-Butynediol
Diethylene glycol dimethylether
Diethylene glycol monomethylether
Ethylene cyanohydrin
Ethylene glycol monoethyl ether
Ethyleneimine
Hexylene glycol
n-Propyl alcohol
Triethanolamine
Allyl alcohol
1,4-Butenediol
Chlorohydrins (crude)
Diethylene glycol monoethyl ether
Diisopropanolamine
1,4-Dioxane
Ethylene glycol monobutyl ether
Ethylene glycol monomethyl ether acetate
Ethylene glycol monomethyl ether
Isobutyl alcohol
Polypropylene glycol methyl ether

NO TREATMENT NECESSARY

Aminoethanolamine
tert-Butyl alcohol
Dextrose solution
Dichloromethane
Diethylene glycol
Ethoxytriglycol
Ethoxylated pentadecanol
Ethoxylated tridecanol
Ethylene glycol
Isobutyl alcohol
Methyl alcohol
Monoisopropanolamine
Propylene oxide
Triethylene glycol
sec-Butyl alcohol
Corn syrup
Diacetone alcohol
Diethanolamine
Dimethyl sulfoxide
Ethoxylated dodecanol
Ethoxylated tetradecanol
Ethyl alcohol
Glycerine
Isopropyl acetate
Monoethanolamine
Propylene glycol
Sorbitol

(Continued)

TABLE 6.2-1. (Continued)

NO DATA AVAILABLE TO MAKE RECOMMENDATIONS

- Dimethyl sulfate
- Dipropylene glycol
- Epichlorohydrin
- Ethyl acrylate
- Methanearsonic acid, sodium salts
- Morpholine
- Sulfolane
- Tetrahydrofuran

The development of solvent extraction treating equipment might be made more attractive, however, if it is built in modules that can be used for other types of responses. For example, the first module, designed for filtering solids, might also serve as a treatment skid for chemical spills subject to amelioration by precipitation. The entire system might also be suitable for use in conjunction with treatment response using a sequestering chelating agent which can then be recovered and recycled by solvent extraction. However, basic data are lacking for meaningful design of such treatment modules at present. The concept appears to be technically feasible but the potential for developing it into a practical field response method is not clear. Further analysis of the extent of environmental damage associated with this class of spills and comparison with treatment methods other than those included in this study should be conducted to determine whether a solvent extraction response system justifies further development.

6.3. PRECIPITATION

No single agent is capable of treating all of the chemical compounds in the list of chemicals suggested for treatment by precipitation. It is not possible for the same type of treatment to be equally effective for both cations and anions. Although a variety of reagents can be employed to precipitate each of these compounds, many of the reagents do not reduce the concentration of the toxic metals to a sufficiently low level. In some cases, the use of a precipitating agent could introduce a new toxic element into the system.

A summary of the recommended treatments for the chemicals subject to precipitation is given in Table 6.3-1. Dibasic sodium phosphate (Na_2HPO_4) is the preferred agent for six of the thirteen chemicals. The others require individual treatment. No treatment is recommended for silver nitrate in marine waters because the high concentration of chloride ion which exists (0.5 $\underline{M}$) is sufficient to precipitate the silver. Titanium tetrachloride reacts with water to liberate hydrochloric acid and, therefore, should be treated by neutralization. At the same time a relatively non-toxic precipitate of white titanium is formed. Treatment of synthetic latex is not recommended because no simple treatment can be

6.3-1. SPILL CHEMICALS SUBJECT TO PRECIPITATION

SPILL CHEMICAL	REAGENT
Cadmium Chloride	Dibasic Sodium Phosphate
Copper Sulfate	Dibasic Sodium Phosphate
Ferrous Sulfate	Dibasic Sodium Phosphate
Nickel Sulfate	Dibasic Sodium Phosphate
Zinc Chloride	Dibasic Sodium Phosphate
Antimony Trifluoride	Dibasic Sodium Phosphate
Silver Nitrate	Sodium Chloride (no treatment in marine waters)
Titanium Tetrachloride	Treat as hydrochloric acid by neutralization
Potassium Dichromate	Sodium Sulfite
Potassium Permanganate	Sodium Sulfite
Chromic Anhydride	Ferrous Sulfate
Latex	No treatment
Sodium Ferrocyanide	Ferric Chloride

guaranteed effective. Also, the effects of treatment may compound the adverse effects of the spill and may depend on the particular latex formulation.

It is difficult to assess whether or not an in situ precipitation is possible for the various chemical/treatment combinations since the settling characteristics of the precipitate depend on its particle size distribution and the turbulence of the water column. If settling does occur, then environmental impacts of precipitate removal by dredging or of leaving the material on the bottom may not be acceptable in some cases. If the precipitate does not settle out, it may continue to move with the water as a colloidal dispersion.

These difficulties can be overcome by pumping the contaminated water into a treatment system where precipitation and precipitate collection occur before treated water is returned to an uncontaminated region of the water body. The equipment required for this purpose is fairly simple, consisting of a pump, a precipitation tank, a solids separator, and a precipitate storage vessel. As discussed in Section 6.2, this equipment might also serve as a module for treating the inlet water to a solvent extraction system.

6.4. CHELATION

Chelate compounds are potentially capable of ameliorating spills of some chemicals because the complexes formed with toxic metals have a lower toxicity than the original spilled chemical. There are two types of chelating agents: sequestrants which bind the metal ion but remain soluble within the water column, and precipitants which, as the name implies, cause precipitation of the chelate-metal complex and, in this manner, remove it from the water column.

A summary of the recommended treatment by chelating agents is given in Table 6.4-1. The most promising sequestrant is ethylenediaminetetraacetic acid (EDTA). This compound forms stable chelate complexes with copper, nickel, zinc, cadmium and iron and can reduce the concentration of these metals to below the water quality criteria at pH of 6 or higher. EDTA is a widely used reagent and has a relatively low toxicity.

EDTA is probably not effective with the metals silver, antimony, and titanium and is not suitable for the other compounds such as potassium

TABLE 6.4-1. SPILL CHEMICALS SUBJECT TO CHELATION

Chemical	Formula	Toxic Ion	Recommended Chelating Agent	
			Sequestrant	Precipitant
Antimony Trifluoride	SbF_3	Sb^{+3}	no suitable reagent	
Cadmium Chloride	$CdCl_2$	Cd^{+2}	EDTA	Oxine
Chromic Anhydride	CrO_3	Cr^{+6}	no suitable reagent	
Copper Sulfate	$CuSO_4 \cdot 5H_2O$	Cu^{+2}	EDTA	Oxine
Ferrous Sulfate	$FeSO_4 \cdot 7H_2O$	Fe^{+2}	EDTA	Oxine
Latex, Liquid Synthetic	---	---	no suitable reagent	
Nickel Sulfate	$NiSO_4$	Ni^{+2}	EDTA	Oxine
Potassium Dichromate	$K_2Cr_2O_7$	Cr^{+6}	no suitable reagent	
Potassium Permanganate	$KMnO_4$	Mn^{+7}	no suitable reagent	
Silver Nitrate	$AgNO_3$	Ag^+	no suitable reagent	
Sodium Ferrocyanide	$Na_4Fe(CN)_6$	$Fe(CN_6)^{-4}$	no suitable reagent	
Titanium Tetrachloride	$TiCl_4$	Ti^{+4}	treat by neutralization	
Zinc Chloride	$ZnCl_2$	Zn^{+2}	EDTA	Oxine

dichromate, potassium permanganate, chromic anhydride and sodium ferrocyanide.

The most promising precipitant is 8-hydroxyquinoline (oxine) which precipitates copper, nickel, zinc, cadmium, and possibly, silver, antimony and titanium. Suitable chelating precipitants for the anions have not been demonstrated. Additional information is needed on reaction rates and effects of pH on reactions before a final conclusion on feasibility can be drawn.

Treatment by sequestering with EDTA might be implemented in the field using the same equipment as that developed for the solvent extraction treatment method. The EDTA could probably be recovered and recycled using solvent extraction with vegetable oil. For the precipitating chelation scheme, the precipitation equipment described in Section 6.3 might be appropriate.

7.0 RECOMMENDATIONS FOR FUTURE RESEARCH

7.1 Neutralization

7.1.1 Introduction

Development of a neutralization response technique should be given a priority above the other response techniques considered in this program. This priority is warranted because (1) spills of acids and bases are common;* (2) such spills can have a severe environmental impact; and, (3) neutralization can be carried out relatively easily with only minor additional environmental impact.

A five step research and development program is proposed, to include the following:

1. Laboratory tests (using natural waters);
2. Spill modeling;
3. Construction of a small test system;
4. Field tests with the test system;
5. Construction and testing of a full-scale system.

The general time frame for these steps is shown schematically in Figure 7.1-1.

Detailed information on the recommended research and development steps is given below.

7.1.2 Specific Recommendations

Step 1 - Laboratory Tests

Objectives: (1) To determine experimentally the quantities of neutralizing reagent needed for each hazardous acid (or base) in various types of natural waters. (2) To recommend, following laboratory studies, what combination of real-time pH monitors and/or indicators will be required. (3) To determine rates of reaction of those chemicals which react with water to form acids and bases.

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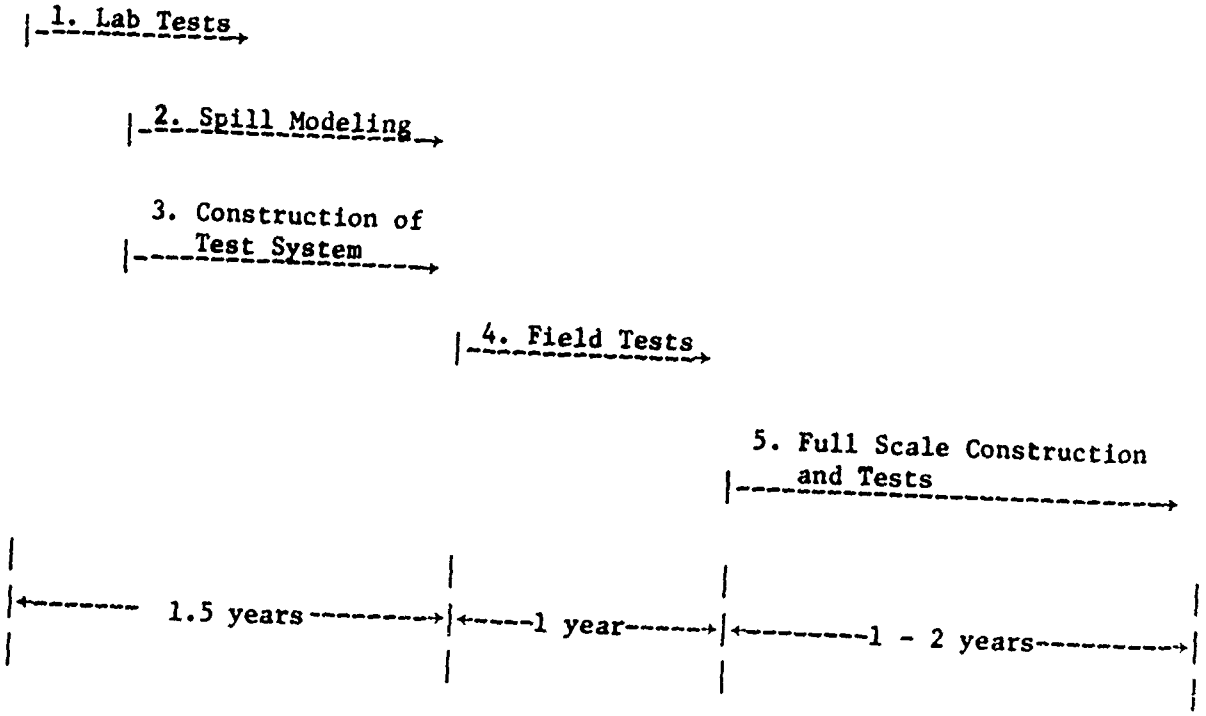
*Spills of acids and bases constituted about one-third of all spills of hazardous chemicals (excluding crude oil and single spills of a chemical) reported to the EPA during the period 1970-1973.

Figure 7.1-1

ORDER AND TIME FRAME FOR DEVELOPMENT OF A NEUTRALIZATION RESPONSE TECHNIQUE



Discussion: While theoretical calculations provide approximate values for the amounts of reagent needed, it is desirable to obtain somewhat more accurate data for each hazardous chemical for which neutralization is the recommended treatment. Especially for spills which are acid and are to be adjusted to within 1 pH unit of neutrality, the natural pH of the water may have a major effect on the quantity of treating agent for neutralization.

Only simple laboratory titrations would be required; a high degree of sophistication is not warranted. The titrations should be carried out in different natural waters (with pure water as a reference point) so that the influence of such parameters as natural pH, suspended solids, salinity, etc., can be understood. The quantities of neutralization agent needed in pure water should be determined for all hazardous chemicals for which neutralization is recommended; a few representative hazardous chemicals may be chosen to investigate the effects of the various parameters mentioned. The results of these tests should be tabulated (and annotated as necessary) for easy reference. The results should also be compared with theory to see if new theoretical correlations need to be developed.

Recommendation for pH monitors and indicators for use in real-time spill monitoring will involve (1) screening-- based on cost, usefulness and reliability-- of portable pH meters, and (2) screening for the most appropriate pH indicators (chemicals that change color at a given pH) or spill markers, based on quantitites needed, toxicity, availability, cost, visibility, and other appropriate factors. It is anticipated that pH meters will be the most useful tool for monitoring. If the required type of pH meter is not commercially available, added requirements should be specified to encourage the development of suitable instrumentation.

Testing requirements for this part of Step 1 need not be extensive; it is expected that much of the testing could be carried out in conjunction with the titrations mentioned above. If toxicity data are not available (from the literature) on the recommended indicators or markers, then the list of indicators should be submitted to expert judgment, and if warranted, actual experiments conducted to determine the aquatic toxicity levels.

Funding: Estimated at 1.5 man years.

Anticipated Difficulties: None

Step 2 - Spill Modeling

Objectives: To develop the capacity in the CHRIS system for accurate modeling of acid and base spills and their subsequent neutralization.

Discussion: A key part of successful spill amelioration is to be able to estimate the approximate location of the contaminated water at the start of treatment, to estimate the amount of treatment chemical required for neutralization and to identify the best application pattern for the treatment chemical. A first step in this direction was taken in this study. Simplified models from CHRIS for dispersion of species in large and small rivers were adapted (see Appendix C) to allow estimates to be made of the effectiveness of various neutralization treatment procedures. However, these models are quite simplistic.

Two alternatives are evident. First, it is possible to develop sophisticated models for specific locations including characterization of three dimensional dispersion effects and specific flow geometrics. Alternatively, one could develop on-line, interactive models to be used in conjunction with spill marking and contaminant detection techniques. For treating agents which are selected on the basis of being environmentally acceptable even if misapplied, the less sophisticated approach might require use of more than the minimum quantity of treatment chemical; however, this approach may prove acceptable in most spill situations.

One aspect presently omitted from the simple dispersion models is the effect of negative or positive buoyancy of the spilled acid or base on the vertical distribution of species. For certain chemicals, such as sulfuric acid, the density relative to water may be an important factor in determining the downstream location of the contaminated zone. This effect could be studied by an analysis based on a limited amount of laboratory and small-scale data and physical models.

Funding: Estimated at 1.0 man year

Anticipated Difficulties: None

Step 3 - Construction of Test System

Objective: To construct a reagent deployment system which can be used for field tests of neutralization as a response technique.

Discussion: A small scale, mobile deployment system should be designed and constructed to simulate the performance of the full-scale deployment system. The system must be sized to correspond with the field tests to be conducted. If, for example, field tests involving spills of up to 100 lbs of acid (or base) were to be carried out, then the system should be capable of delivering about 500 lbs /hr of reagent to the zone of hazardous concentration.

The system should be mounted on a boat for the subsequent tests.

Funding: Estimated at 1 man year (plus equipment)

Anticipated Difficulties: None

Step 4 - Field Tests with Test System

Objectives: To (1) test the neutralization response technique; (2) identify problems with equipment logistics, materials, and procedures; and (3) make recommendations concerning a full-scale system.

Discussion: Tests in small rivers or streams should be carried out for a limited number of simulated and/or actual spills; they should be conducted in conjunction with input from the model developed in Step 2. The tests should attempt to (1) demonstrate that the system is practical; (2) identify problems to be addressed in the construction and operation of a full-scale system; and, (3) assess the probable treatment efficiency. Once the field test prototype is developed, some additional tests in wide rivers or lakes should be conducted to provide information for verification and improvement of models for these types of water bodies.

Monitoring of any actual spill will be required; documentation (e.g., film and slides) would be desirable.

Funding: Estimated at 2 man years (plus equipment)

Anticipated Difficulties: No major difficulties anticipated. Actual spills will require permits from federal and/or state authorities; there may be some difficulty in obtaining a permit for an actual spill into a stream of navigable size. If a permit cannot be obtained, then testing (on a real spill) may have to wait until an accidental spill occurs. Dispersion models, however, might still be checked using some environmentally safe type of trace chemical.

Step 5 - Construction and Testing of a Full-Scale System

Objective: To construct and test a neutralization system capable of handling major spills of acids and bases.

Discussion: The output from this task will be (1) a full-scale neutralization system; (2) an operation and maintenance manual; and, (3) training material (reports, films, slides) for potential response teams. When possible, USCG/EPA spill response personnel should be invited to participate in the testing of this equipment.

The details of the design will be formulated after the results of the field tests of Step 4 have been assessed. The designing of the main deployment system will have to be coordinated with the capabilities of available transport services and ships upon which it will be used. The system should have mobility at least equivalent to the Coast Guard's ADAPTS*.

Testing of the system can take place with simulated spills; again this should be done in conjunction with spill-modeling input to further familiarize personnel with the capabilities and limitations of the system.

Funding: Estimated at 2-3 man years (plus equipment).

Anticipated Difficulties: No major difficulties anticipated.

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*Air Deliverable Anti-Pollution Transfer System-- for transferring oil from ships in distress.

7.2 SOLVENT EXTRACTION

7.2.1 Introduction

The results of this program have shown that solvent extraction is possible for some-- but not all-- of the water soluble organic chemicals on the CHRIS list. There is, at present, a relatively high degree of uncertainty about the practicality of carrying out such a procedure. Nevertheless, a significant number of spills of water soluble organic chemicals do occur, and some additional developmental work seems warranted.** As will be seen below, we are recommending that the basic evaluation of solvent extraction-- following certain laboratory studies-- be made in comparison with activated carbon adsorption.*** Solvent extraction and carbon adsorption have roughly similar capabilities for extracting organic chemicals from aqueous solution; if the results of the research recommended in Step 1 below indicate that solvent extraction offers little additional spill treatment capability over carbon, then no further research will be warranted.

No spill modeling is being recommended here. Should solvent extraction be developed as a response technique, the models developed for neutralization can be modified for use here.

A four step research and development program is proposed, to include the following:

1. Final solvent selection and laboratory investigations; comparison with activated carbon;

   (2-4 only if solvent extraction is found to be practical and to offer advantages over carbon)

2. Construction of a small test system;
3. Pilot tests with test system; and,
4. Construction and testing of a full-scale system.

The general time frame of these steps are shown schematically in Figure 7.2-1.

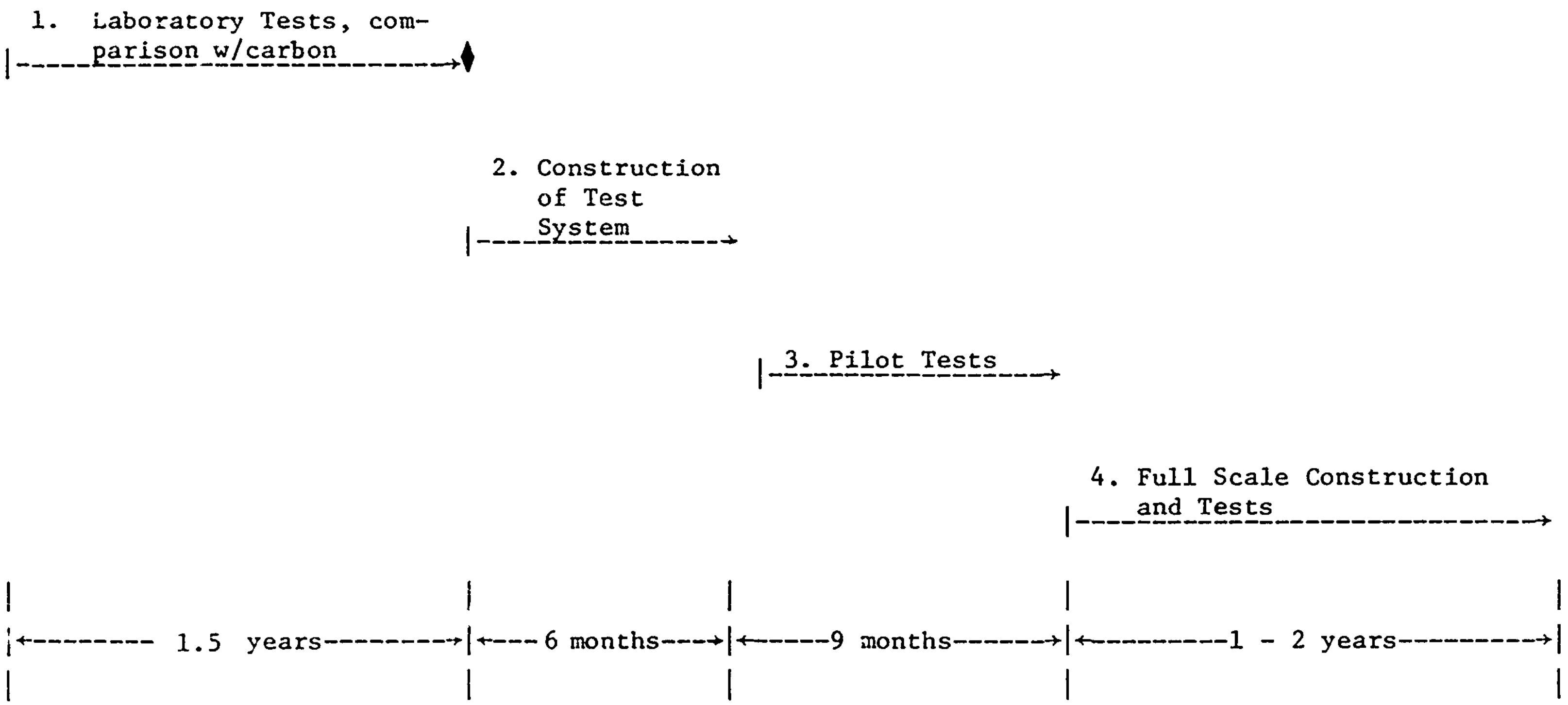
**The fact that solvent extraction would also be applicable to spills of slightly soluble or "insoluble" organic chemicals should not be overlooked. Such chemicals were not on the specific list of chemicals to be considered in this program. Solvent extraction would be, in general, much more efficient for the low solubility organic chemicals.

***At least two mobile spill treatment units incorporating activated carbon currently exist; in addition, the use of carbon in floating bags (thrown into a spill plume) is being considered.

Figure 7.2-1

ORDER AND TIME FRAME FOR DEVELOPMENT OF A SOLVENT EXTRACTION RESPONSE TECHNIQUE

(◆ = major decision point)



7.2.2. Specific Recommendations

Step 1 - Laboratory Tests

Objectives: To determine the degree of efficiency and practicality that can be expected with a solvent extraction system and to compare this with what can be expected from a carbon adsorption system.

Discussion: The investigations should include the following:

1. A review of the extensive data base of Leo and co-workers* to obtain vegetable oil/water, oleyl alcohol/water, and (possibly) octanol/water partition coefficients for those chemicals for which data were not available in the data source used in this program.

2. Data relating to the ternary (solvent/solute/water) equilibrium diagrams for selected hazardous chemicals should be obtained (from the literature, if possible).

3. Laboratory tests with the chosen solvent-- on selected hazardous chemicals-- should be carried out to determine:

- the likely efficiency of extraction from water in a centrifugal extractor;
- the effectiveness of countercurrent flow extractors vs. those where fresh solvent is used in each stage;
- the optimum solvent-to-spill ratio;
- the effects of temperature and suspended solids on the extraction;
- the effects of some chemicals interfering with the extraction of others;
- the extent of solvent losses into the water;
- the best method for solvent recovery;
- the efficiency of solute removal from the solvent;
- the stability of the solvent; and,
- other tests, as necessary.

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*Professor Albert J. Leo and co-workers at Pomona College (Claremont, California) have a continuing project to collect and tabulate partition coefficient data. At present, their data base contains over 11,500 such values in 83 solvent systems with octanol/water predominating. The data base is available at a reasonable cost in the form of hard copy, microfiche or magnetic tape.

4. The overall perceived practicality, efficiency and cost of solvent extraction should then be compared with carbon adsorption. (Some additional research on carbon adsorption may also be needed at this point.) A final decision can then be made concerning additional work on solvent extraction.

Funding: Estimated at 2 man years

Anticipated Difficulties: No major difficulties anticipated.

Step 2 - Construction of a Test System

Objective: To construct a bench (or small pilot) scale test system to be used for tests of solvent extraction as a response technique.

Discussion: Design to be based on results of Step 1 and considerations of the probable features of a full-scale system. A treatment capacity of about one gal/min would probably be sufficient. The Podbielniak Model A-1 centrifugal extractor (max. capacity of 3 gal/min) would be acceptable for this unit.

Funding: Estimated at 0.5 man years (Equipment cost ≃ $25,000)

Anticipated Difficulties: None

Step 3 - Pilot Tests

Objective: To (1) test the solvent extraction response technique, (2) identify problems with equipment, materials and procedures, and (3) make recommendations concerning a full-scale system.

Discussion: Pilot test should be conducted with several representative hazardous chemicals at various concentrations. Actual spill treatment is not necessary. The tests should be sufficient to (1) demonstrate that the system is practical (or can be made so); (2) identify problems to be addressed in the construction and operation of a full-scale system; and, (3) quantify the expected treatment efficiency.

Funding: Estimated at 1.5 man years

Anticipated Difficulties: None

Step 4 - Construction and Testing of a Full-Scale System

Objective: To construct and test a solvent extraction system capable of handling major spills of soluble organic chemicals.

Discussion: The output from this task will be (1) a (mobile) full-scale solvent extraction unit; (2) an operation and maintenance manual; and, (3) training material (reports, films, slides) for potential response teams. When possible, USCG/EPA spill response personnel should be invited to participate in the testing of this equipment.

The details of the design will be formulated after the results of the pilot tests in Step 3 have been assessed. The sizing of the main unit will have to be coordinated with the capabilities of available transport services.

Testing of the system may take place with actual or simulated spills. The design of the final system will determine to some degree the nature of spills that may be treated (e.g., confined versus unconfined, high concentration versus low concentration, etc.). When pertinent, modeling may also be used to assist in such tests and actual use.

Funding: Estimated at 2-3 man years (plus equipment)

Anticipated Difficulties: No major difficulties anticipated.

7.3. PRECIPITATION

7.3.1. Introduction

There is little doubt that precipitation can be developed into a spill response technique that is both effective and environmentally safe, but further research and development involving both laboratory and field tests is necessary.

The following questions related to the need for this technique should be answered first.

- The need for development of precipitation as a spill response technique

  This should include a consideration of the frequency of spills, the size of the spills, the response times that would have to be met for effective treatment, and the actual impact of an untreated spill (not known at present). There are some indications that the spill frequency is low, the quantities small, and thus the response time short. Impacts may not be major. Would development of a response capability be cost effective?

- <u>The implications of short response times</u>

  Short response times require the use of personnel near the spill site. The EPA has suggested that local firemen be trained to respond to certain spills and be supplied in advance with a precipitating agent. If the Coast Guard response teams cannot direct the spill response, is it necessary for the Coast Guard to develop a better spill response technique?

- <u>Competition with chelation as a spill response technique</u>

  Since precipitation and chelation are both being considered for (essentially) the same list of hazardous chemicals, a decision may be made indicating preferential development of these two response techniques. (Other techniques may also be competitors.)

- <u>Coordination with the EPA's R & D Efforts</u>

  Since the EPA has conducted some investigations[39] with regard to developing precipitation as a response technique, coordination of further efforts is clearly desirable.

If, after considering the above, it is considered desirable to develop precipitation as a spill response technique, then we recommend that a five-step research and development program be carried out. The steps include:

1. Laboratory tests
2. Spill modeling
3. Construction of a small test system
4. Field tests
5. Development of final recommendations for spill response. Training of response personnel.

The general order and time frame for these steps are shown schematically in Figure 7.3-1.

The recommended order of priority for the development of a response technique with different reagents is as follows (highest priority first):

1. Precipitation with Na_2HPO_4

   For Cd, Cu, Fe, Ni, Zn and Sb compounds
2. Precipitation with $FeCl_3$

   For sodium ferrocyanide
3. Precipitation with NaCl

   For silver nitrate
4. Precipitation with $FeSO_4$

   For chromic anhydride.
5. Precipitation with Na_2SO_3

   For potassium permanganate
   For potassium dichromate.

This order of priority was thought appropriate after a consideration of (1) the number of hazardous chemicals that could be treated with each reagent, (2) the risk involved in a spill of each hazardous chemical, and (3) the relative degree of confidence that a viable response technique could be developed.

The possibility of treating other water soluble (and commercially important) compounds that precipitate the same toxic cation or anion may be included.

Detailed information on the recommended research and development steps are given below.

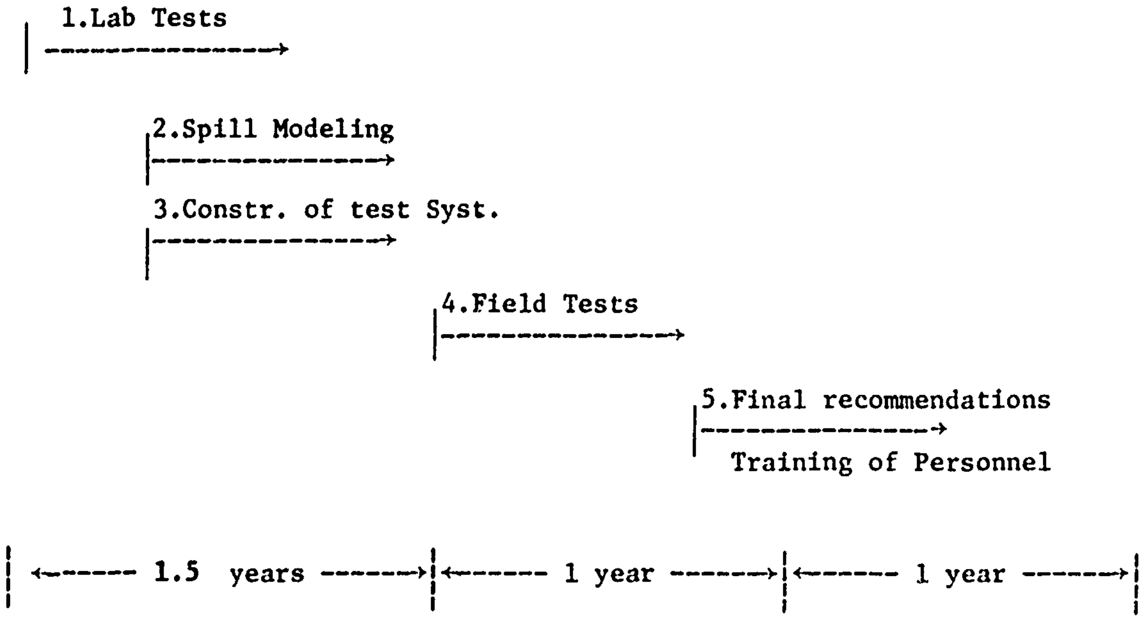
7.3.2. Specific Recommendations

Step 1 - Laboratory Tests

Objectives: To (1) obtain accurate data on the quantities of reagent needed in natural waters; (2) investigate the influence of such factors as mixing and suspended solids; (3) investigate precipitate settling rates, resulting pH and other factors; and, (4) to recommend spill indicators.

FIGURE 7.3-1

ORDER AND TIME FRAME FOR DEVELOPMENT OF A PRECIPITATION RESPONSE TECHNIQUE



Discussion: While theoretical calculations are capable of giving values for the amounts of reagent needed in pure water, it is desirable to obtain somewhat more practical information relating to the quantities required in a range of natural waters. There are numerous parameters which may have some influence on the quantity needed: natural levels of metals in the water, suspended particles and sediments, mixing rate, pH, concentrations of natural precipitants (carbonates, phosphates, sulfides), spill concentration at time of treatment, method of reagent addition, ionic strength, etc. The effect of all these parameters need not be investigated in detail; one option would be to simulate (e.g., in a fish tank) a variety of surface waters and conduct the experiments in these "typical" waters. A second option would be to design a statistical (factorial) experiment to determine the effect of varying each major parameter. These experiments should yield more accurate reagent-to-spill ratios, indicate the limitations of the technique, and the most favorable (or desirable) treatment methods.

Treatment efficiencies, settling characteristics and pH (at a minimum) should be monitored in these tests. The possible use of flocculating agents to aid the settling process could be investigated.

The "no treatment" recommendation for $TiC\ell_4$ should be verified by determining the reaction products following a spill into water.

Recommendations should be made concerning the most appropriate spill and spill-treatment indicators that can be used. Both instrumental and chemical indicators should be considered. Instruments that may be useful would include portable conductivity meters, pH meters and other more specific analytical instruments. Chemicals that may be useful are pH indicators or a precipitating reagent, which may be the recommended reagent for the treatment. These indicators would be used to help locate a spill, estimate its concentration, and monitor the course of treatment.

Funding: Estimated at 1.5 man years

Anticipated Difficulties: None

Step 2 - Spill Modeling

Objectives: To develop the capacity in the CHRIS system for accurate modeling of spills of the subject chemicals and their subsequent precipitation.

Discussion: A clear need exists for a model which can be used for spills and their subsequent treatment by precipitation. A computer model, for incorporation into CHRIS, should be prepared to allow calculations of (1) the concentrations following a spill of known size into a given waterbody, (2) the amounts of reagent needed for different chemicals and response times, and (3) the area, or distance, affected at given times following a spill.

The work here should give specific consideration to the chemical and physical interactions of chemical species both before and after treatment. Specifically, interactions with natural levels of dissolved, suspended and sedimented chemicals must be included. The results of Step 1, will be required here before this portion can be completed.

The final output should not only include the program (and training manual), but several sample calculations on various chemicals and water body types to serve as an instructional tool for others who will use the model.

Funding: Estimated at 1.0 man years

Anticipated Difficulties: The incorporation of realistic chemical rate and equilibrium data (relating to natural precipitation, chelation, cation exchange as well as other processes) may be difficult. The current state of development of modeling for such interactions is not known though some work is ongoing (e.g., at Oak Ridge and Sandia Labs) and a survey of such work would be advisable.

Step 3 - Construction of a Small Test System

Objective: To construct a reagent deployment system which can be used for field tests of precipitation as a response technique.

Discussion: A small scale, mobile deployment system should be designed and constructed. The size of the system may be close to full size if most spills of the subject chemicals are small in quantity. A delivery capacity of 500 lbs (of reagent) would seem quite adequate.

It seems likely that the test system recommended for neutralization can be used here with little or no modification.

Funding: Estimated at 1 man year (plus equipment); none if system constructed for neutralization tests is available.

Anticipated Difficulties: None

Step 4 - Field Tests

Objectives: To (1) test the precipitation response technique; and (2) identify problems with logistics.

Discussion: Tests (in small rivers or streams) should be carried out for a limited number of simulated and/or actual spills; they should be carried out in conjunction with input from the model developed in Step 2. The tests should be sufficient to (1) demonstrate that the system is practical (or can be made so); (2) identify problems to be addressed in the treatment of actual spills; and (3) assess the probable treatment efficiency.

Monitoring of any actual spill will be required; documentation (e.g., films and slides) would be desirable.

Funding: Estimated at 2 man years (plus equipment).

Anticipated Difficulties: No major difficulties anticipated. Actual spill will require permits from state and/or federal authorities.

Step 5 - Development of Final Recommendations for Spill Response and Training of Personnel

Objective: To develop a final set of recommendations with respect to the use of precipitation as a spill response technique and to train response personnel as required.

Discussion: It is not clear at this time whether or not sophisticated deployment devices will be required (since most spills may be small and require short response times); thus no "full scale" hardware development can be recommended. More likely deployment will require only simple equipment and thus the emphasis here is on detailed recommendations and training.

Funding: Uncertain; if just USCG response teams are to be trained cost will be low; if a large number of personnel is to be trained (e.g., local firemen as suggested by the EPA) then there would be a significant cost.

Anticipated Difficulties: Training local personnel (e.g., firemen) to respond to certain spills can be expected to involve problems relating to (1) poor understanding of the problems associated with a spill and the required response, (2) legal responsibilities, (3) frequent need for retraining.

7.4. CHELATION

7.4.1. Introduction

The information presently available is insufficient to assess the possibility of developing an in situ spill-response technique based on chelation that is both effective and environmentally safe. The use of a chelate in a closed-loop solvent extraction system would be environmentally safe but there are substantial questions relating to effectiveness.

In addition the following questions should be addressed prior to any research program:

- The need for development of chelation as a spill response;
- The implications of short response times; and
- Competition with precipitation as a spill response technique.

If it is desirable to develop further chelation as a spill response technique, then we recommend that a four-step research and development program be carried out. The steps include:

1. System selection and laboratory tests;
2. Construction of a small test system;
3. Pilot tests with system; and
4. Construction and testing of a full-scale system.

(Steps 2-4 only if chelation is found to be practical.)

The general order and time frame for the steps are shown schematically in Figure 7.4-1.

The recommended order of priority for R & D for different methods of chelation is as follows (highest priority first):

1. Chelation in closed-loop solvent extraction system;
2. Sequestering with the EDTA chelate; and
3. Precipitation with the oxine chelate.

This order is based primarily on environmental considerations; items 2 and 3 above involve the possibility of adverse environmental impact as a result of treatment, and this fact, along with a consideration of the extensive and costly testing that would be required to establish reliable, safe limits (toxicity thresholds)-- puts them substantially below 1 on the priority list. Consequently no specific recommendations are given for methods 2 and 3.

There is no need for any special order of priority amongst the list of chemicals subject to chelation. The metal cations formed by these chemicals are Ag^+, Ni^{++}, Cd^{++}, Zn^{++}, Cu^{++}, Fe^{++}, Ti^{+4} (no treatment recommended), and Sb^{3+}. Nevertheless, the work should also include chemicals with Cr, Hg, Pb (and other toxic metal cations).

No spill modeling is recommended. Should the solvent/chelate technique be developed the models developed for solvent extraction can be modified for use here.

Detailed information on the recommended research and development steps are given below.

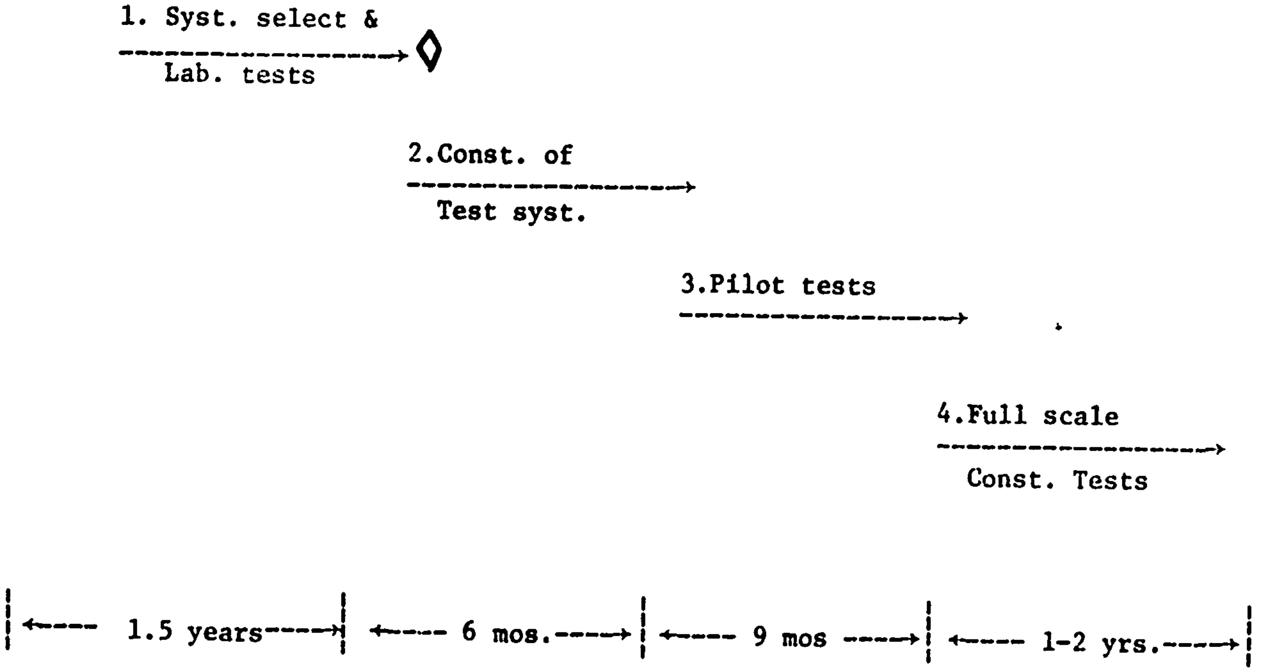
7.4.2. Specific Recommendations

Step 1 - System Selection and Laboratory Tests

Objectives: To select a solvent/chelate system (presumably using oxine) and to determine the degree of efficiency and practicality that can be expected with a solvent/chelate extraction system. Compare results with precipitation.

FIGURE 7.4-1

ORDER AND TIME FRAME FOR DEVELOPMENT OF A CHELATION RESPONSE TECHNIQUE
(◇ = major decision point)



Discussion: A solvent must be found that can be used with the recommended chelate (oxine). Vegetable oils (as recommended for the solvent extraction of organics) should certainly be investigated since the environmental impact of losses of small amounts from the extraction system would be negligible. If they are not practical then other solvents should be considered.

Data relating to the full ternary equilibrium diagrams for a few selected hazardous chemicals should be obtained (from the literature, if possible).

Laboratory tests with the chosen solvent/chelate-- on a few selected hazardous chemicals-- should be carried out to determine:

- the likely efficiency of extraction from water and the number of extraction stages required;
- the optimum solvent/chelate-to-spill ratio;
- the effects of temperature, suspended solids, pH, and natural levels of other cations (e.g., Ca^{++}, Mg^{++}) on the extraction;
- the extent of solvent losses into water;
- the best method for solvent recovery (i.e., removal of the chelated metals from the solvent);
- the stability of the solvent; and
- other tests as necessary

The overall perceived practicality, efficiency, cost and required response time of a chelation response technique should then be assessed and compared with the precipitation response technique. A final decision must then be made as to the desirability of additional work on the solvent/chelate system.

Funding: Estimated at 2 man years.

Anticipated Difficulties: None. Similar processes have been commercialized for use in water pollution control and metal recovery.

Step 2 - Construction of a Test System

Objective: To construct a bench (or small pilot) scale test system to be used for tests of the solvent/chelate system as a response technique.

Discussion: Design will be based on the results of Step 1 and considerations of the probable features of a full-scale system. The possibility of using the same test system as that for the solvent extraction of organics (see Section 7.2.2) should not be overlooked. A treatment capacity of about one gal/min would probably be sufficient.

Funding: Estimated at 0.5 man years; less if a system developed for solvent extraction of organics is suitable.

Anticipated Difficulties: None

Step 3 - Pilot Tests

Objectives: To (1) test the solvent/chelation response technique, (2) identify problems with equipment, materials and procedures, and (3) make recommendations concerning a full-scale system.

Discussion: Pilot tests should be conducted with a few representative hazardous chemicals at various concentrations. The tests should be sufficient to (1) demonstrate that the system is practical; (2) identify problems to be addressed in the construction and operation of a full-scale system; and (3) quantify the expected treatment efficiency.

Funding: Estimated at 1.5 man years

Anticipated Difficulties: None

Step 4 - Construction and Testing of a Full-Scale System

Objective: To construct and test a solvent/chelation system capable of handling large spills of the subject hazardous [illegible]

Discussion: The output from this step will be (1) a full-scale extraction/chelation unit (mobile); (2) an operation and maintenance manual; and (3) training material (reports, films, slides) for potential response teams. When possible USCG/EPA spill response personnel should be invited to participate in the testing of this equipment.

The details of the design will have to be formulated after the results of the pilot tests in Step 3 have been assessed. The sizing of the main unit will have to be coordinated with the capabilities of available transport services.

Testing of the system may take place with actual or simulated spills. When pertinent, modeling may also be used to assist in such tests.

Funding: Estimated at 2-3 man years (plus equipment)

Anticipated Difficulties: No major difficulties anticipated.

APPENDIX A: LIST OF CHEMICALS CONSIDERED

A.1 Chemicals Subject to Neutralization

CHEMICALS

1. Acetic acid
2. Acetic anhydride
3. Acetophenone
4. Acrylic acid
5. Aluminum chloride
6. Aminoethanolamine
7. Ammonium hydroxide
8. Anhydrous Ammonia
9. Aniline
10. Benzoyl chloride
11. Bromine
12. Caustic potash solution
13. Caustic soda solution
14. Chlorosulfonic acid
15. Cyclohexylamine
16. Diethanolamine
17. Diethylamine
18. Diethylenetriamine
19. Diisopropanolamine
20. Dimethylformamide
21. 1,1 - Dimethylhydrazine
22. Ethyleneimine
23. Ethylenediamine
24. Formic acid
25. Hexamethylenediamine
26. Hexamethylenetetramine
27. Hydrazine
28. Hydrochloric acid
29. Hydrofluoric acid
30. Hydrogen chloride
31. Hydrogen cyanide
32. Hydrogen fluoride
33. Lithium aluminum hydride
34. Maleic anhydride
35. Methylethylpyridine
36. Monoethanolamine
37. Monoisopropanolamine
38. Morpholine
39. Nitrogen tetroxide
40. Nitric acid
41. Nitrosylchloride
42. Oleum
43. Oxalic acid
44. Phosphoric acid
45. Phosphorour oxychloride
46. Phosphorous pentasulfide
47. Phosphorous trichloride
48. Polyphosphoric acid
49. Potassium hydroxide
50. Propionic acid
51. Pyridine
52. Sodium
53. Sodium amide
54. Sodium hydride
55. Sodium hydroxide
56. Sulfur monochloride
57. Sulfuric acid
58. Sulfuric acid (spent)
59. Sulfuryl chloride
60. Titanium tetrachloride
61. Triethanolamine
62. Triethylamine
63. Triethylenetetramine
64. Trimethylamine
65. Urea

A.2 Chemicals Subject to Solvent Extraction

CHEMICALS

1. Acetone cyanohydrin
2. Allyl alcohol
3. Aminoethanolamine
4. n-Amyl alcohol
5. 1,4-Butanediol
6. 1,4-Butenediol
7. n-Butyl acetate
8. n-Butyl alcohol
9. sec-Butyl alcohol
10. tert-Butyl alcohol
11. 1,4-Butynediol
12. Carbon bisulfide
13. Chloroform
14. Chlorohydrins (crude)
15. Corn syrup
16. Dextrose solution
17. Diacetone alcohol
18. Dichloromethane
19. Diethanolamine
20. Diethylene glycol
21. Diethylene glycol dimethyl ether
22. Diethylene glycol monoethyl ether
23. Diethylene glycol monomethyl ether
24. Diisopropanolamine
25. Dimethyl sulfate
26. Dimethyl sulfoxide
27. 1,4-Dioxane
28. Dipropylene glycol
29. Epichlorohydrin
30. Ethoxytriglycol
31. Ethoxylated dodecanol
32. Ethoxylated pentadecanol
33. Ethoxylated tetradecanol
34. Ethoxylated tridecanol
35. Ethyl acetate
36. Ethyl acrylate
37. Ethyl alcohol
38. Ethylene cyanohydrin
39. Ethylene glycol
40. Ethylene glycol monobutyl ether
41. Ethylene glycol monoethyl ether
42. Ethylene glycol monomethyl ether acetate
43. Ethylene glycol monomethyl ether
44. Ethyleneimine
45. Formaldehyde solution
46. Glycerine
47. Hexylene glycol
48. Isoamyl alcohol
49. Isobutyl alcohol
50. Isopropyl acetate
51. Isopropyl alcohol
52. Methanearsonic acid, sodium salts
53. Methyl acrylate
54. Methyl alcohol
55. Methyl amyl alcohol
56. Methyl isobutyl carbinol
57. Methyl methacrylate
58. Monoethanolamine
59. Monoisopropanolamine
60. Morpholine
61. Paraformaldehyde
62. Polypropylene glycol methyl ether
63. n-Propyl acetate
64. n-Propyl alcohol
65. Propylene glycol
66. Propylene glycol methyl ether
67. Propylene oxide
68. Sodium alkyl
69. Sodium alkyl sulfates
70. Sorbitol
71. Sulfolane
72. Tetrahydrofuran
73. Triethanolamine
74. Triethylene glycol
75. Vinyl acetate

A.3 Chemicals Subject to Precipitation and/or Chelation

CHEMICALS

1. Antimony trifluoride
2. Cadmium chloride
3. Chromic anhydride
4. Copper sulfate
5. Ferrous sulfate
6. Latex, liquid synthetic
7. Nickel sulfate
8. Potassium dichromate
9. Potassium permanganate
10. Silver nitrate
11. Sodium ferrocyanide
12. Titanium tetrachloride
13. Zinc Chloride

APPENDIX B: NEUTRALIZATION STUDIES

B.1 Neutralization of Acids with Sodium Bicarbonate

In order to check and confirm the findings associated with our choice of sodium bicarbonate as a good neutralizing agent for acid spills, and to investigate potential problems associated with carbon dioxide evolution, the following laboratory tests were carried out.

B.1.1 Properties of the Sodium Bicarbonate Solution

A 1.0 molar solution of $NaHCO_3$ cannot be made (at room temperature) as this is just above the ultimate solubility. Thus all subsequent work was done with a 0.7$\underline{M}$ solution of $NaHCO_3$. The pH and specific gravity of such a solution were measured and found to be:

pH (0.7$\underline{M}$ soln.) = 7.95→7.98 (a drift upwards in time was noticed)

Specific gravity (0.7$\underline{M}$ soln.) = 1.038 (22°C)

B.1.2 Titration of 0.1M Hydrochloric Acid

Three different titrations of 50 ml samples of 0.1$\underline{M}$ HCl were carried out with the 0.7$\underline{M}$ $NaHCO_3$ solution. The titrations were carried out in an open stirred beaker using an Orion Model 801A digital analyzer, and a Sargeant automatic (i.e., constant rate) titrator.

The evolution of bubbles (carbon dioxide) did take place in all titrations and was first seen about one to two minutes after the start of the titration. (The rate of titration was generally 1 ml/min.) The rate of bubble formation was not high (up to a few bubbles/second), but a monolayer of bubbles did exist on most surface areas at the end of the titration.

One titration curve is shown in Figure B.1-1. In this case the titration was stopped when pH 6 was reached. In the second titration, the addition of sodium bicarbonate was stopped at pH 5. In the third titration, an initial slug of 5ml of the bicarbonate solution was added from a pipette followed by a continuing of the titration at the rate of 1 ml/min. until pH 7 was reached.

After each titration was stopped, the pH in the open beaker was monitored. The pH continued to slowly rise in each case, and in the "worst" case (the titration to pH 7) reached a pH of 8.35 after standing overnight. The pertinent facts from these three titrations are summarized in Table B.1-1 below.

FIGURE B.1-1

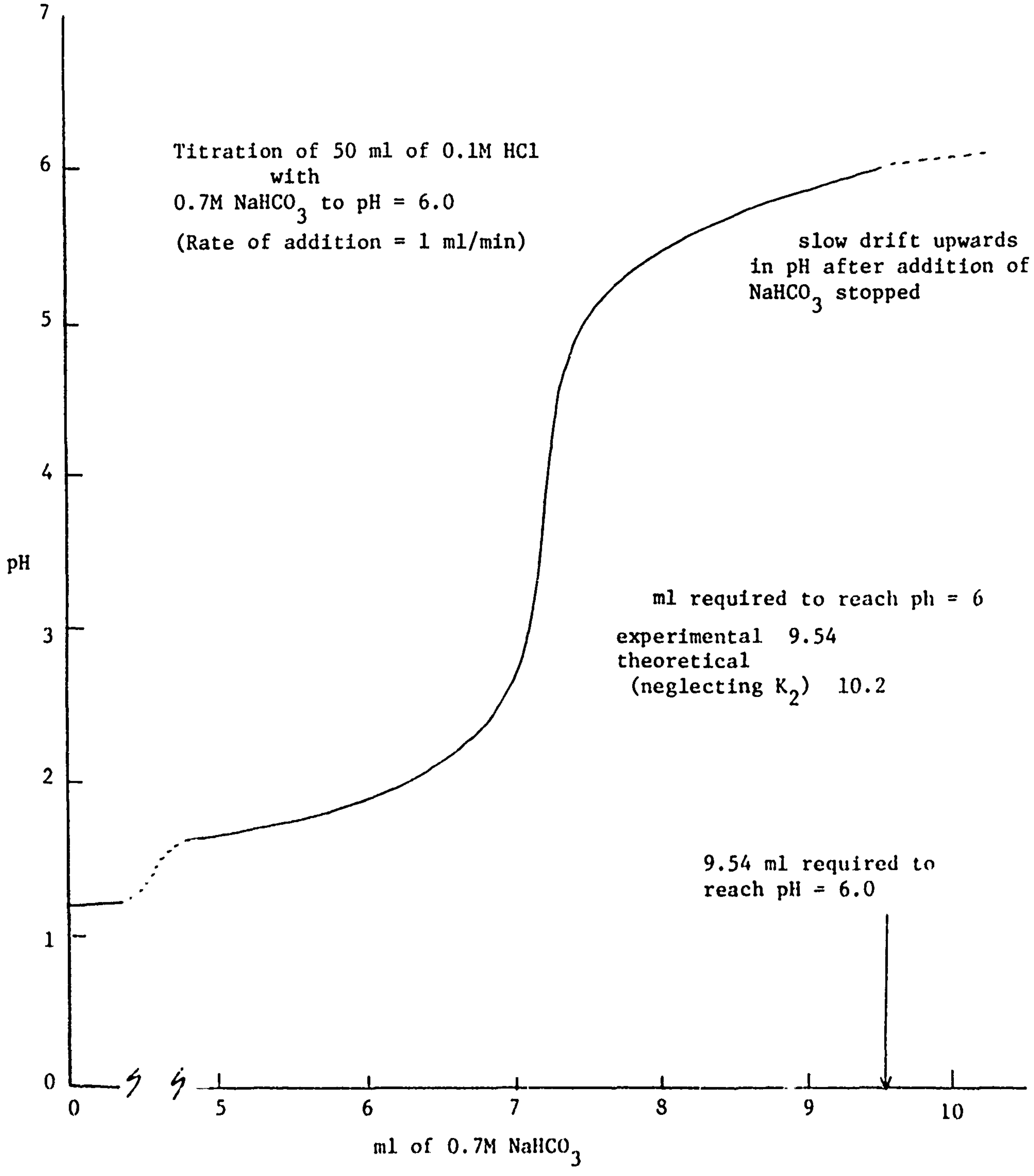

Titration of 50 ml of 0.1M HCl
with
0.7M NaHCO$_3$ to pH = 6.0
(Rate of addition = 1 ml/min)
slow drift upwards in pH after addition of NaHCO$_3$ stopped
ml required to reach ph = 6
experimental 9.54
theoretical (neglecting K$_2$) 10.2
9.54 ml required to reach pH = 6.0
pH
7
6
5
4
3
2
1
0
0
5
6
7
8
9
10
ml of 0.7M NaHCO$_3$

TABLE B.1-1

TITRATION OF 0.1M HCl (50ml) WITH 0.7M $NaHCO_3$

Titration to pH	Rate of Addition	Amount of Solution to Reach Specified pH	pH Drift After: 10 min.	pH Drift After: Overnight
5	1ml/min.	7.53ml	5.31	7.09
6	1ml/min.	9.54ml	6.23	8.14
7	5ml slug, then 1ml/min.	22.3ml	7.10	8.35

The amount of bicarbonate solution that one would expect to be required on a theoretical basis may be approximately calculated. If the effect of the second dissociation ($HCO_3^- \rightleftarrows H^+ + CO_3^=$) is neglected, as is reasonable since K_2 (5.6×10^{-11}) is much less than K_1 (4.3×10^{-7}), then the following equation may be used:

$$H^3 + H^2\,[(b-a) + K_1] - H\,(aK_1 + K_w) - K_1K_w = 0 \qquad \text{B.1-2}$$

where:

H = hydrogen ion concentration B.1-3

a = acid concentration (moles/l)

b = base concentration (moles/l)

$K_1 = 4.3 \times 10^{-7}$

$K_w = 10^{-14}$

Using this equation, the amount of bicarbonate solution required to reach pH 6 is calculated as 10.2ml. This is only slightly greater than the experimental value of 9.54ml given in Table B.1-1. The calculated value exceeds the experimental value because K_2 was neglected in the calculations.

B.2 Neutralization of Bases with Sodium Dihydrogen Phosphate

For reasons similar to those given above, a titration with sodium dihydrogen phosphate was carried out. In this case, there is no carbon dioxide evolution to complicate the analysis.

B.2.1 Properties of the Sodium Dihydrogen Phosphate Solution

A 1.0M NaH_2PO_4 solution was made up and found to have the following properties:

pH (1.0M soln.) = 4.07 B.2-1

Specific gravity (1.0M soln.) = 1.078 (25°C)

We had expected a pH of 4.5 from our calculations (see Table 2.4-5).

B.2.2 Titration of a 0.1M Sodium Hyroxide Solution

A 0.1M NaOH solution (50 ml) was titrated with the 1.0M NaH_2PO_4 solution in the same manner described above for the sodium bicarbonate titrations. In this case, the titration was continued well past the "safe" pH of 9 in order to determine the shape of the curve. The results are shown in Figure B.2-1. It required 5.05 ml of solution to reach pH 9.

This titration should yield the same results as the example in Table 2.4-4, where calculations are given for the titration of 0.1M KOH with 1.0M NaH_2PO_4. From that example we can calculate the amount of NaH_2PO_4 solution that should have theoretically been required to reach pH 9 in our laboratory experiment. The amount is 50 ml x ($.102M^3/1M^3$) or 5.10 ml, which is quite close to the actual value of 5.05 ml.

B.3 Relative Rates of Neutralization for Sodium Bicarbonate and Calcium Carbonate

The purpose of these experiments was to see if, as expected, the rate of neutralization of acids was higher with sodium bicarbonate than with limestone (calcium carbonate).

Two 50 ml portions of 0.1 M HCl and two of 0.1 M H_2SO_4 were prepared. To one 0.1 M HCl portion was added, all at once, 0.300 g of dry powdered $CaCO_3$*; to the other portion was added 0.5605 g of dry powdered $NaHCO_3$**. The two 0.1 M H_2SO_4 portions received, respectively, 0.600 g of dry powdered $CaCO_3$ and 1.121 g of dry powdered $NaHCO_3$. These quantities were calculated to allow the pH to eventually reach 6.0.

The pH of each solution was monitored versus time with an Orion 801A Digital Analyzer. The solutions were stirred at a constant rate.

The times required to reach a specified pH for each neutralization are given in Table B.3-1 and Table B.3-2 below:

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* Mallinckrodt, Analytical Grade

** Fisher, certified ACS

FIGURE B.2-1

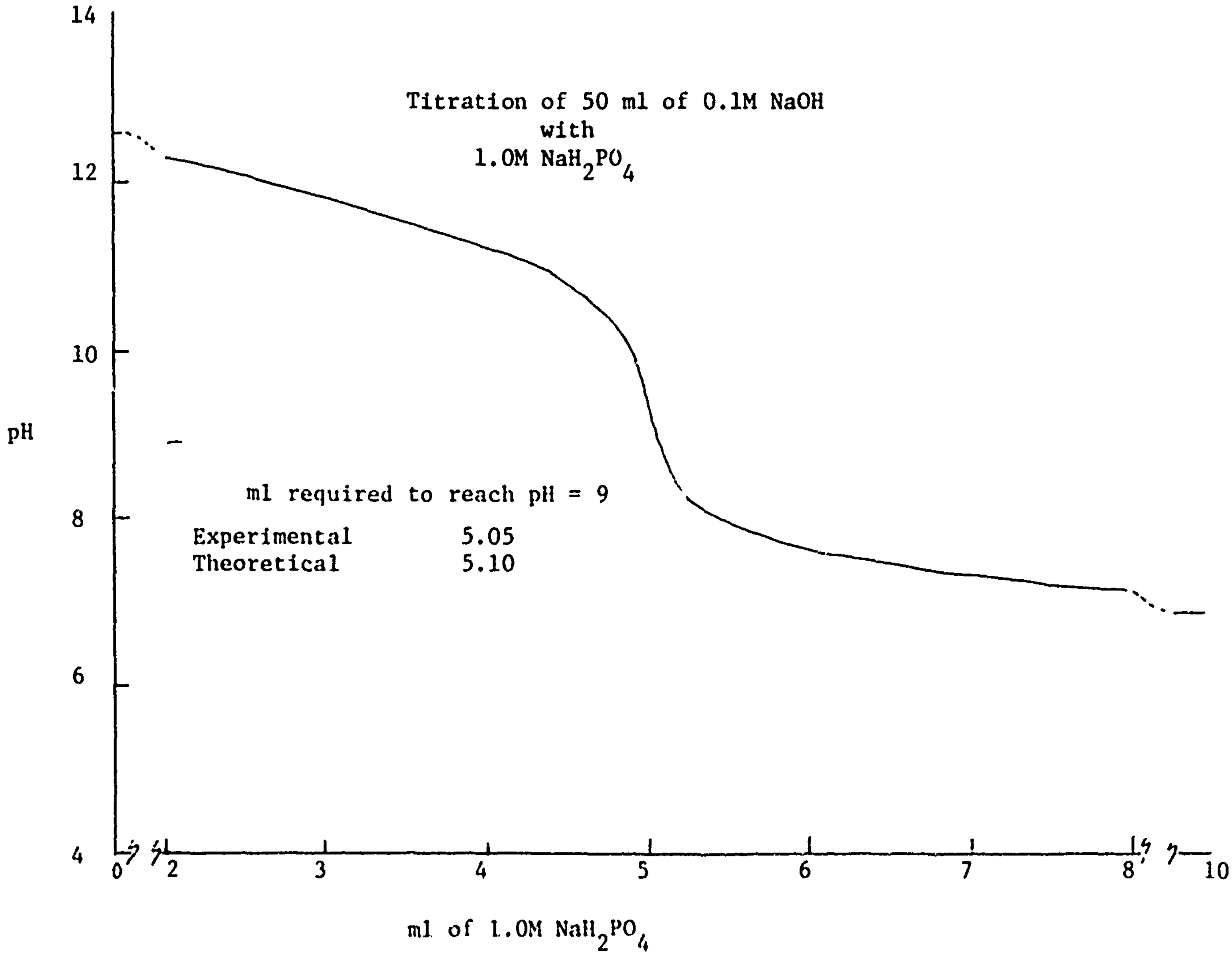
Titration of 50 ml of 0.1M NaOH
with
1.0M NaH_2PO_4
ml required to reach pH = 9
Experimental 5.05
Theoretical 5.10
pH
14
12
10
8
6
4
0
2
3
4
5
6
7
8
10
ml of 1.0M NaH_2PO_4

TABLE B.3-1

NEUTRALIZATION OF 50 ml of 0.1 M HCl

	Time Required (min.) to Reach pH after Addition of:	
pH	$CaCO_3$ (0.300 g)	$NaHCO_3$ (0.5605 g)
1.02	0 min	0 min.
2	.17	.03-
3	.30	.03+
4	.48	.04-
5	3.55	.04+
6	21.1	.35
6.12	24.	-
6.38	-	6.6

TABLE B.3-2

NEUTRALIZATION OF 50 ml of 0.1 M H_2SO_4

	Time Required (min.) to Reach pH after Addition of:	
pH	$CaCO_3$ (0.600 g)	$NaHCO_3$ (1.12[illegible] g)
.96	0 min.	0 min.
2	.1	.01
3	.23	.04-
4	.38	.04
5	2.3	.04+
5.5	10.	-
5.8	20.	-
6.0	-	.06
6.6	-	10.

The data show that sodium bicarbonate allows a more rapid neutralization of HCl and H_2SO_4 than calcium carbonate, if both are added in equivalent stoichiometric amounts. (This assumes there were no significant differences due to particle size in the powders used; the particle sizes for the powders used were not given by the manufacturer.)

The difference in time (on an absolute scale) required to reach pH 4 is not significant - 2 to 3 seconds for $NaHCO_3$ versus 23 to 29 seconds for $CaCO_3$ - but is significant for higher pH values. For example, to reach pH 5.5 takes 3 to 4 seconds with $NaHCO_3$ versus 10 to 12 minutes with $CaCO_3$.

A recent paper by Carton and Vatanatham on the kinetics of limestone neutralization of acid waters concludes that "the rate of neutralization of sulfuric acid by limestone particles is...controlled by hydrogen diffusion in the pH range of 2-6". No evidence was found that would substantiate a concern relating to possible coating of the limestone surface with flocculant metal precipitates. Their experiments were carried out (1) with somewhat weaker sulfuric acid solutions (initial pH ∿2); (2) with larger particle sizes; and, (3) with an amount of limestone that was twice the stoichiometric amount needed to balance the acidity (resulting in an eventual pH of about 7.9). They investigated, in part, (1) the effect of particle size; (2) the effect of temperature; and, (3) the effect of the presence of metal ions on reaction times. Some data extracted from their studies of the effects of particle size and temperature are given in Table B.3-3 and Table B.3-4 below:

TABLE B.3-3

EFFECT OF LIMESTONE PARTICLE SIZE ON REACTION RATE

Particle Size (mm)	Time Required to Reach pH=6 (approximate)
.037 - .044	3.3 min.
.063 - .074	5.
.125 - .149	12.
.250 - .297	22.
.500 - .595	60.

TABLE B.3-4

EFFECT OF TEMPERATURE ON REACTION RATE

(particle sizes: .250 - .297 mm)

Temperature (°C)	Time Required to Reach pH=5 (approximate)
0.6	67 min.
25.2	25
50.2	17
74.6	12

B.4 Titration of 1.0 M NaH_2PO_4 with 0.1 M NaOH

The purpose of this experiment was to determine the amount of dilute caustic required to neutralize a concentrated NaH_2PO_4 solution.

20 ml of 1.0 M NaH_2PO_4 (initial pH of 4.10) were titrated with 0.1 M NaOH using a constant rate (1 ml/min.) titrator. The pH was monitored versus time with an Orion 801A Digital Analyzer.

TABLE B.4-1

NEUTRALIZATION OF 20 ml OF 1.0 M NaH_2PO_4

pH	Amount of 0.1 M NaOH Solution Required to Reach pH
5.0	9.7 ml
5.5	20.
5.95	40.

B.5 Estimated Amounts of Neutralizing Reagents Needed for Acid and Base Spills of Known Amounts

There are at least two ways to estimate, in advance, the approximate amount of reagent needed to neutralize a spill of an acid or base:

1. If the identity, amount, and purity of the spilled material are known, appropriate equations - in conjunction with some approximations - may be used to estimate the amount of reagent needed.
2. If the identity of the spilled material and resulting pH are known (but not necessarily the quantity spilled) then different equations - again with some approximations - may be used to estimate the amount of spilled material in a given volume; this is then followed by the use of the equations given for the first method.

This appendix presents, in Tables B.5-2 and B.5-3, sample calculations relating to the first method mentioned above.

The second method, mentioned above, can also be used in conjunction with these tables. Since the pH is known (presumably measured) and the dissociation constant is known*, the concentration (C) may be estimated by use of the appropriate equation in Table B.5-1. Once the concentration (C, moles/liter) has been estimated, the amount (A) of the acid or base present in the volume (V, liters) is obtained from:

$$A = C \cdot V \cdot MW \qquad \text{B.5-1}$$

where A is in kg, and MW is the molecular weight of the chemical in kg/mole.

Tables B.5-2 and B.5-3 give the estimated amounts (in kg) of reagent needed to neutralize a specific (known) amount of spilled material. If the material spilled is normally transported as a liquid, the spill amount chosen was 1,000 liters; if normally transported as a solid, the amount chosen was 1,000 kg. Since, for each material, the amount of reagent needed is directly proportional to the amount of material spilled, the tables may be used to find the estimated amount of reagent for spills greater or smaller than 1,000 liters (or kilograms). For example, a spill of 10,000 liters of a material would require 10 times the amount of reagent given for a 1,000 liter spill.

The total amount of reagent needed is essentially independent of the concentration of the spilled material in the pH ranges we are concerned with, 0-5 for acid spills and 10-14 for base spills. Thus, if the total volume affected by the spill is to be treated, the total amount of reagent needed is the same for a given spill amount, no matter how large or small the affected volume is. At the spill site, however, the reagent should be added in amounts that are proportional to the local spill concentration which may vary considerably throughout the volume affected. In an actual spill, with time, treatment quantities will decrease as some material will be diluted by dispersion and not require chemical amelioration. The use of pH meters or indicators can be of some assistance here.

The specific scenarios for which calculations were carried out included:

B.5.1 Neutralization of Acids with Sodium Bicarbonate

The amount needed to return the pH to 6 was first estimated and then an additional 20% added.

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* e.g., from Tables 2.2-8 and 2.2-9.

Table B.5-1

ESTIMATION OF ACID OR BASE CONCENTRATION AFTER SPILL INTO WATER, GIVEN IDENTITY OF CHEMICAL AND pH

Note: $[H^+]$ = hydrogen ion concentration = $10^{(-pH)}$

C = concentration of acid or base (moles/liter)

K = acid or base dissociation constant

1. For strong acids (monobasic); e.g., HCl, HNO_3

$C \approx [H^+]$ (for $Ka > 10^{-4}$) (1)

2. For strong bases (monoacid); e.g., KOH, $NaOH$

$C \approx 10^{-14}/[H^+]$ (for $Kb > 10^{-4}$) (2)

3. For weak acids (monobasic); e.g., acetic acid

$C \approx [H^+]^2/Ka$ (for $Ka \approx 10^{-5}$ to 10^{-8}) (3)

4. For weak bases (monoacid); e.g., ammonium hydroxide

$C \approx \dfrac{10^{-28}}{Kb \cdot [H^+]^2}$ (for $Kb \approx 10^{-5}$ to 10^{-8}) (4)

5. For dibasic acids, strong in K_1 and K_2; e.g., sulfuric acid

$C \approx [H^+]/2$ (5)

6. For dibasic acids, strong in K_1 only; e.g., maleic acid

$C \approx [H^+]$ ($K_2 < \sim 10^{-5}$) (6)

7. For dibasic acids, weak in K_1 and K_2 ($K_1 > K_2$); e.g., glutaric acid

a.) If $K_1 > 10^{-7}$, $C \approx [H^+]^2/(K_1 + K_2)$ (7a)

b.) If $K_1 < 10^{-7}$, $C \approx ([H^+]^2 - 10^{-14})/(K_1 + K_2)$ (7b)

8. For tribasic acids, weak in K_3; e.g., phosphoric acid

Ignore K_3 and use equations #5, 6, 7a, or 7b, as appropriate.

9. For polyacid bases; e.g., diethylenetriamine

Use equations #5 - #8, as appropriate, but first replace $[H^+]$ with $\dfrac{10^{-14}}{[H^+]}$ in the equation.

Table B.5-2

ESTIMATED AMOUNTS OF SODIUM BICARBONATE NEEDED TO NEUTRALIZE ACID SPILLS

(Amount Needed = Amount to Reach pH=6 + Excess of 20%)

	SHIPPING INFORMATION		AMOUNT OF CHEMICAL SPILLED			
CHEMICAL	Physical State as Shipped	Assumed Concentration of Chemical	Liters of Liquid or Solution	kg of Pure Chemical	Estimated Amount of $NaHCO_3$ Needed for Neutralization (Amount to Reach pH 6 + 20%) kg	Notes
Acetic Acid	Liquid	100%	1,000	1,050	2,360	
Acetic Anhydride	Liquid	100%	1,000	1,080	1,440	
Acrylic Acid	Liquid	100%	1,000	1,050	2,060	
Aluminum Chloride	Solid	100%	---	1,000	3,240	
Benzoyl Chloride	Liquid	100%	1,000	1,210	2,460	
Bromine	Liquid	100%	1,000	3,120	5,640	1
Chlorosulfonic Acid	Liquid	100%	1,000	1,750	4,340	
Formic Acid	Liquid	100%	1,000	1,220	3,830	
Hydrochloric Acid	Liquid	35%	1,000	441	1,630	
Hydrofluoric Acid	Liquid	50%	1,000	599	4,330	
Hydrogen Chloride	Liquid*	100%	1,000	1,190	4,720	
Hydrogen Fluoride	Liquid*	100%	1,000	992	7,160	
Maleic Anhydride	Solid	100%	---	1,000	2,150	
Nitrogen Tetroxide	Liquid*	100%	1,000	1,450	2,280	
Nitric Acid	Liquid	100%	1,000	1,490	3,420	
Nitrosyl Chloride	Liquid*	100%	1,000	1,360	6,000	
Oleum	Liquid	100%	1,000	2,000	6,540	2
Oxalic Acid	Solid	100%	---	1,000	2,270	

---

*Liquefied compressed gas.

Table B.5-2

(continued)

CHEMICAL	SHIPPING INFORMATION: Physical State as Shipped	SHIPPING INFORMATION: Assumed Concentration of Chemical	AMOUNT OF CHEMICAL SPILLED: Liters of Liquid or Solution	AMOUNT OF CHEMICAL SPILLED: kg of Pure Chemical	Estimated Amount of $NaHCO_3$ Needed for Neutralization (Amount to Reach pH 6 ± 20%) kg	Notes
Phosphoric Acid	Liquid	80%	1,000	1,306	2,030	
Phosphorous Oxychloride	Liquid	100%	1,000	1,675	6,400	
Phosphorous Pentasulfide	Solid	100%	---	1,000	2,780	3
Phosphorous Trichloride	Liquid	100%	1,000	1,575	7,010	
Polyphosphoric Acid	Liquid	see note	1,000	2,360 (as H_3PO_4)	3,660	4
Propionic Acid	Liquid	100%	1,000	995	1,820	
Sulfur Monochloride	Liquid	100%	1,000	1,680	7,180	5
Sulfuric Acid	Liquid	98%	1,000	1,800	5,290	
Sulfuric Acid (spent)	Liquid	60%	1,000	899	2,640	
Sulfuryl Chloride	Liquid	100%	1,000	1,670	7,140	
Titanium Tetrachloride	Liquid	100%	1,000	1,726	2,630	6

---

1. All Bromine is assumed to be eventually converted to Bromic Acid ($HBrO_3$), a strong acid.
2. Free SO_3 content is assumed to be 50%. Normal range is 20% - 65%.
3. Only 1/5 of H_2S formed (in reaction with water) is assumed to remain in solution where it will contribute slightly to the acidity.
4. Assumes that concentration is equivalent to 115% Phosphoric Acid.
5. Assumes equivalent of 2 moles of HCl and 1 mole of H_2SO_4 formed in the reaction of 1 mole of S_2Cl_2 with water.
6. Assumes 2 moles of HCl formed in the reaction of 1 mole of $TiCl_4$ with water.

TABLE B.5-3

ESTIMATED AMOUNTS OF SODIUM DIHYDROGEN PHOSPHATE NEEDED TO NEUTRALIZE BASE SPILLS

(Amount Needed = Amount to Reach pH=9 + Excess of 20%)

CHEMICAL	SHIPPING INFORMATION		AMOUNT CHEMICAL SPILLED		Estimated Amount of NaH_2PO_4 Needed for Neutralization (Amount to Reach pH 9 + 20%)	Notes
	Physical State as Shipped	Assumed Concentration of Chemical	Liters of Liquid or Solution	kg of Pure Chemical	kg	
Aminoethanolamine	Liquid	100%	1,000	1,028	1,120	
Ammonium Hydroxide	Liquid	25% (as NH_3)	1,000	227 (as NH_3)	1,260	
Anhydrous Ammonia	Liquid*	100%	1,000	682	3,750	
Caustic Potash Solution	Liquid	50%	1,000	757	1,980	
Caustic Soda Solution	Liquid	60%	1,000	978	3,580	
Cyclohexylamine	Liquid	100%	1,000	865	1,270	
Diethanolamine	Solid	100%	---	1,000	630	
Diethylamine	Liquid	100%	1,000	708	1,420	
Diethylenetriamine	Liquid	100%	1,000	954	1,750	
Diisopropanolamine	Solid	100%	---	1,000	530	
1,1-Dimethylhydrazine	Liquid	100%	1,000	791	180 - 960	1
Ethyleneimine	Liquid	100%	1,000	832	2,160	
Ethylenediamine	Liquid	100%	1,000	909	2,020	
Hexamethylenediamine	Solid	100%	---	1,000	1,260	
Hydrazine	Liquid	50%	1,000	522	570	
Lithium Aluminum Hydride	Solid	100%	---	1,000	3,860	
Monoethanolamine	Liquid	100%	1,000	1,016	1,860	

---

*Liquefied compressed gas.

Table B.5-3

(continued)

CHEMICAL	SHIPPING INFORMATION		AMOUNT OF CHEMICAL SPILLED		Estimated Amount of NaH_2PO_4 Needed for Neutralization (Amount to Reach pH 9 + 20%)	Notes
	Physical State as Shipped	Assumed Concentration of Chemical	Liters of Liquid or Solution	kg of Pure Chemical	kg	
Monoisopropanolamine	Liquid	100%	1,000	961	1,480	
Morpholine	Liquid	100%	1,000	1,000	300	
Potassium Hydroxide	Solid	90%	---	900	2,350	
Sodium	Solid	100%	---	1,000	6,510	
Sodium Amide	Solid	100%	---	1,000	6,150	
Sodium Hydride	Solid	55%	---	550	3,260	
Sodium Hydroxide	Solid	100%	---	1,000	3,660	
Triethanolamine	Liquid	100%	1,000	1,130	80	
Triethylamine	Liquid	100%	1,000	729	1,040	
Triethylenetetramine	Liquid	100%	1,000	982	1,480	
Trimethylamine	Liquid*	100%	1,000	633	1,340	

---

*Liquefied compressed gas.

1. Range in estimated amount of NaH_2PO_4 needed for neutralization is due to uncertainty in the dissociation constant. The pKa is estimated to be in the range of 8-9.

For the neutralization of strong (monobasic) acids, the general equation relating the hydrogen ion concentration (H) to the concentrations of acid (a) and sodium bicarbonate (b) is:

$$H^3 + H^2 [(b-a) + K_1] - H(aK_1 + K_w) = 0 \qquad \text{B.5-2}$$

where a and b are in moles/liter, $K_1 = 4.3 \times 10^{-7}$ and $Kw = 10^{-14}$. This equation neglects the effect of the second dissociation constant of sodium bicarbonate ($K_2 = 5.6 \times 10^{-11}$). This is reasonable since K_2 is about 10,000 times less than K_1. Under the conditions of interest here, equation B.5-2 can be simplified to

$$b \approx a(K_1 + H)/H \qquad \text{B.5-3}$$

because several terms are negligible in relation to others. If we let X be the amount of the pure chemical spilled (in kg) and A the amount of sodium bicarbonate needed (in kg), then equation B.5-3 reduces to:

$$A \approx X \cdot 120/MW \qquad \text{(for pH 6)} \qquad \text{B.5-4}$$

where MW is the molecular weight of the acid (in g/mole).

In one laboratory experiment conducted in this program, the amount of sodium bicarbonate required to return the pH of solution containing a strong (monobasic) acid to 6 (excluding pH drift*) was 6.5% less than the amount calculated by the method described above; if pH drift is included for a small time period (10-15 minutes), then the actual amounts needed are probably about 10% less than the calculated amounts. This is not a significant error.

There are likely to be somewhat larger uncertainties associated with the estimated amounts of sodium bicarbonate needed to neutralize the weak acids since the appropriate equations are not given in any of the reference documents available to us. To estimate the amount needed, the equation relating to the neutralization of a weak acid with a strong (monoacid) base was used to calculate the relative amount needed for neutralization of the weak acid in comparison with a strong acid. For example, it might be calculated that neutralization of a given weak acid took only 50% as much reagent (strong base) as it did for a strong acid. The ratio (e.g., 50%) was then applied to the amount of sodium bicarbonate needed (per mole of acid) to neutralize a strong acid to obtain the amount needed for the weak acid. In actuality, the lowest ratio used was 94%, and, thus, the additional uncertainty due to the use of this method is not expected to be large.

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* The pH of the titrated solutions continued to drift up after the addition of sodium bicarbonate was stopped.

B.5.2 Neutralization of Bases with Sodium Dihydrogen Phosphate

The amount needed to return the pH to 9 was first estimated and then an additional 20% added.

For the neutralization of strong (monoacid) bases, the general equation relating the hydrogen ion concentration (H) and the concentration of base (b) and sodium dihydrogen phosphate (a) is:

$$H^5 + H^4 (a + b + K_1) + H^3 (K_{12} - Kw + K_1 b) [K_{23} - Kw - K_2 (a - b)] - HK_{12} [Kw + K_3 (2a - b)] - K_{123} Kw = 0 \qquad \text{B.5-5}$$

where a and b are in moles/liter

$$K_1 = 7.59 \times 10^{-3} \qquad K_{12} = K_1 \cdot K_2$$

$$k_2 = 6.7 \times 10^{-8} \qquad K_{23} = K_2 \cdot K_3 \qquad \text{B.5-6}$$

$$K_3 = 2.14 \times 10^{-13} \qquad K_{123} = K_1 \cdot K_2 \cdot K_3$$

$$K_w = 10^{-14}$$

As in B.5.1, equation B.5-5 may be simplified by neglecting the smaller terms to yield

$$A \simeq X \cdot 122/MW \qquad (\text{for pH} = 9) \qquad \text{B.5-7}$$

Here, A is the amount (kg) of anhydrous sodium dihydrogen phosphate required to return the pH to 9 after the spill (X kg) of a strong (monoacid) base whose molecular weight is MW (kg/mole).

In one laboratory experiment conducted in this program, the amount of sodium dihydrogen phosphate required to return the pH of a solution containing a strong (monoacid) base to 9.0 was only 1% less than the amount calculated by the method described above.

Again, there are likely to be somewhat larger uncertainties associated with the estimated amounts of sodium dihydrogen phosphate needed to neutralize weak bases because appropriate equations were not available. The actual calculations assumed a constant ratio with strong bases for which equations are available. The ratios used were above 40% in all cases except three: triethanol amine (∿7%), the lower range value for 1,1-dimethyl-hydrazine (∿9%), and hydrazine (∿24%). The error in the estimated amounts associated with these three chemicals could be substantial; the error in the estimated amounts for the remaining chemicals is not expected to be serious.

B.5.3 Assumptions

Equations B.5-4 and B.5-7 should be applied only to those chemicals that do not react with water. When a reaction with water is involved, the equations may be applied to each of the acid or base reaction products. For example, in a spill of sodium, X would be the amount of sodium hydroxide formed and MW would be the molecular weight of sodium hydroxide.

There are other assumptions inherent in the calculations carried out. Some specific ones are spelled out in the notes for Tables B.5-2 and B.5-3. Others of a more general nature are as follows:

1. All of the spill is assumed to dissolve in water.
2. If the initial material reacts with water, it is assumed that all material reacts and that the acids or bases produced by the reaction remain in solution.
3. If a material was commonly shipped in a relatively pure form ($\geq$ 95%) then, for ease in calculation, 100% purity was usually assumed.
4. Activity coefficients are all assumed to be unity.
5. The ionic strength and buffer capacity of the water into which the material is spilled are assumed to be low.
6. Chemical and physical transformations of the spilled material (aside from any initial reaction with water) are ignored. Such transformations might include adsorption, precipitation, ion exchange, oxidation, evaporation, boiling, etc.

APPENDIX C: COMPUTER MODELS FOR NEUTRALIZATION RESPONSES

C.0 Summary

C.0.1 Objective

As part of a study to assess the feasibility of neutralizing acidic or basic spills in a waterway, we have developed a methodology for use in evaluating various treatment procedures. The analysis includes models for dispersion in water of both the spilled chemical and the treating chemical as well as a model of their interaction. These models can be used to evaluate the effectiveness of each combination of response time, reagent deployment method, and initial spill scenario.

A computer program has been written to study the problem of the simultaneous dispersion and reaction of two chemical species spilled and dissolved in succession in a flowing river. The generality of the solution has been constrained from the beginning in several respects, namely:

1. The program is based on CHRIS[15] models for dispersion in wide and narrow rivers, under ideal conditions. For such cases, no variation of the concentration profiles in the vertical direction has been considered since on the time scale of interest, vertical (z-direction) mixing is essentially complete. It is crucial to realize that the chemicals are assumed to dissolve instantly and completely in the water. Whether these species in fact sink or float or aggregate is not considered in this idealized model. However, since the program includes models for both instantaneous and continuous spills, a slowly-dissolving chemical might be modeled as a continuously emitting source.

2. Four types of source terms, describing idealized potential spill and reagent deployment scenarios, are provided.

3. The computer programs presently available refer specifically to acid-base interactions between spills of either an acid or a base and the two neutralizing agents identified in our feasibility study: sodium bicarbonate and sodium dihydrogen

phosphate. Other reagents, as well as other species which are not amenable to acid-base neutralization, could be handled by modifying the computer subroutines involved.

C.0.2 Source Models

Four types of source terms are developed, corresponding to idealized spill scenarios and reagent deployment methods.

1. The instantaneous point source. This might correspond to the overturn of an open barge or tank car, or to a massive leak in a container which will empty it in a short time.
2. The instantaneous line source. This would most likely represent a deployment technique, such as the use of an airplane or marine craft to lay down a region of neutralizing agent which is far longer than it is wide.
3. The continuous point source. This might be a barge anchored in the waterway or discharge from an outlet at a fixed position along the shore, emitting a chemical at a constant rate for a specified period of time.
4. The floating continuous point source. This could represent a barge drifting with the current and releasing a chemical at a constant rate for a specified period of time.

A further option for both spill and treatment allows the user to specify the profiles of concentration at the time in question, thus permitting more complex source types to be described empirically.

C.0.3 Analysis

The general method of attack is as follows. First, the concentration profiles of the spilled chemical are calculated for the time of interest, assuming that it alone is present in the water; the equations for the different types of sources described above are discussed in the following sections. Second, the concentration profiles for the subsequently deployed treating chemical are calculated at the time of interest, again as if only that species were present in the river. Third, the two species are allowed to interact, instantaneously and to their equilibrium (which at each point generally results in the annihilation of the less concentrated species). Regions which are still dangerous due to excess of spilled material or treating agent and the degree of danger according to prescribed water quality criteria (for acid-base systems, a pH range of 6 - 9 is considered safe) are delineated. The efficacy of a given treatment procedure - method of application, quantity of reagent, etc. - may then be assessed. Models of the four source types, which describe the concentration profiles of spill and treatment chemicals as they spread independently through the river, are discussed in Section C.1 for wide rivers and Section C.2 for narrow rivers. These include both the CHRIS point source models and simple extensions to line and continuous sources. The interaction of the acid and base species is modeled in Section C.3. In this section, the spill must be a monoacid or base, and may be either strong or weak.

The procedure described in the preceding paragraph requires the two species to disperse through the river independently until the time of interest. Then they interact; the neutralization is instantaneous and proceeds to equilibrium. This is the same as assuming that the eddy diffusivity of each specie depends only on river turbulence, not on chemical concentration or other molecular properties.

This set of assumptions is required for two reasons. First, the alternative approach of solving the coupled differential equations for dispersion plus reaction, even for simple point sources, appeared infeasible without major development of new analytical models. Such effort was beyond the scope of the present project, which was limited to very modest development of new mathematical procedures. Further, considering that the treatment of the behavior of the river itself and of the different sources is somewhat idealistic, the mathematical accuracy implied by such solutions would have been deceptive, and the effort expended thereon not justified.

A second approach might have been to allow dispersion to proceed for a short time; permit interaction to take place, neutralizing some of each species; and step along in time, first dispersing the solutes, then allowing them to react. This would have meant that each time step after the first would be essentially an independent dispersion problem with a specified, non-ideal source distribution. It was clear, as can be seen from the material which follows, that even a simple point source had a very complicated dispersion relation; it would have been extremely complex to study dispersion from the array of complex distributed sources that would have resulted from each step of this procedure.

The method first described was therefore adopted. The results obtained are believed to be adequate for the purpose of comparing different treatment techniques, especially since in practice, such treatments will be subject to both the nonidealities which we have ignored and the possibility of human error.

C.0.4 Required Data

Several kinds of information are needed for a particular calculation. These may be divided into three categories: information about the problem, information about the spill, and information about the treatment. They are discussed below. The coordinate system to be used and the references for the times mentioned are provided in detail in the introductions to the first two sections.

1. Information about the problem: river width, depth and velocity; time of interest.
2. Information about the spill: name of chemical, acid or base, strong or weak; molecular weight, mole fraction composition, density, pKa; source type, volume spilled, distance from center of river to spill site; if a line source, the half length and angle with the river centerline; if continuous, the time at which the source is depleted.
3. Information about the treatment: source type, volume used, distance from spill site and center of river to treatment

site, time of treatment; if a line source, the half length and angle with the river centerline; if continuous, the time at which the source is depleted.

C.0.5 Results of Calculations

A sample of the computer program output appears in Section C.4. The basic river parameters and calculated directional diffusivities are printed, and the scenario under study is described. The pH level of the river at the time under study is shown graphically, with downstream distance shown on the abscissa and cross stream distance on the ordinate; pH values are rounded to the nearest integer and safe areas are shown as blanks. The danger areas (if any) resulting from the spill alone, the treatment alone, and the neutralization process are separately charted.

In Section C.5, some calculations of the theoretical amount of neutralizing agent needed and of the extent of the damaged areas are made. These are based on the simplest case, a spill which behaves like an instantaneous point source. The correlation between spill size, elapsed time, and amount of neutralizing agent required is shown in parametric plots.

C.1 Wide River Models

Consider a river of width w and depth d: Distance y is measured from y=0 at the centerline to $y = \pm \frac{w}{2}$ at the edges; distance z from z = 0 at the river surface to z = d on the bottom*. The river is flowing with velocity u in the x-direction, and because of the assumed turbulent nature of the flow, it is taken to have a flat velocity profile (plug flow) over its entire cross-section. Since mixing is assumed to proceed entirely by eddy diffusion, no important error is introduced by the use of a constant velocity. It is emphasized that the idealized models used in this analysis are different from real rivers; bends, irregular bottoms and shores, islands and other irregularities affect the mixing pattern, and may in fact be as important in determining the overall behavior as the turbulent diffusion considered here. For example, bends and islands can be expected to increase both axial and radial dispersion, while narrow channels would increase the river velocity at points. These models may be considered a first, conservative approximation, and are useful because they simplify the analysis.

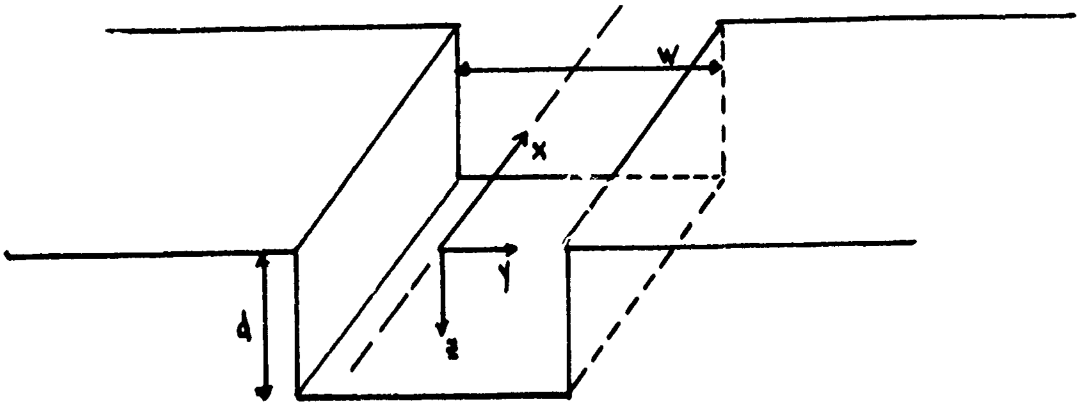

FIGURE C.1-1 An Idealized River

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*all x distances are measured from the x-position of the spill, y from the river centerline, z from the river surface.

No z-variation of these equations is permitted, since, in preliminary calculations, vertical diffusion proved to be essentially complete in the time scale of interest for soluble species. In the case of continuous sources (section C.1.3 and C.1.4 below), terms in z were retained throughout the integration and eliminated at the end for mathematical convenience; it is simplest to evaluate these equations at the river surface ($z = 0$).

From work done in the CHRIS manual on eddy diffusion in wide rivers, correlations for the eddy diffusivities, e, in the three-dimensional systems are obtained. For wide rivers, they reduce to:

$$e_x = e_y = 0.00063\, u\, d^{5/6} \qquad \text{C.1-1}$$

$$e_z = 10\, e_x$$

Four types of source terms will now be discussed. Note that they may be applied to either the spill or the treatment.

C.1.1 Instantaneous Point Source

Consider any point source placed at (x_1, y_1) at time t_1 consisting of M moles of a chemical which dissolves in water practically instantly. It is important to clearly understand the coordinate system. If the source referred to is the spill, $x_1 = 0$ and $t_1 = 0$, by definition - time is measured from the occurrence or initiation of the spill, x is the distance from the position of the spill. If the source under consideration is the treating agent, x_1 is the distance from the spill site to the treatment application point and t_1 is the subsequent time at which application takes place - typically within a day after the spill occurs. We are in a fixed coordinate system - the origin is the point at which the spill occurred.

Concentration profiles for this source in a long river of width w and depth d are:

$$C(x,y,z,t) = \frac{2M}{(4\pi(t-t_1))^{3/2}\sqrt{e_x e_y e_z}}\, e^{-\frac{(x-x_1-u(t-t_1))^2}{4e_x(t-t_1)}} \left[e^{-\frac{(y-y_1)^2}{4e_y(t-t_1)}} + e^{-\frac{(y+y_1+w)^2}{4e_y(t-t_1)}} + e^{-\frac{(y+y_1-w)^2}{4e_y(t-t_1)}} \right] \left[e^{-\frac{z^2}{4e_z(t-t_1)}} + e^{-\frac{(z-2d)^2}{4e_z(t-t_1)}} \right], \qquad \text{C.1-2}$$

However, it is known that the diffusion times for the z-direction are of the same order as the time scale for treatment response (less than 6 hours). Even if equation C.1-2 were modified to include "reflection terms," so that a spill could disperse to the river bottom and be "reflected" back, 30-50% of the source mass would be "lost" in the first 6 hours due to the inherent errors involved in summing such multiple reflections. To avoid this error we assume that there is no variation of concentration in the z-direction; this assumption is implemented by taking the average of the profile with respect to z:

$$C(x,y,t) = \frac{M}{4\pi d\,(t-t_1)\sqrt{e_x e_y}}\, e^{-\frac{(x-x_1-u(t-t_1))^2}{4e_x(t-t_1)}} \left[e^{-\frac{(y-y_1)^2}{4e_y(t-t_1)}} + e^{-\frac{(y+y_1+w)^2}{4e_y(t-t_1)}} + e^{-\frac{(y+y_1-w)^2}{4e_y(t-t_1)}} \right] \qquad \text{C.1-3}$$

To examine the improvement which has been made, consider a typical case; let $w = 3200$ m, $d = 20$ m, $u = 1$ m/s; e_z is obtained as 0.076 m^2/s. The total obtained by integration of the concentration profile over the whole river should equal M, the number of moles initially placed in the river. A balance on equation C.1-2 shows that in seven minutes, 1% of the initial source is unaccounted for; in 12 minutes, 5%. Using equation C.1-3 corresponding losses occur in seven and 12 years, respectively (these losses result from interference due to "reflections" from the river banks, which occur on a much longer time scale). The new equation remains valid for times far in excess of any likely to be encountered.

C.1.2 Instantaneous Line Source

Consider a line source of length 2L and total charge M moles (where $\dot{M}$ is a charge per unit length M/2L moles/m), placed with its center at (x_1, y_1) at time t_1. It makes an angle θ with the river centerline, where $-\frac{\pi}{2} < \theta \leq \frac{\pi}{2}$. The defining equation is obtained by integrating the point source equation over the length of the line source; here the dummy variable s represents distance along the line:

$$C(x,y,t) = \frac{\dot{M}}{4\pi d\,(t-t_1)\sqrt{e_x e_y}} \int_{-L}^{L} e^{-\frac{(x-x_1-s\cos\theta-u(t-t_1))^2}{4e_x(t-t_1)}} \qquad \text{C.1-4}$$

$$\left[e^{-\frac{(y-y_1-s\sin\theta)^2}{4e_y(t-t_1)}} + e^{-\frac{(y+y_1-s\sin\theta+w)^2}{4e_y(t-t_1)}} + e^{-\frac{(y+y_1-s\sin\theta-w)^2}{4e_y(t-t_1)}}\right] ds$$

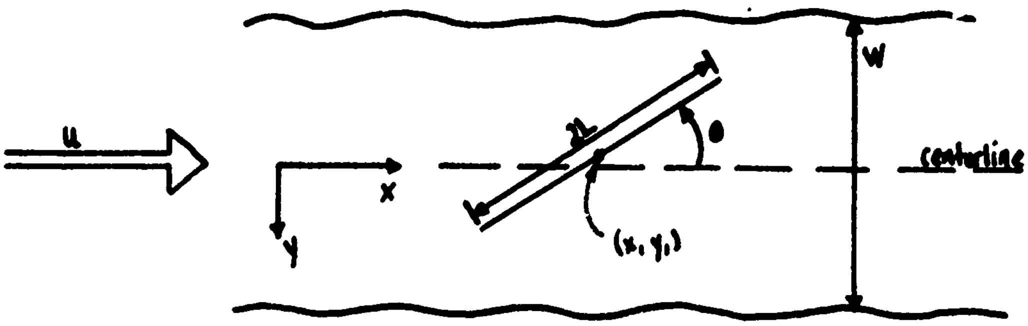


FIGURE C.1-2 A Line Source in a Wide River

The calculations proceed through the product of the x-term and the first y-term remembering that the other y-terms are handled identically. First, the product is expanded in powers of s, noting that $e_x = e_y$:

$$\int_{-L}^{L} e^{-s^2\left[\frac{1}{4e_x(t-t_1)}\right] + 2s\left[\frac{x-x_1-u(t-t_1)}{4e_x(t-t_1)}\cos\theta + \frac{y-y_1}{4e_y(t-t_1)}\sin\theta\right]} ds \times e^{-\left[\frac{(x-x_1-u(t-t_1))^2}{4e_x(t-t_1)} + \frac{(y-y_1)^2}{4e_y(t-t_1)}\right]} \qquad \text{C.1-5}$$

Next, the square is completed; terms which are not dependent on s are removed from the integral. In terms of the dummy variable of integration, $\xi = A's - B'$, the form of the result is:

$$\int_{-L}^{L} e^{-[A's-B']^2 - C'} ds = \frac{1}{A'} e^{-C'} \int_{-A'L-B'}^{A'L-B'} e^{-\xi^2} d\xi \qquad \text{C.1-6}$$

$$= \frac{\sqrt{\pi}}{2A'} e^{-C'} \left[\operatorname{erf}(A'L+B') + \operatorname{erf}(A'L-B')\right]$$

The coefficients A', B' and C' are obtained from equation C.1.5 when the square is completed. The expanded result for this term is:

$$C(x,y,t) = \frac{\dot{M}}{4d\sqrt{\pi e_x (t-t_1)}} e^{-\frac{((x-x_1-u(t-t_1))\sin\theta-(y-y_1)\cos\theta)^2}{4e_x(t-t_1)}} \left\{ \operatorname{erf}\left[\frac{(x-x_1+L\cos\theta-u(t-t_1))\cos\theta+(y-y_1+L\sin\theta)\sin\theta}{\sqrt{4e_x(t-t_1)}}\right] - \operatorname{erf}\left[\frac{(x-x_1-L\cos\theta-u(t-t_1))\cos\theta+(y-y_1-L\sin\theta)\sin\theta}{\sqrt{4e_x(t-t_1)}}\right]\right\} \qquad \text{C.1-7}$$

The concentration profile is the sum of this expression and two similar expressions corresponding to the other two y-terms. Two interesting limits can be obtained:

1) $\theta = 0$, $L \to \infty$ (very long x-direction line source):

$$C(y,t) = \frac{\dot{M}}{2d\sqrt{\pi e_y (t-t_1)}} e^{-\frac{(y-y_1)^2}{4e_y(t-t_1)}} \qquad \text{C.1-8}$$

2) $\theta = \frac{\pi}{2}$, L and $w \to \infty$ (very long y-direction line source in a very wide river):

$$C(x,t) = \frac{\dot{M}}{2d\sqrt{\pi e_x (t-t_1)}} e^{-\frac{(x-x_1-u(t-t_1))^2}{4e_x(t-t_1)}} \qquad \text{C.1-9}$$

C.1.3 Continuous Point Source

A point source is placed at (x_1,y_1) at time t_1. It emits a chemical at a rate $\dot{M}$ until time t_2, when it becomes depleted (here $\dot{M} = M/(t_2 - t_1)$ moles/sec, where M is the total quantity released in moles). The resulting concentration profiles for times $t > t_2$ are calculated by integrating the instantaneous point source expression over the duration of the emission, using the dummy variable of integration τ to represent time since inception of the point source:

$$C(x,y,z,t) = \frac{\dot{M}}{4\pi^{3/2}\sqrt{e_x e_y e_z}} \int_{t_1}^{t_2} (t-\tau)^{-3/2} e^{-\frac{(x-x_1-u(t-\tau))^2}{4e_x(t-\tau)}} \left[e^{-\frac{(y-y_1)^2}{4e_y(t-\tau)}} + e^{-\frac{(y+y_1+w)^2}{4e_y(t-\tau)}} + e^{-\frac{(y+y_1-w)^2}{4e_y(t-\tau)}} \right] \left[e^{-\frac{z^2}{4e_z(t-\tau)}} + e^{-\frac{(z-2d)^2}{4e_z(t-\tau)}} \right] d\tau \qquad \text{C.1-10}$$

Note that the z-dependence is retained only because it makes the equation integrable, although it is quite possible that an analytical solution to the two-dimensional case also exists. Since it has been assumed that the concentration does not vary with z, it should be permissible to retain all three dimensions, evaluating the results at z = 0 when finished.

Consider the product of the x-term and the first y- and z-terms, noting that the other (five) combinations are analogous. Expand this product into terms in $(t - \tau)$ and $1/(t - \tau)$:

$$\int_{t_1}^{t_2} (t-\tau)^{-3/2} e^{-(t-\tau)\frac{u^2}{4e_x} + \frac{u(x-x_1)}{2e_x} - \frac{1}{t-\tau}\left[\frac{(x-x_1)^2}{4e_x} + \frac{(y-y_1)^2}{4e_y} + \frac{z^2}{4e_z}\right]} d\tau \qquad \text{C.1-11}$$

Let:

$$b = \frac{u^2}{4e_x} \qquad \text{C.1-12}$$

$$g = \frac{(x-x_1)^2}{4e_x} + \frac{(y-y_1)^2}{4e_y} + \frac{z^2}{4e_z}$$

and transform the variables according to:

$$\eta^2 = b(t-\tau) \qquad \text{C.1-13}$$

$$c^2 = bg$$

so that there results:

$$-\int_{\sqrt{b(t-t_1)}}^{\sqrt{b(t-t_2)}} 2\sqrt{b}\, e^{\frac{u(x-x_1)}{2e_x}} \frac{1}{\eta^2} e^{-\eta^2-\frac{c^2}{\eta^2}}\, d\eta \qquad \text{C.1-14}$$

Now

$$\int \frac{1}{\eta^2} e^{-\eta^2-\frac{c^2}{\eta^2}}\, d\eta = -\frac{1}{2c}\frac{\partial}{\partial c}\int e^{-\eta^2-\frac{c^2}{\eta^2}}\, d\eta \qquad \text{C.1-15}$$

The right hand side is:

$$\int e^{-\eta^2-\frac{c^2}{\eta^2}}\, d\eta = \frac{\sqrt{\pi}}{4}\left[e^{2c}\,\mathrm{erf}\left(\eta+\frac{c}{\eta}\right)+e^{-2c}\,\mathrm{erf}\left(\eta-\frac{c}{\eta}\right)\right] \qquad \text{C.1-16}$$

Thus:

$$\int \frac{1}{\eta^2} e^{-\eta^2-\frac{c^2}{\eta^2}}\, d\eta = \frac{-\sqrt{\pi}}{8c}\left\{e^{2c}\left[2\,\mathrm{erf}\left(\eta+\frac{c}{\eta}\right)+\frac{1}{\eta}e^{-\left(\eta+\frac{c}{\eta}\right)^2}\right]-e^{-2c}\left[2\,\mathrm{erf}\left(\eta-\frac{c}{\eta}\right)+\frac{1}{\eta}e^{-\left(\eta-\frac{c}{\eta}\right)^2}\right]\right\} \qquad \text{C.1-17}$$

The first term thus becomes:

$$C(x,y,t) = \frac{\dot{M}e^{\frac{u(x-x_1)}{2e_x}}}{8\pi\sqrt{e_x e_y e_z g}}\left\{e^{2\sqrt{bg}}\,\mathrm{erf}\left[\sqrt{b(t-\tau)}+\sqrt{\frac{g}{t-\tau}}\right]-e^{-2\sqrt{bg}}\,\mathrm{erf}\left[\sqrt{b(t-\tau)}-\sqrt{\frac{g}{t-\tau}}\right]\right\}\Bigg|_{\tau=t_1}^{\tau=t_2} \qquad \text{C.1-18}$$

For computational purposes, the error function erf(z) is defined as $1 - e^{-Z^2}F(Z)$, where the function F(Z) is given for non-negative Z by Abramowitz and Stegun.[1] For $Z < 0$, $\mathrm{erf}(Z) = -1 + e^{-Z^2}F(-Z)$. The error function is expanded in this manner so that small differences between numbers of similar magnitude can be calculated accurately.

The concentration profiles are the sum of this first term and five others like it, representing other combinations of y- and z-terms.

The steady state limit, which can be obtained by allowing t and t_2 to become infinite, represents a continuous source of constant emission rate. Here we consider only the case where both t and t_2 become large, since t is constrained to exceed t_2. This steady state limit is:

$$C(x,y) = \frac{\dot{M} e^{\frac{u(x-x_1)}{2e_x}}}{4\pi \sqrt{e_x e_y e_z}} \frac{e^{-2\sqrt{bg}}}{\sqrt{g}} \qquad \text{C.1-19}$$

As the point source is approached, $g \to 0$ and the concentration becomes infinite, as one would expect.

If a continuous source is still emitting at the time of interest, then the integrals given above are evaluated from $\tau = t_1$ to $\tau = t$ (the upper limit is no longer $\tau = t_2$); the value of the upper limit is now zero instead of $t - t_2$. This procedure is allowed for all continuous sources.

C.1.4 Floating Continuous Point Source

If the point source of the preceding section is allowed to drift with the current in the river, the analysis is carried out in a completely similar manner to that in section C.1.3. For any floating source, the x-coordinate of the source equals the location downstream at which it was inserted in the river plus the distance it has drifted since then, $x_1 + u\,(t-t_1)$; this location is fixed during the integration performed in C.1-11. The x-dependence is written as:

$$e^{-\frac{(x-x_1-u(t-t_1))^2}{4e_x(t-\tau)}} \qquad \text{C.1-20}$$

where $(t - t_1)$ replaces $(t - \tau)$ in the numerator of the exponent. The coefficient $b = 0$; for the combination of the first -y and z-terms, g is defined by:

$$g = \frac{(x-x_1-u(t-t_1))^2}{4e_x} + \frac{(y-y_1)^2}{4e_y} + \frac{z^2}{4e_z} \qquad \text{C.1-21}$$

The completed integral is of the form:

$$C(x,y,t) = \frac{\dot{M}}{4\pi\sqrt{e_x e_y e_z}\, g}\ \mathrm{erf}\left[\sqrt{\frac{g}{t-\tau}}\right]\Bigg|_{\tau=t_1}^{\tau=t_2} \qquad \text{C.1-22}$$

The concentration profiles consist of six such terms, one for each combination of the y- and z-terms. In the limit as the point source is approached $(g \to 0)$, this profile reduces to:

$$C(t) = \frac{\dot{M}}{2\pi\sqrt{\pi e_x e_y e_z (t-\tau)}}\Bigg|_{\tau=t_1}^{\tau=t_2} \qquad \text{C.1-23}$$

C.2 Narrow River Models

Consider a narrow river of depth d and width w. The river is flowing in the x-direction with uniform velocity u. In the CHRIS models of eddy diffusion, appropriate diffusivities are given:

$$e_x = 0.00063\, u\, R_h^{5/6} \qquad \text{C.2-1}$$

$$e_y = 0.021\, u\, R_h^{5/6}$$

$$e_z = 10\, e_x$$

where the hydraulic radius R_h is defined as:

$$R_h = \frac{wd}{w + 2d} \qquad \text{C.2-2}$$

These rivers have a width-to-depth ratio less than about 100. As is clear from equation C.2-1, in narrow rivers both the y- and z-diffusivities greatly exceed the x-diffusivity. Hence, dispersion in these rivers can be taken to be one-dimensional (well-mixed in the y- and z-directions and traveling as a plug whose length is slowly extended by dispersion in the x-direction). Because of this reduction of order, many of the results cited below are less complex than those described in Section C.1.

Concentration profiles for the four source types previously derived will now be discussed in relation to the narrow river model. This section relies on the material and methods presented in C.1, and only the results are cited.

C.2.1 Instantaneous Point Source

Assuming that the concentration profiles are constant in the y- and z-directions, the equation describing them can be obtained from equation C.1-2 by calculating the average with respect to y and z:

$$C(x,t) = \frac{M}{2dw\sqrt{\pi e_x (t-t_1)}}\, e^{-\frac{(x-x_1-u(t-t_1))^2}{4e_x(t-t_1)}} \qquad \text{C.2-3}$$

Since the river is assumed to be infinitely long (no end effects need be considered), the mass balance is identically satisfied at all points. The x-direction concentration profiles are bell-shaped; at a distance $(4e_x(t-t_1)\ln \varepsilon)^{1/2}$ from the point of peak concentration (either upstream or downstream), the concentration is reduced to $1/\varepsilon$ of its peak value.

C.2.2 Instantaneous Line Source

In narrow rivers, we have assumed that y-direction mixing is complete. Thus, all line sources can be represented by only their x-component. A cross-river source becomes the same as a point source in this model; an arbitrary line source is replaced by an x-direction line source of shorter length and having the same center (the length is the product of the original length and the cosine of its angle of inclination to the centerline).

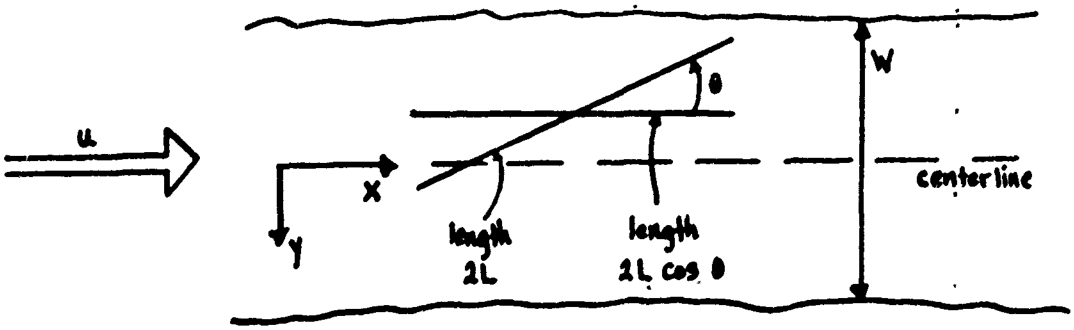


FIGURE C.2-1: A Line Source in a Narrow River

The resulting concentration profiles are:

$$C(x,t) = \frac{\dot{M}}{2dw}\left[\operatorname{erf}\left\{\frac{x-x_1+L-u(t-t_1)}{\sqrt{4e_x(t-t_1)}}\right\} - \operatorname{erf}\left\{\frac{x-x_1-L-u(t-t_1)}{\sqrt{4e_x(t-t_1)}}\right\}\right] \qquad \text{C.2-4}$$

where L is the half-length of the corresponding x-direction line source.

For the case of a very long line source, this reduces to a constant value over the whole river:

$$C(x,t) = \frac{\dot{M}}{dw} \qquad \text{C.2-5}$$

C.2.3 Continuous Point Source

Using the same methods as in section C.1, we must integrate equation C.2-3 and describe the point source over the duration of the continuous source emission:

$$C(x,t) = \frac{\dot{M}}{2dw\sqrt{\pi e_x}} \int_{t_1}^{t_2} (t-\tau)^{-1/2} e^{-\frac{(x-x_1-u(t-\tau))^2}{4e_x(t-\tau)}} \, d\tau \qquad \text{C.2-6}$$

Letting

$$b = \frac{u^2}{4e_x} \qquad \text{C.2-7}$$

$$g = \frac{(x-x_1)^2}{4e_x}$$

$$\eta^2 = b(t-\tau)$$

$$c^2 = bg$$

the integral becomes:

$$C(x,t) = \frac{-\dot{M} e^{\frac{u(x-x_1)}{2e_x}}}{dw\sqrt{\pi e_x b}} \int_{\sqrt{b(t-t_1)}}^{\sqrt{b(t-t_2)}} e^{-\eta^2-\frac{c^2}{\eta^2}} \, d\eta \qquad \text{C.2-8}$$

Notice the absence of the $1/n^2$ factor which was present in the integrand of equation C.1-14; this factor disappears because only terms in x (instead of x, y and z) are present. This integral is:

$$C(x,t) = \frac{-\dot{M} e^{\frac{u(x-x_1)}{2e_x}}}{4dw\sqrt{e_x b}} \Bigg\{ e^{2\sqrt{bg}} \operatorname{erf}\left[\sqrt{b(t-\tau)} + \sqrt{\frac{g}{t-\tau}}\right] + e^{-2\sqrt{bg}} \operatorname{erf}\left[\sqrt{b(t-\tau)} - \sqrt{\frac{g}{t-\tau}}\right] \Bigg] \Bigg|_{\tau=t_1}^{\tau=t_2} \qquad \text{C.2-9}$$

For computation purposes, the function F(z) (defined in the material Preceding equation C.1-19) is again used to evaluate the error function.

In the steady state limit, the source emits steadily for all time and the concentration at all points in the river attains a constant value:

$$C = \frac{\dot{M}}{dwu} \qquad \text{C.2-10}$$

C.2.4 Floating Continuous Point Source

Writing $(x - x_1 - u(t-t_1))$ in equation C.2-6 for the x-dependence (instead of $x-x_1-u(t-\tau)$) and integrating, the result obtained is:

$$C(x,t) = \frac{-\dot{M}}{dw\sqrt{e_x}} \left[\sqrt{\frac{t-\tau}{\pi}}\, e^{-g/t-\tau} + \sqrt{g}\, \operatorname{erf}\left(\sqrt{\frac{g}{t-\tau}} \right) \right] \Bigg|_{\tau=t_1}^{\tau=t_2} \qquad \text{C.2-11}$$

C.3 Neutralization with Sodium Bicarbonate and Sodium Dihydrogen Phosphate

In the calculations in section C.1 and C.2, it is necessary to determine the pH of the water in different parts of a river when concentrations [A] of acid and [B] of base are present; after neutralization has proceeded to equilibrium, the water is either neutral or there is an excess of one species. The equations to be solved are described below, and are valid for the neutralization of both strong and weak acids and bases; the assumptions made are that the species present are sufficiently dilute, that their activity coefficients may be considered as unity, and that the spill chemical is either monoacidic or monobasic.

C.3.1 Sodium Bicarbonate

For mixtures of sodium bicarbonate of concentration [B] and strong acids of concentration [A], the function $G_{st}([H^+])$ is defined

$$G_{st}([H^+]) = [H^+]^4 + [H^+]^3 ([B] - [A] + K_1) - [H^+]^2 (K_1[A] - K_1K_2 + K_w) - [H^+]K_1 (K_2([A] + [B]) + K_w) - K_1K_2K_w \qquad \text{C.3.1}$$

The hydrogen ion concentration at equilibrium is calculated by setting $G_{st} = 0$. For weak acids of concentration [A], the function $G_{wk}([H^+])$ is defined by:

$$G_{wk}([H^+]) = [H^+]G_{st}([H^+])\Big|_{[A]=0} + K_a G_{st}([H^+]) \qquad \text{C.3.2}$$

The hydrogen ion concentration at equilibrium in this case is calculated by setting $G_{wk} = 0$.

In these equations, all concentrations are in gmoles/liter. $K_w = 10^{-14}$ is the dissociation constant for water, and the sodium bicarbonate dissociation constants are $K_1 = 4.3 \times 10^{-7}$, $K_2 = 5.61 \times 10^{-11}$. The solution is achieved by a rapidly convergent Newton-Raphson iteration, using an initial value obtained by trial-and-error.

C.3.2 Sodium Dihydrogen Phosphate

For mixtures of sodium dihydrogen phosphate of concentration [A] and strong bases of concentration [B], the function $G_{st}([H^+])$ is defined by:

$$G_{st}([H^+]) = [H^+]^4 + [H^+]^3 \left([A]+[B]+K_1\right) + [H^+]^2 \left(K_1K_2-K_w + K_1[B]\right) - [H^+]K_1 \left(K_w+K_2([A]-[B])\right) - K_1K_2K_w \qquad \text{C.3.3}$$

The hydrogen ion concentration at equilibrium is calculated by setting $G_{st} = 0$. For weak bases of concentration [B], the function $G_{wk}([H^+])$ is defined by:

$$G_{wk}([H^+]) = K_w G_{st}([H^+])/K_b \Big|_{[B]=0} + [H^+]G_{st}([H^+]) \qquad \text{C.3.4}$$

The hydrogen ion concentration at equilibrium in this case is calculated by setting $G_{wk} = 0$.

In these equations, all concentrations are in gmoles/liter. $K_w = 10^{-14}$ is the dissociation constant of water, and the dissociation constants of sodium dihydrogen phosphate are $K_1 = 7.59 \times 10^{-3}$ and $K_2 = 6.17 \times 10^{-8}$. A third dissociation constant ($K_3 = 2.14 \times 10^{-13}$) has been assumed negligible and dropped from the calculation. The solution is achieved by a rapidly convergent Newton-Raphson iteration, using an initial value obtained by trial-and-error.

C.4 Sample Output

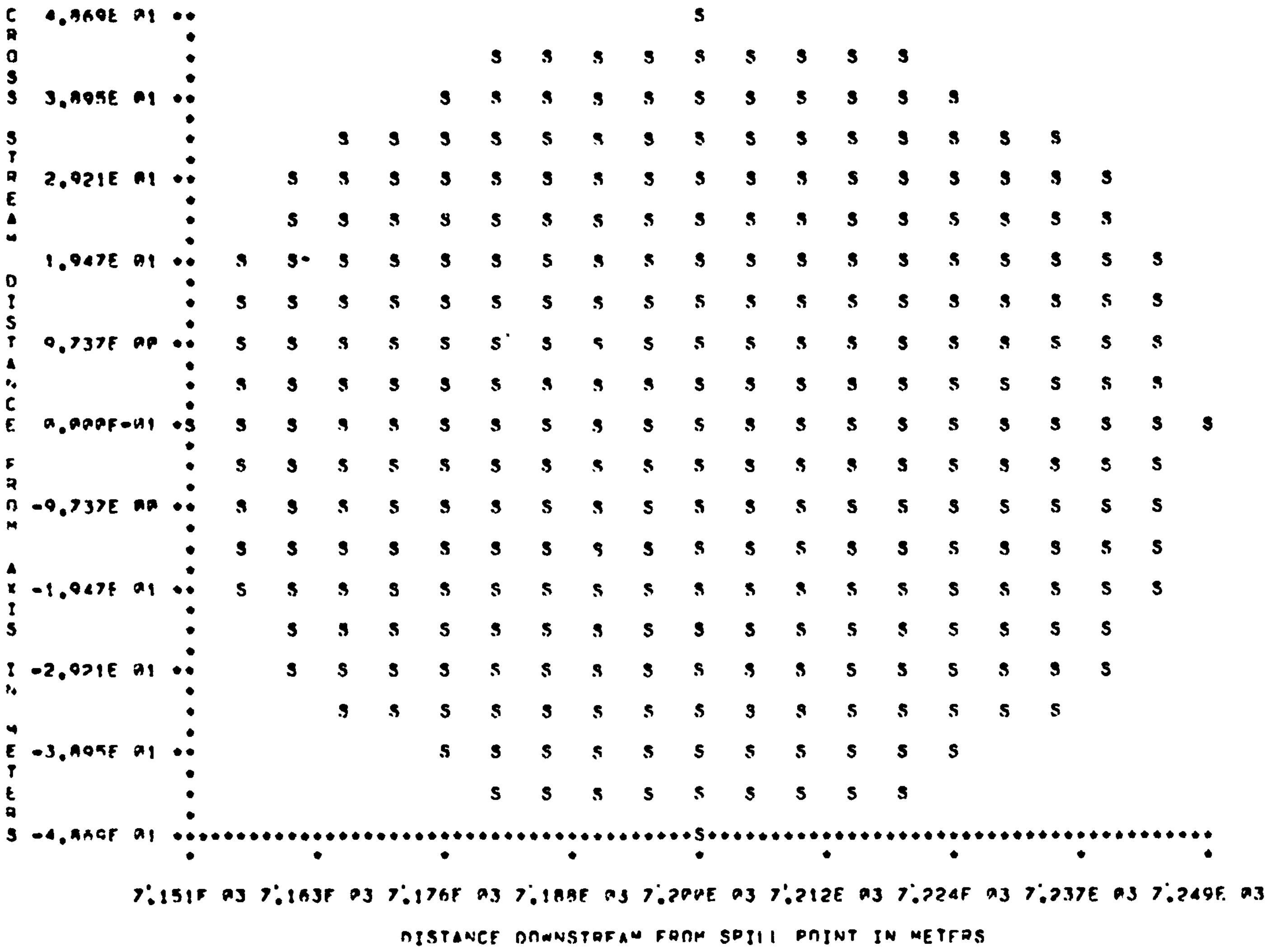
```
THIS IS A MEDIUM SPILL = 1.900E 04 GALLONS; 4.000E 03 GALLONS OF REAGENT ARE ADDED

SPILL:    37% HYDROCHLORIC ACID
REAGENT: 100% SODIUM BICARBONATE

 U = 1.000E 00 METERS/SEC      US = 5.684E-02 METERS/SEC       W = 3.200E 03 METERS           D = 2.000E 01 METERS
RH = 1.975E 01 METERS          EX = 7.616E-03 SQ.METERS/SEC  EY = 7.616E-03 SQ.METERS/SEC  EZ = 7.616E-02 SQ.METERS/SEC
A1 = 6.733E 05 GMOLES          A2 = 3.946E 05 GMOLES          YS = 0.000E-01 METERS         XR = 3.610E 03 METERS
YR = 1.020E 01 METERS          AM = 9.900E-04 MOLES/CU.METER RM = 0.000E-01 MOLES/CU.METER SK = 0.000E-01 1/SEC
RK = 0.000E-01 1/SEC           TF = 7.200E 03 SEC            TSR = 3.600E 03 SEC            TM = 1.127E 01 YEARS
DA =-6.000E 00

THE  SPILL  IS AN INSTANTANEOUS POINT SOURCE
THE REAGENT IS AN INSTANTANEOUS POINT SOURCE

AT TIME = 3.600E 03 SEC WHEN THE REAGENT WOULD BE ADDED, THE LOCUS OF DANGEROUS CONCENTRATION IS
    A CIRCLE WITH CENTER AT (3.600E 03, 0.000E-01) METERS AND RADIUS 3.551E 01 METERS
NOTE THAT THE RIVER WIDTH IS 3.200E 03 METERS
THE CONCENTRATION AT THE CENTER IS 9.670E 04 TIMES THE DANGEROUS CONCENTRATION

** IN ACID-BASE SYSTEMS, DANGEROUS CONCENTRATIONS ARE DEFINED AS THOSE PRODUCING A PH OUTSIDE THE RANGE 6 - 9

    U   RIVER VELOCITY
    US  SHEAR VELOCITY
    W   RIVER WIDTH
    D   RIVER DEPTH
    RH  HYDRAULIC RADIUS
    EX  X-DIFFUSIVITY
    EY  Y-DIFFUSIVITY
    EZ  Z-DIFFUSIVITY
    A1  SPILL SIZE
    A2  TREATMENT SIZE
    YS  Y-COORDINATE OF SPILL
    XR  X-COORDINATE OF TREATMENT
    YR  Y-COORDINATE OF TREATMENT
    AM  DANGEROUS CONCENTRATION OF SPILL
    RM  DANGEROUS CONCENTRATION OF REAGENT
    SK  SPILL DECAY RATE
    RK  REAGENT DECAY RATE
    TF  TIME OF INTERST
    TSR TIME TREATMENT BEGINS
    TM  UNASSISTED SPILL DISPERSION TIME
    DA  PKA OF SPILL
```

HYDROCHLORIC ACID

LOCUS OF DANGEROUS CONCENTRATION IN GMOLES/CU.METER BEFORE REACTION OCCURS

TIME = 7.200E 03 SEC, RATIO OF MAXIMUM CONCENTRATION TO DANGEROUS CONCENTRATION = 4.935E 04 AT (7.200E 03, 0.000E-01)

DANGER AREA = 7.419E 03 SQ.METERS, AVERAGE CONCENTRATION RATIO = 4.583E 03

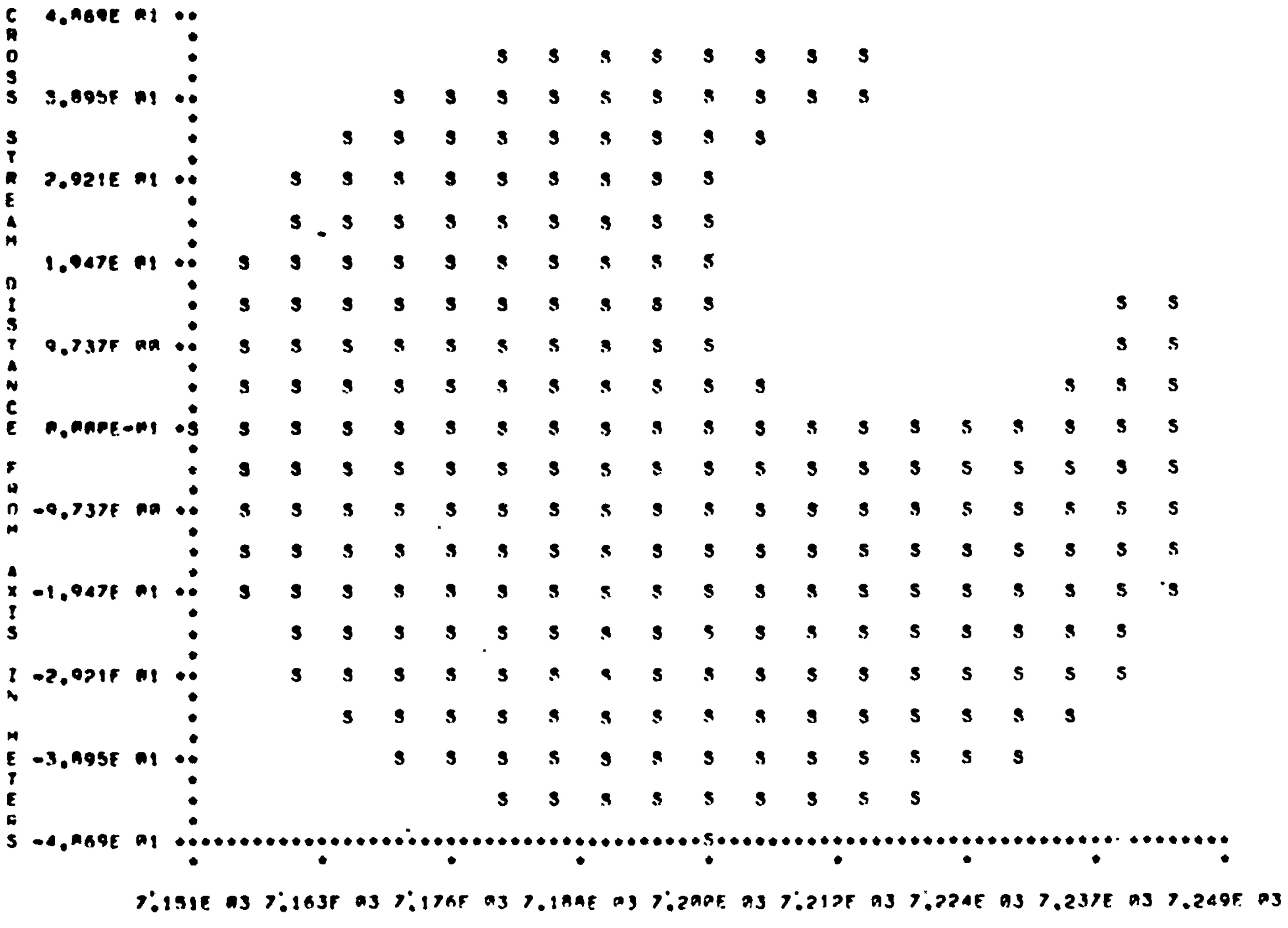


HYDROCHLORIC ACID

LOCUS OF DANGEROUS CONCENTRATION IN GMOLES/CU.METER AFTER REACTION OCCURS

TIME = 7.200E 03 SEC, MOST EXTREME PH VALUE = 1.309E 00 AT (7.195E 03, 0.000E-01)

DANGER AREA = 6.107E 03 SQ.METERS



```
                                        PH VALUES (ROUNDED)

                 PH VALUES GREATER THAN 6 BUT LESS THAN 9 ARE REPRESENTED BY BLANKS


C  4.869E 01 ••
R             •
O             •                 6  6  5  5  5  5  5  6
S             •
S  3.895E 01 ••           6  5  5  5  5  4  4  5  5  6
              •
S             •        6  5  5  4  4  4  4  4  5
T             •
R  2.921E 01 ••     6  5  5  4  4  3  3  3  4
E             •
A             •     5  5  4  4  3  3  3  3  5
M             •
   1.947E 01 ••  6  5  4  4  3  3  2  2  2  6
D             •
I             •  6  5  4  3  3  2  2  2  2  5                       6  6
S             •
T  9.737E 00 ••  5  5  4  3  3  2  2  2  2  2                       5  5
A             •
N             •  5  4  4  3  3  2  2  2  1  2  2                 5  5  5
C             •
E  0.000E-01 ••  5  4  4  3  2  2  2  2  1  1  2  2  5  6  5  4  4  4  5
              •
F             •  5  4  4  3  3  2  2  2  1  1  1  2  2  2  3  3  4  4  5
R             •
O -9.737E 00 ••  5  5  4  3  3  2  2  2  2  2  2  2  2  2  3  3  4  5  5
M             •
              •  6  5  4  3  3  2  2  2  2  2  2  2  2  2  3  3  4  5  6
A             •
X -1.947E 01 ••  6  5  4  4  3  3  2  2  2  2  2  2  2  3  3  4  4  5  6
I             •
S             •     5  5  4  4  3  3  3  3  2  3  3  3  3  4  4  5  5
              •
I -2.921E 01 ••     6  5  5  4  4  3  3  3  3  3  3  3  4  4  5  5  6
N             •
              •        6  5  5  4  4  4  4  4  4  4  4  4  5  5  6
M             •
E -3.895E 01 ••           6  5  5  5  5  4  4  4  5  5  5  5  6
T             •
E             •                 6  6  5  5  5  5  5  6  6
R             •
S -4.869E 01 ••••••••••••••••••••••••••••••••••••••••••••••••••••••••••••••
              •       •      •       •      •       •      •       •      •

          7.151E 03 7.163E 03 7.176E 03 7.188E 03 7.200E 03 7.212E 03 7.224E 03 7.237E 03 7.249E 03

                             DISTANCE DOWNSTREAM FROM SPILL POINT IN METERS
```

C.5 Estimation of Quantities of Neutralization Agent Needed

In our comparison of various methods of spill neutralization, it is necessary to consider the quantities of treating agent required to respond to various types and sizes of acidic or basic spills. Since spills will continue to be diluted in any unconfined water body, the amount of treating agent is also a function of how rapidly treatment can be initiated. In the case of small spills, for example, dispersion by natural dilution may occur before a response treatment can be initiated; such spills would not be worth treating. Even with larger spills, less treating agent is required at longer times since some of the hazardous chemical is dispersed safely by dilution.

Models developed from the basic CHRIS models for dispersion in wide and narrow rivers (see section C.1 and C.2) can be employed to estimate spill sizes above which amelioration treatment is required as well as the recommended amounts of treating agent for various response time intervals. The volume of the water body made hazardous by the spill residue can also be estimated as a function of time.

This section describes the methods used for making such estimates and presents generalized results for typical chemicals and typical rivers, which will be used to study the feasibility of different application methods.

C.5.1 Wide River Models

Equation C.1-3 describes the concentration profiles resulting from the placement of a point source in a wide river. It would be desirable to derive some simple relationships from this expression to facilitate consideration of different treatment schemes. For example, the maximum concentration in the spill area will only depend on the spill size and elapsed time in any given river; this quantity could easily be represented parametrically on a graph and would provide an idea of the speed with which a given spill disperses.

For this analysis, the terms in w in equation C.1-3 are described as negligible; this is valid for sources somewhere "near" the center of the river. The maximum concentration C_m occurs at the center of the dispersion pattern. At any time, this center is at $x=x_1+u(t-t_1)$, $y=y_1$:

$$C_m = \frac{M}{4\pi d t \sqrt{e_x e_y}} \qquad \text{C.5-1}$$

Another useful quantity would be the volume of river water adversely affected by the spill. To quantify this, some critical level of concentration C_d must be specified, such that all areas whose concentration is below this level are considered "not affected." Such a volume would not measure the severity of the damage inflicted by a spill, but, for different spills, the extent of the damage could be compared. Concentrations of acid producing pH values less than 6 are dangerous (for bases, pH > 9). A danger volume may therefore be derived:

$$V_d = 4\pi d t e_x \ln \frac{C_m}{C_d} \qquad \text{C.5-2}$$

An average concentration can be obtained by integration of equation C.1-3 over the danger volume; the average value of the concentration in the danger area can be shown to equal:

$$C_{ave} = \frac{C_m - C_d}{\ln C_m - \ln C_d} \qquad \text{C.5-3}$$

To calculate the quantity of neutralizing agent needed for a given spill, which is proportional to spill size and decreases with the passage of time, it is necessary to assume that both the spilled chemical and neutralizing agent are uniformly spread throughout the "danger zone" described above. The amount of neutralizing agent needed to reduce this average concentration to the value C is:

$$C_{ave,n} = a_n (C_{ave} - C_d) \qquad \text{C.5-4}$$

where the constant a_n has dimensions of gmol neutralizing agent/gmol spilled chemical and equals 1.430 for sodium bicarbonate and 1.016 for sodium dihydrogen phosphate.* Using equations C.5-2 and C.5-3, this implies a total amount of neutralizing agent M_n (gmoles):

$$M_n = 4\pi d t e_x a_n \left(C_m - C_d \left[1 + \ln \frac{C_m}{C_d} \right] \right) \qquad \text{C.5-5}$$

In the limit of short times or large spills, such that most of the spilled chemical is still in the danger zone (very little dispersion has occurred), this expression reduces to:

$$M_n = a_n M \qquad \text{C.5-6}$$

C.5.2 Narrow River Models

The development in this section will exactly parallel that in section C.5.1. The concentration profiles, which are now only functions of x and t because of the different properties of narrow rivers, are described by equation C.2-3. The maximum concentration value occurs at the center of the area over which the spill has dispersed and is given by:

$$C_m = \frac{M}{2dw\sqrt{\pi e_x t}} \qquad \text{C.5-7}$$

In terms of a critical or dangerous concentration C_d, such that waters with $C > C_d$ are unsafe, the volume of water endangered can be calculated:

---

*These values are obtained by solving equation C.3-1 for the ratio [B]/[A] when the pH = 6, and equation C.3-3 for [A]/[B] when the pH = 9. They apply to strong, monoacids and bases only.

$$V_d = 2dw\sqrt{4e_x t \ln \frac{c_m}{c_d}} \qquad \text{C.5-8}$$

The average concentration within this volume is obtained by integration of equation C.2-3 over the volume V_d:

$$C_{ave} = \frac{\sqrt{\pi}}{2}\,\frac{c_m}{\sqrt{\ln\frac{c_m}{c_d}}}\operatorname{erf}\left[\sqrt{\ln\frac{c_m}{c_d}}\right] \qquad \text{C.5-9}$$

where erf (x) is the error function. Calculation of the amount of neutralizing agent needed proceeds as in section C.5.1. The necessary average concentration is given by:

$$c_{ave,n} = a_n\left(c_{ave} - c_d\right) \qquad \text{C.5-10}$$

where a_n = 1.430 for sodium bicarbonate and 1.016 for sodium dihydrogen phosphate. Using equations C.5-8 and C.5-9 the total amount of neutralizing agent needed can be estimated:

$$M_n = 4dw\sqrt{e_x t}\,a_n\left\{c_m\frac{\sqrt{\pi}}{2}\operatorname{erf}\left[\sqrt{\ln\frac{c_m}{c_d}}\right] - c_d\sqrt{\ln\frac{c_m}{c_d}}\right\} \qquad \text{C.5-11}$$

In the limit where treatment response is very prompt and little dispersion has occurred, this reduces to:

$$M_n = a_n M \qquad \text{C.5-12}$$

C.5.3 Sample Calculations

Wide river

Let the river parameters be:

$w = 3200$ m
$d = 20$ m
$u = 1$ m/s C.5-13
$e_x = 0.00752$ m^2/s
$e_y = 0.00752$ m^2/s

Then the maximum concentration is:

$$C_m = 0.529 \frac{M}{t} \qquad \text{C.5-14}$$

Assuming that the spill is a strong acid, concentrations in excess of .001 gmol/m^3 produce a pH < 6. The danger volume is:

$$V_d = 1.39\,t \left[6.23 + \ln \frac{M}{t}\right] \qquad \text{C.5-15}$$

The average concentration within this volume is:

$$C_{ave} = 0.529 \frac{M/t - 0.00177}{\ln M/t + 6.28} \qquad \text{C.5-16}$$

The average sodium bicarbonate concentration needed is:

$$C_{ave,n} = 0.756 \frac{M/t - 0.00187}{\ln M/t + 6.28} - 0.00141 \qquad \text{C.5-17}$$

The total amount of sodium bicarbonate needed is:

$$M_n = 1.43\,M - 0.0194\,t - 0.0027\,t \ln {}^{M}/t \qquad \text{C.5-18}$$

Narrow river

$w = 50$ m
$d = 5$ m
$u = 1$ m/s C.5-19
$e_x = 0.00206$ m^2/s

$$C_m = 0.0249 \frac{M}{\sqrt{t}} \tag{C.5-20}$$

$$V_d = 45.9 \sqrt{t(3.23 + \ln M/\sqrt{t})} \tag{C.5-21}$$

$$C_{ave} = \frac{0.0221\, M/\sqrt{t}}{\sqrt{3.23 + \ln M/\sqrt{t}}} \operatorname{erf}\left[\sqrt{3.23 + \ln M/\sqrt{t}}\right] \tag{C.5-22}$$

$$C_{ave,n} = \frac{0.316\, M/\sqrt{t}}{\sqrt{3.23 + \ln M/\sqrt{t}}} \operatorname{erf}\left[\sqrt{3.23 + \ln M/\sqrt{t}}\right] - 0.00141 \tag{C.5-23}$$

$$M_n = 1.43 M \operatorname{erf}\left[\sqrt{3.23 + \ln M/\sqrt{t}}\right] - 0.0642\sqrt{t(3.23 + \ln M/\sqrt{t}} \tag{C.5-24}$$

Numerical values

Let M = 1000 gmol (for example, 80.3 lb pure HCl) and t = 21,600 sec (6 hr):

	wide	narrow
C_m (gmol/m^3)	0.0245	0.169
V_d (m^3)	1.31×10^5	1.51×10^4
C_{ave} (gmol/m^3)	0.00733	0.0663
$C_{ave,n}$ (gmol/m^3)	0.00906	0.0933
M_n (gmol)	1188	1409

C.5-25

Let M = 10,000 gmol and t = 43,200sec (12 hr):

	wide	narrow
C_m	0.122	1.198
V_d	3.93×10^5	2.51×10^4
C_{ave}	0.0252	0.399
$C_{ave,n}$	0.0345	0.569
M_n	13,630	14,260

C.5-26

C.5.4 Applications

Partial dispersion of spills

Figure C.5-1 is obtained from equation C.5-1. For each curve, C_m is set to the value corresponding to a pH of 5 (acids) or 10 (bases). The equation is solved for M as a function of t. Since M is in gram moles and t is seconds, appropriate constants are inserted to yield pounds versus hours (these constants differ for different chemicals). Clearly, a figure could be obtained for any choice of pH value (degree of dispersion) and chemical.

Figure C.5-2 is obtained from equation C.5-7 in an identical manner. Curves like those appearing in Figure C.5-1 and C.5-2 can be drawn to suit any particular set of requirements. Note that they refer to the amount of the pure chemical present; spills of solutions require calculation of the actual amount of the pure species involved. They provide information about the size spill which will disperse to a "satisfactory" degree within the time typically required for amelioration response. Determination of an acceptable level is largely a matter of opinion. The standard adopted in this work has been that waters whose pH lies between 6 and 9 are safe. Therefore, in the construction of Figure C.5-1 and C.5-2, somewhat weaker criteria were used for the most extreme pH in the spill area. If the most extreme pH were 5 for acids (or 10 for bases) at the time when treatment became available, treatment might be withheld on the grounds that the danger to the environs from further exposure to the spill would be less than that resulting from a sudden change of pH such as neutralization might cause. The precise choice of pH is clearly a matter of preference, since little data is available, but at some level, this kind of thought is justified.

Figure C.5.3 is related to Figure C.5-1 and C.5-2. For a spill of a given size M, the time required for partial dispersion (to pH = 5 or pH = 10) can be read from Figure C.5-1 or C.5-2. This time is used in Figure C.5-3 to read the danger volume, that is, the volume of water whose pH is between 5 and 6 or between 9 and 10. Equations C.5-2 and C.5-8 were used to draw Figure C.5-3; C_m was taken as the value corresponding to pH = 5 (or 10) and C_d as the value corresponding to pH = 6 (or 9).

Danger volumes of spills

Figures C.5-4 and C.5-5 are obtained from equation C.5-2 (for wide rivers) for hydrogen chloride and sodium hydroxide respectively. C_d is the concentration corresponding to pH = 6 for hydrogen chloride, pH = 9 for sodium hydroxide. Appropriate conversion factors have been applied to yield spill sizes in pounds and times in hours.

Figures C.5-6 and C.5-7 are obtained from equation C.5-8 (for narrow rivers) and are analogous to Figures C.5-4 and C.5-5.

Danger volumes calculated in this manner increase with time as a spill spreads, attain a maximum, and then decrease as the center, maximum concentration falls toward a safe level. In wide rivers, this maximum volume is reached when $C_m = 2.7\ C_d$; the time required for the danger volume to return to zero after this maximum is reached is 2.7 times the time required to reach the maximum value. By this time, pH values are within 0.4 of levels considered safe (assuming a strong acid or base was spilled). What this means is that, of the whole time for which any areas are dangerous, the danger volume is increasing for 27% of the time and decreasing for 73% of the time. For narrow rivers, the principle is similar. The volume begins to decrease when $C_m = 1.6\ C_d$; at this point 38% of the time required to completely disperse the spill has elapsed. Water pH values are already within 0.2 of safe levels.

Amount of neutralizing agent

Figure C.5-8 and C.5-9 are obtained from equation C.5-5 with both spill sizes and amounts of neutralizing agent (sodium bicarbonate or sodium dihydrogen phosphate) converted to pounds. These amounts are approximate, and correspond to reduction to pH = 6 for hydrogen chloride and pH = 9 for sodium hydroxide. This is not complete neutralization to pH = 7.

Corresponding curves could be drawn from equation C.5-11 (for narrow rivers). However, for the range of spill sizes considered, for periods less than 48 hours all such lines would be straight and horizontal. Hence equation C.5-12 is adequate in this regime.

It should be noted that various factors will affect the amount of neutralizing agents used. The calculation provides a value, assuming that the entire supply of both reagents is contained in the same volume, uniformly distributed, well-mixed. Since some of the treatment agent could be misplaced, could sink and be lost, or could fail to dissolve, one might want to exceed the recommended amount. On the other hand, to lessen shock to the environs, one might want to use less than the amount suggested and apply it carefully to the worst, central region; natural dispersion will eventually take care of what remains. The decision is a matter of judgment.

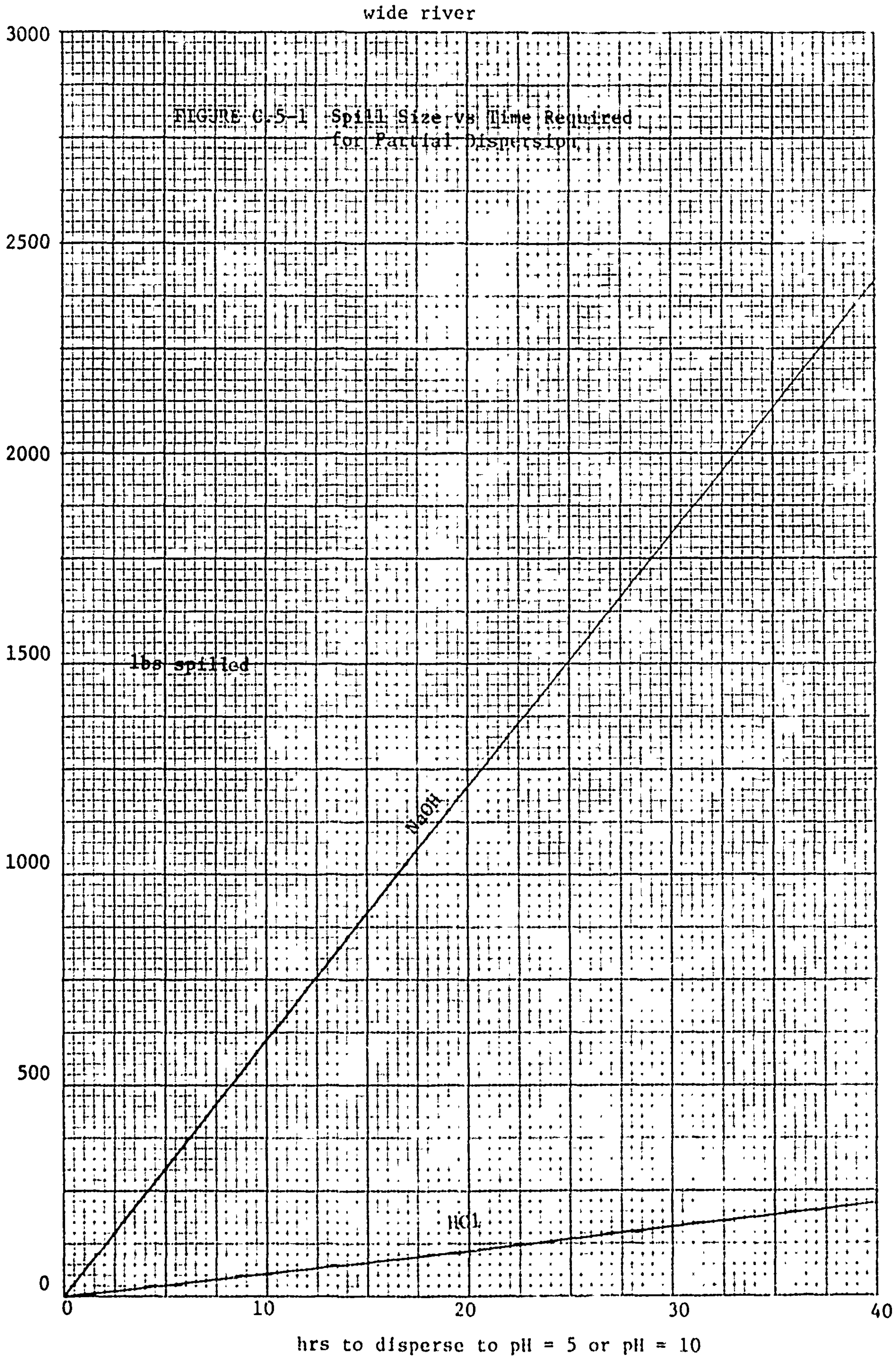


FIGURE C.5-1 Spill Size vs Time Required for Partial Dispersion

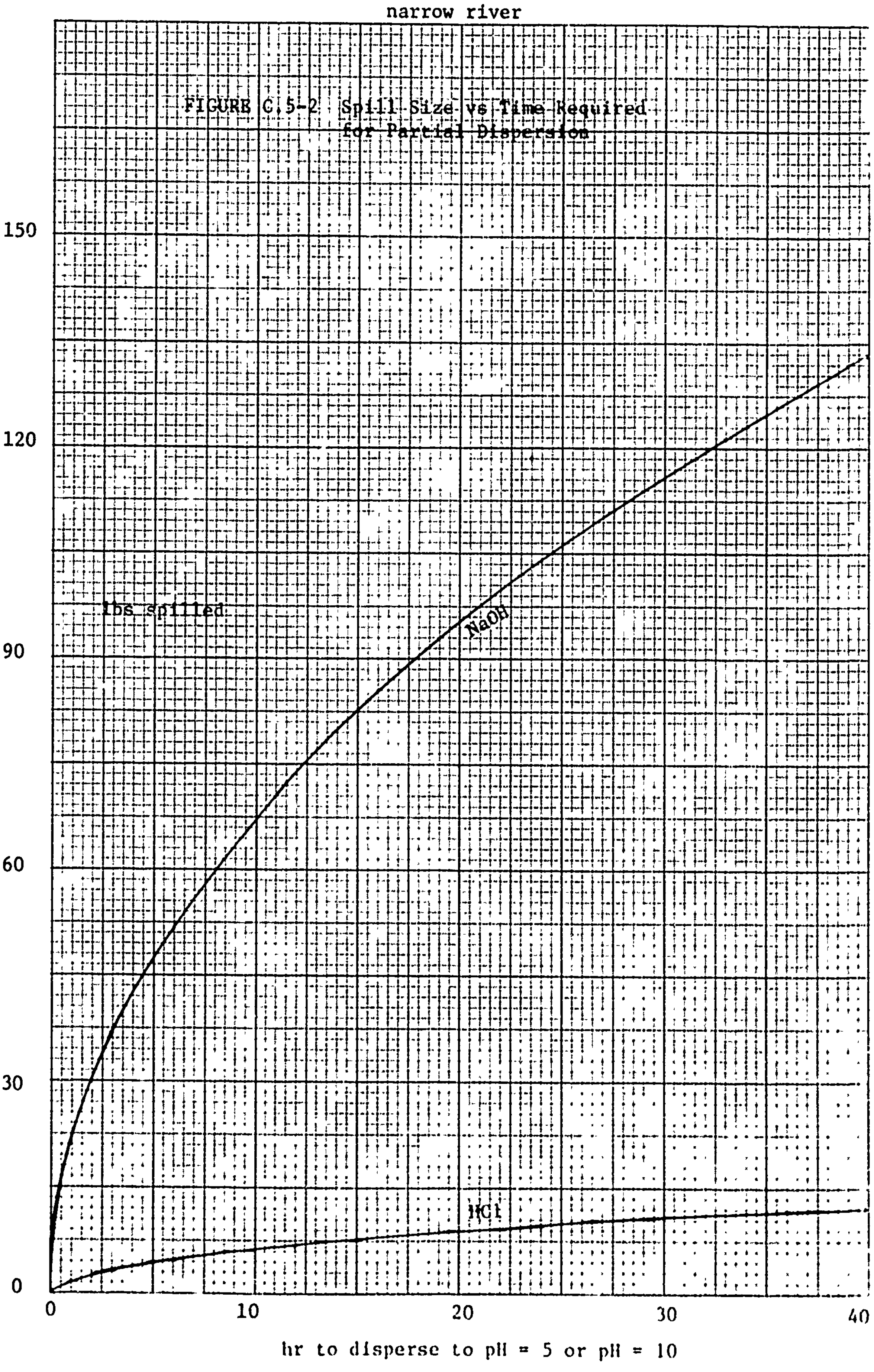


FIGURE C.5-2 Spill Size vs Time Required for Partial Dispersion

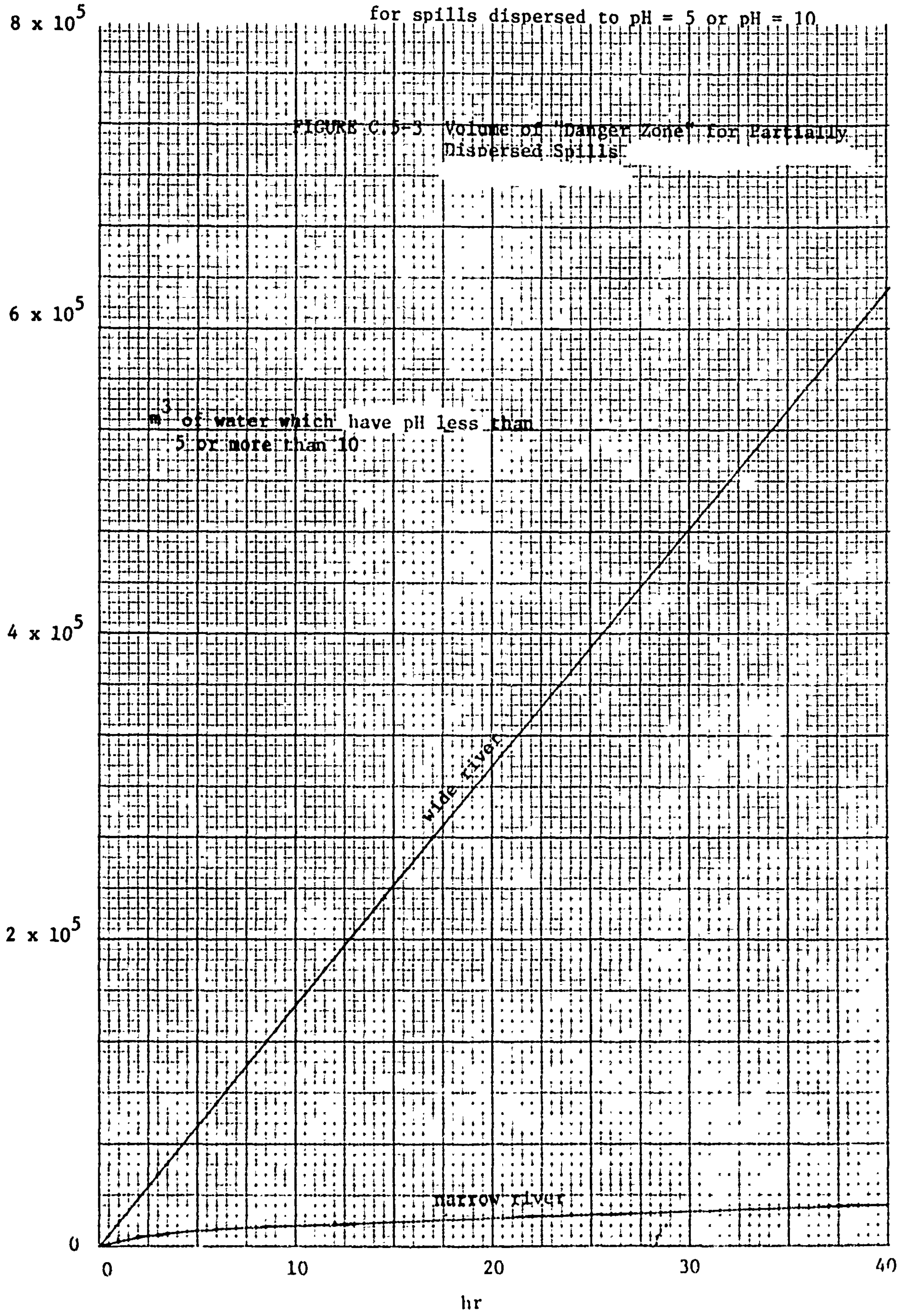


FIGURE C.5-3 Volume of "Danger Zone" for Partially Dispersed Spills

for spills dispersed to pH = 5 or pH = 10

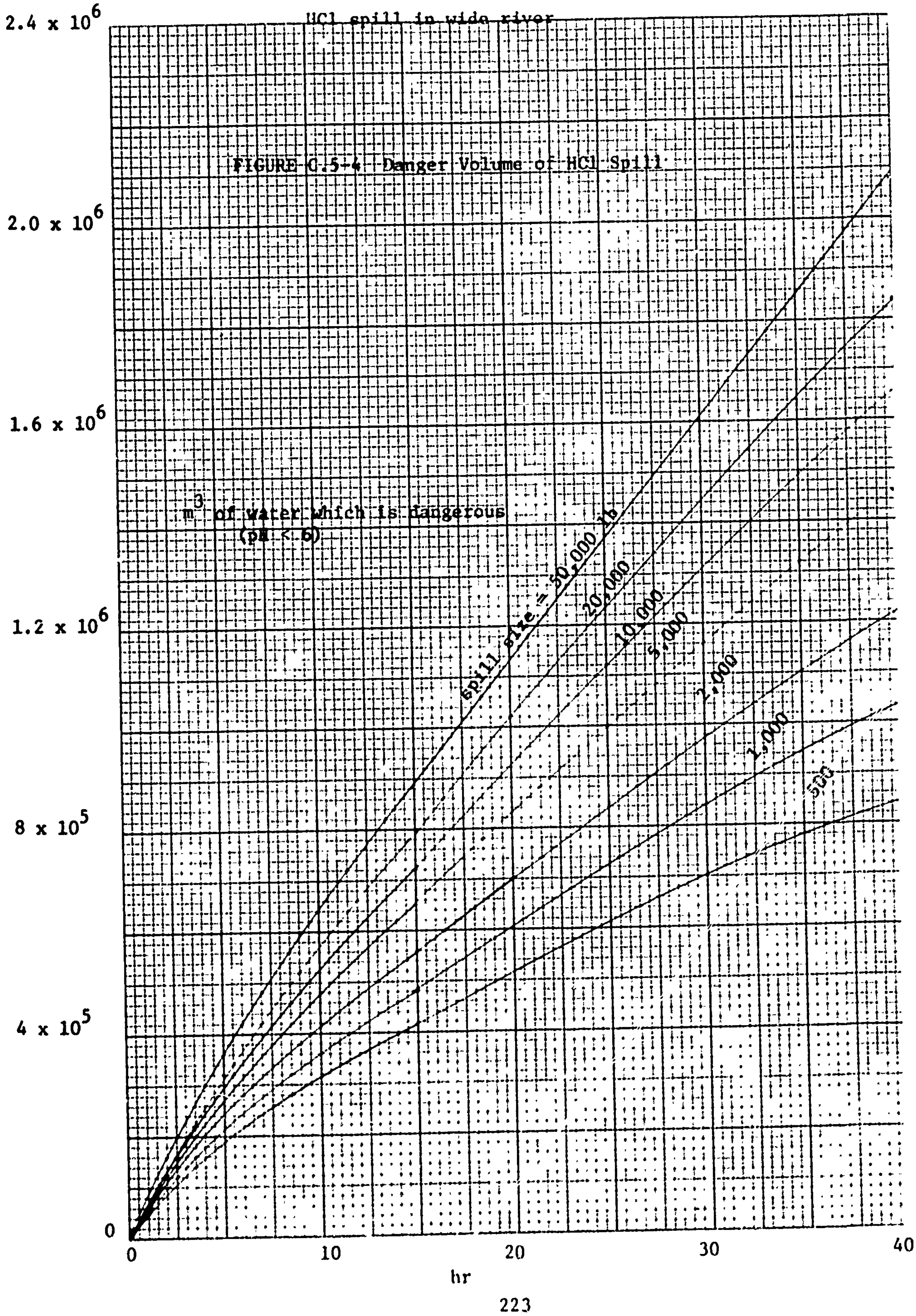


FIGURE C.5-4 Danger Volume of HCl Spill

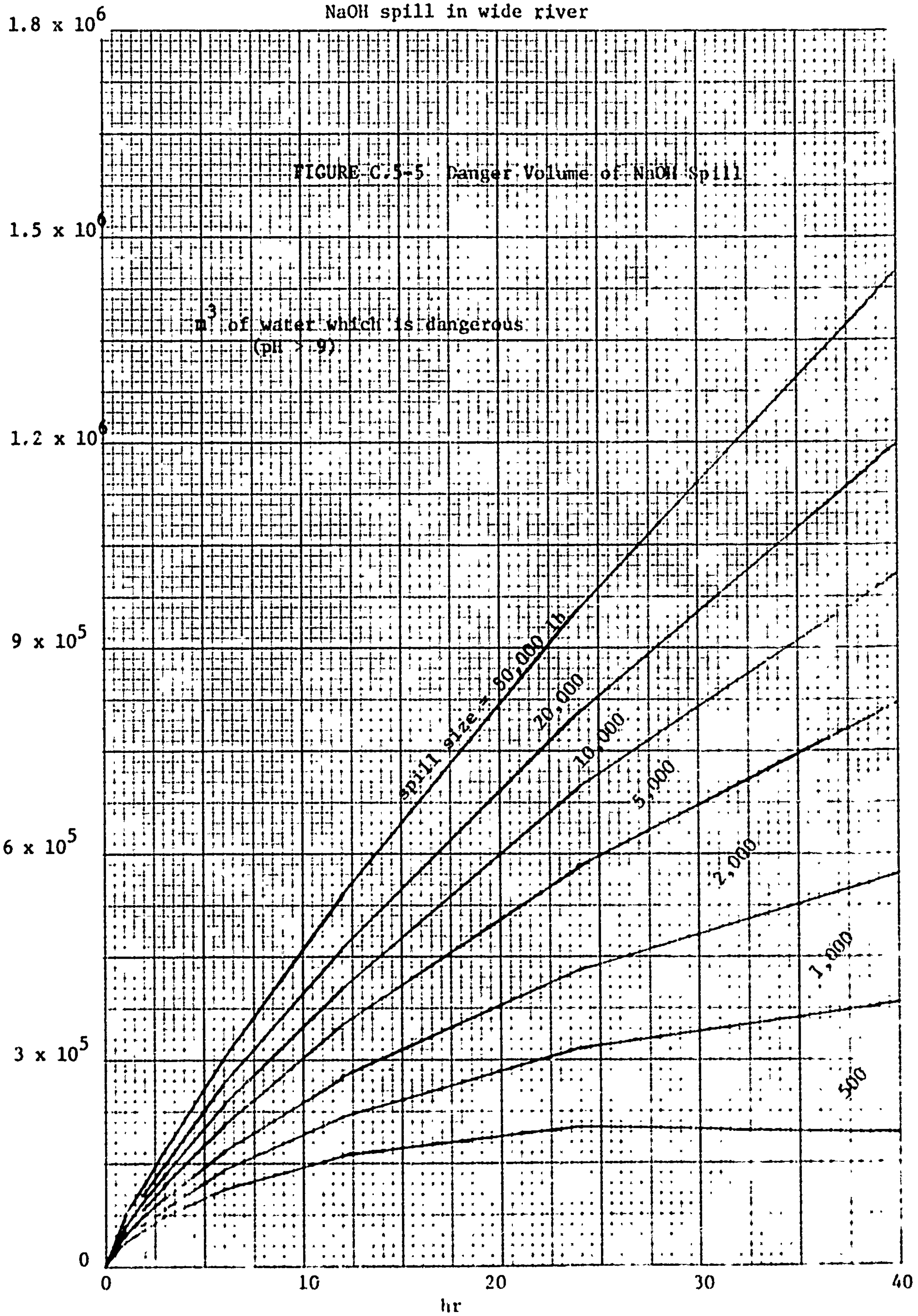


FIGURE C.5-5 Danger Volume of NaOH Spill

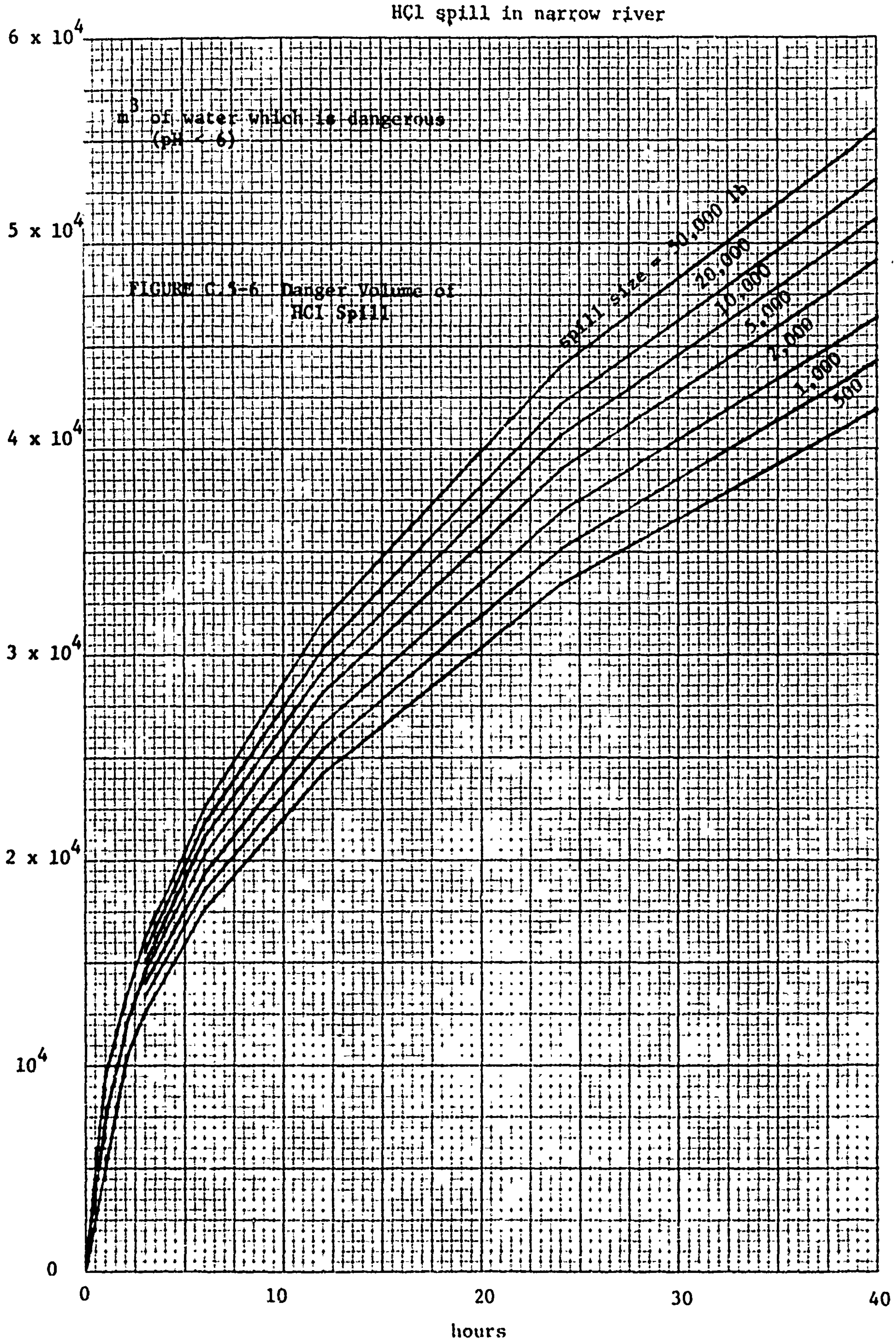


FIGURE C.5-6 Danger Volume of HCl Spill

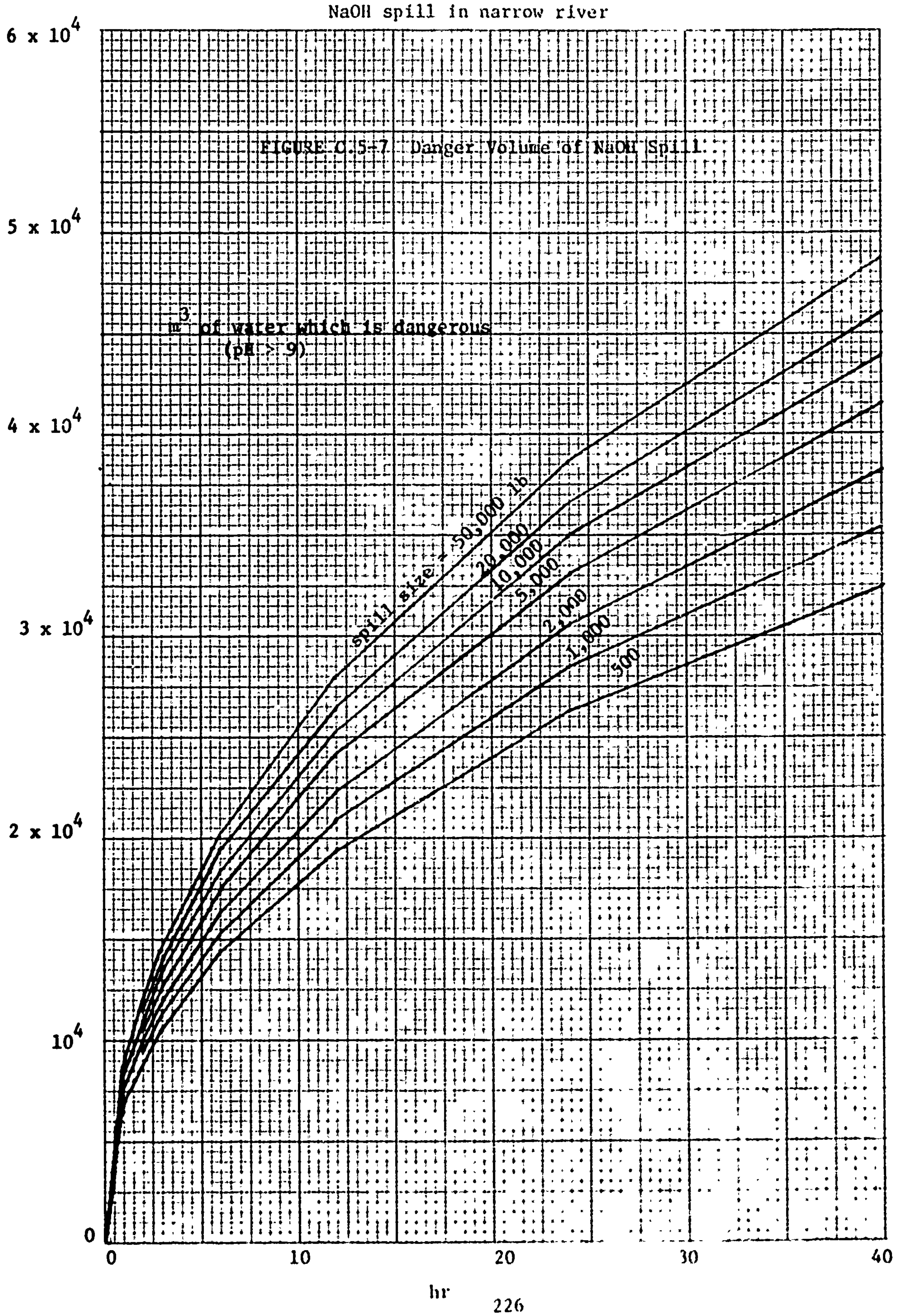


FIGURE C.5-7 Danger Volume of NaOH Spill

HCl spill in wide river

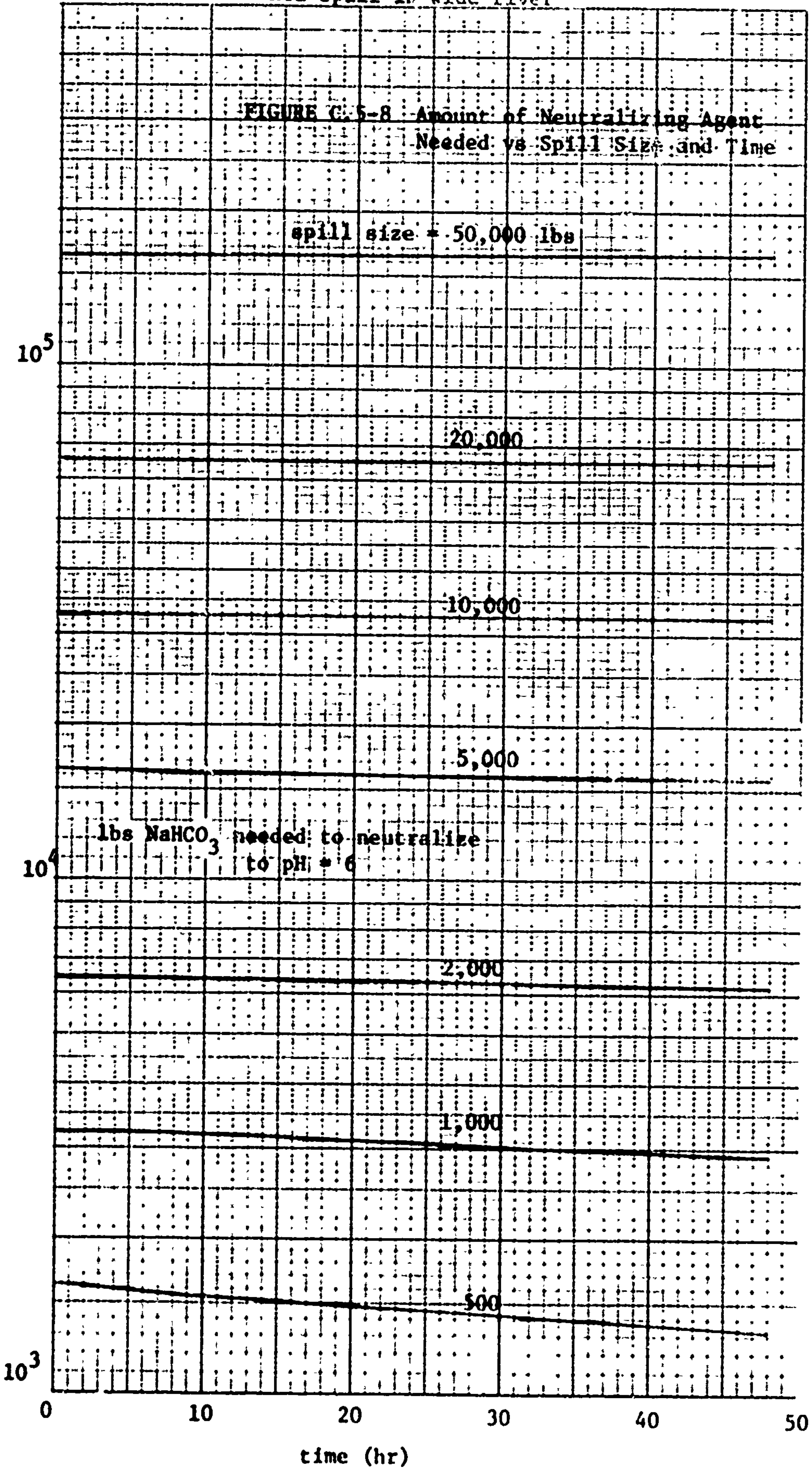


FIGURE C.5-8 Amount of Neutralizing Agent Needed vs Spill Size and Time

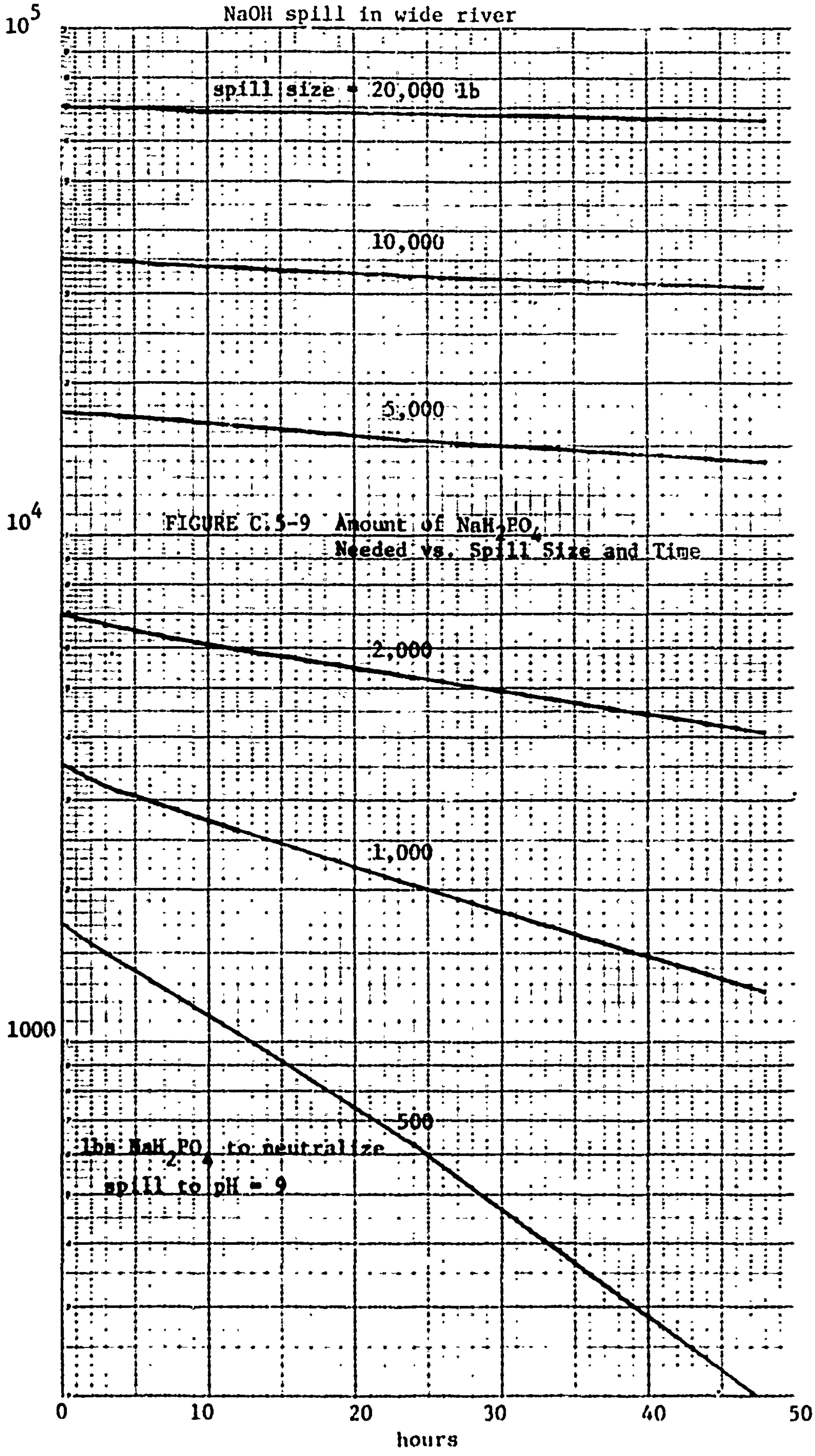


FIGURE C.5-9 Amount of NaH_2PO_4 Needed vs. Spill Size and Time

Nomenclature

Equation numbers refer to the first use of a symbol.

A	acid species	
A'	coefficient in equation C.1-6	
A_n	moles treatment needed/mole spilled	
B	base species	
b	coefficient introduced in C.1-12	
B'	coefficient in equation C.1-6	
C	concentration	gmoles/m^3
c	integration coefficient introduced in C.1-13	
C'	coefficient in equation C.1-6	
C_{ave}	average concentration	gmoles/liter
$C_{ave,n}$	average concentration of neutralizing agent	gmoles/liter
C_d	dangerous concentration	gmoles/liter
C_m	maximum concentration	gmoles/liter
d	river depth	m
e_x	x-diffusivity	m^2/s
e_y	y-diffusivity	m^2/s
e_z	z-diffusivity	m^2/s
F(z)	function in definition of erf(z)	
g	coefficient introduced in C.1-12	
G_{st}	function defined in equations C.3-1, C.3-3	
G_{wk}	function defined in equations C.3-2, C.3-4	
H^+	hydrogen ions	

K_a	acid dissociation constant	gmoles/liter
K_b	base dissociation constant	gmoles/liter
K_1	dissociation constant	gmoles/liter
K_2	dissociation constant	gmoles/liter
K_w	water dissociation constant	(gmoles/liter)^2
L	half-length of line source	m
M	charge	gmoles
$\dot{M}$	charge/unit length or charge/unit time	gmoles/m, gmoles/s
M_n	moles of neutralizing agent needed	gmoles
R_h	hydraulic radius	m
s	distance parameter introduced in C.1-4	
t	time	s
t_1	time any source begins	s
t_2	time continuous sources end	s
u	velocity	m/s
V_d	danger volume	m^3
w	river width	m
x	downstream direction	m
x_1	x-coordinate of source	m
y	cross-river direction	m
y_1	y-coordinate of source	m
z	vertical direction	m
[ ]	concentration	gmoles/liter
η	integration parameter introduced in C.1-13	
τ	time parameter introduced in C.1-10	
θ	angle from centerline	degrees

APPENDIX D: PARTITION COEFFICIENTS FOR WATER-SOLUBLE ORGANIC COMPOUNDS BETWEEN WATER AND (1) VEGETABLE OILS*, (2) OCTANOL AND (3) OLEYL ALCOHOL

The following table gives the log of the partition coefficient ("Log P"), when available, for all organic compounds considered as possible candidates for solvent extraction after a spill into water. The data have been extracted from tables given by Leo, Hansch and Elkins.

The partition coefficient (P) is the equilibrium ratio of the concentration of the solute in the solvent (vegetable oils*, octanol, or oleyl alcohol) to the concentration in water. Thus, if the concentration of a solute was equal in the solvent and water phases, P=1 and log P=0. When the solute is more concentrated in the solvent, P is greater than 1 and thus log P is positive; when the solute is more concentrated in water, P is less than 1 and log P is negative.

The following should be kept in mind when using this table:

- A blank indicates no data were available.
- "∿" indicates that two or more values appearing in the original reference have been averaged. This sign is placed <u>over</u> the number to avoid confusion with the negative (-) sign.
- A superscript "A", "B" or "C" after a value for log P (octanol) indicates that the value has been calculated, or derived, from a log P measurement with a different solvent. The method of calculation is given in the original reference.

The table is split up into two basic groups as follows:

Class I - Includes those chemicals that contain no more than one hydrophylic group.

Class II- Includes those chemicals that contain two or more hydrophylic groups.

Within each group, the chemicals are separated by chemical class (e.g., alcohols, ketones, aldehydes, etc.); within each class the chemicals are listed in order of increasing empirical formula subscripts using the order C, H, X, N, O (X=halogen).

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*The data source used did not differentiate between different types of vegetable oils used as solvents.

TABLE D-1

CLASS I

	EMPIRICAL FORMULA	LOG P VEGETABLE OILS	OCTANOL	OLEYL ALCOHOL
A. ALCOHOLS				
Methyl alcohol	CH_4O	-2.0	- .74	--
Ethyl alcohol	C_2H_6O	-1.4	- .32	-1.00
Allyl alcohol	C_3H_6O	--	-0.17	--
Isopropyl alcohol	C_3H_8O	-1.18	0.0^A	--
n-Propyl alcohol	C_3H_8O	- .85	0.34	- .45
Isobutyl alcohol	$C_4H_{10}O$	- .3	.74	--
n-Butyl alcohol	$C_4H_{10}O$	- .24	0.88	- .19
sec-Butyl alcohol	$C_4H_{10}O$	- .51	.61	--
tert-Butyl alcohol	$C_4H_{10}O$	- .65	.37	--
Isoamyl alcohol	$C_5H_{12}O$	.30	1.16	--
n-Amyl alcohol	$C_5H_{12}O$	.36	1.40	--
Methyl amyl alcohol	$C_6H_{14}O$	.88	2.03	--
Methyl isobutyl carbinol	$C_6H_{14}O$	.88	2.03	--
B. ETHERS AND ALKYLENE OXIDES				
Chlorohydrins (crude)	C_3H_5ClO	--	--	--
Propylene oxide	C_3H_6O	--	--	--
Tetrahydrofuran	C_4H_8O	--	--	--
Epichlorohyrin	C_3H_5ClO	--	--	-
C. KETONES				
Acetone	C_3H_6O	- .81	- .24	--
Methylethyl ketone	C_4H_8O	--	- .28	--
Cyclohexanone	$C_6H_{10}O$	--	.81	--
Methylisobutyl ketone	$C_6H_{10}O$	--	--	--
D. ALDEHYDES				
Acetaldehyde	C_2H_4O	--	$.43^B$	--
Propionaldehyde	C_3H_6O	--	$.38^A$	--
iso-Butyraldehyde	C_3H_8O	--	--	--

TABLE D-1 (continued)

CLASS I

(continued)

	EMPIRICAL FORMULA	LOG P		
		VEGETABLE OILS	OCTANOL	OLEYL ALCOHOL
D. ALDEHYDES (continued)				
Formaldehyde solution	$C_2H_6O_2 \cdot H_2O$	--	0.00[B]	--
Crotonaldehyde	C_4H_6O	--	--	--
n-Butyraldehyde	C_4H_8O	--	1.18[C]	--
Valeraldehyde	$C_5H_{10}O$	--	--	--
E. ESTERS				
Methyl acrylate	$C_4H_6O_2$	--	--	--
Vinyl acetate	$C_4H_6O_2$	--	--	--
Ethyl acetate	$C_4H_8O_2$	.50	.70	--
Methyl methacrylate	$C_5H_8O_2$	--	--	--
Ethyl acrylate	$C_5H_8O_2$	--	--	--
Isopropyl acetate	$C_5H_{10}O_2$	--	--	--
n-Propyl acetate	$C_5H_{10}O_2$	--	~1.5	--
n-Butyl acetate	$C_6H_{12}O_2$	--	--	--
F. ACIDS (organic)				
Formic acid	CH_2O_2	-1.84	- .54	--
Acetic acid	$C_2H_4O_2$	-1.47	- .24	--
Acrylic acid	$C_3H_4O_2$	.37	--	--
Propionic acid	$C_3H_6O_2$	- .82	.29	--
G. AMINES				
Ethyleneimine	C_2H_5N	--	--	--
Trimethylamine	C_3H_9N	--	.27	--
Diethylamine	$C_4H_{11}N$	--	~.50	--
Pyridine	C_5H_5N	- .02	.64	--
Aniline	$C_6H_5NH_2$	--	~.94	~3.5
Cyclohexylamine	$C_6H_{13}N$	--	--	--

TABLE D-1 (continued)

CLASS I

(continued)

	EMPIRICAL FORMULA	LOG P		
		VEGETABLE OILS	OCTANOL	OLEYL ALCOHOL
G. AMINES (continued)				
Triethylamine	$C_6H_{15}N$	--	1.44	--
Methylethylpyridine	$C_8H_{11}N$	--	--	--
H. NITRILES AND NITRATES				
Cyanogen bromide	CBrN	--	--	--
Nitromethane	CH_3NO_2	- .32	- .13	--
Acetonitrile	C_2H_3N	--	- .34	--
Acrylonitrile	C_3H_3N	--	- .92	--
I. HALOGENATED HYDROCARBONS				
Chloroform	$CHCl_3$	1.86	1.97	--
Dichloromethane	CH_2Cl_2	--	--	--
J. ORGANO-METALLIC SALTS				
Methanearsonic acid, sodium salts	CH_4O_3AsNa or $CH_3O_3AsNa_2 \cdot 6H_2O$	--	--	--
Sodium alkyl sulfates	$C_nH_{2n+1}O_4SNa$ $n=12-18$	--	1.60	--
Sodium alkylbenzene sulfonates	$C_{6+n}H_{2n+6}O_3SNa$ $n=12-18$	--	--	--
K. SULFUR CONTAINING				
Carbon bisulfide	CS_2	1.89	2.0^B	--
Dimethyl sulfoxide	C_2H_6SO	--	-2.03	--
Dimethyl sulfate	$C_2H_6SO_4$	--	--	--
Sulfolane	$C_4H_8SO_2$	--	--	--

TABLE D-1 (continued)

CLASS I

(continued)

	EMPIRICAL FORMULA	LOG P VEGETABLE OILS	LOG P OCTANOL	LOG P OLEYL ALCOHOL
L. PHENOLS				
Phenol	C_6H_6O	∿.74	∿1.47	∿1.21
o-Cresol	C_7H_8O	1.34	1.95	1.80
m-Cresol	C_7H_8O	∿1.25	∿1.98	1.79
p-Cresol	C_7H_8O	1.21	∿1.93	1.80

TABLE D-2

CLASS II

		LOG P		
	EMPIRICAL FORMULA	VEGETABLE OILS	OCTANOL	OLEYL ALCOHOL
A. ALCOHOL-AMINES				
Monoethanolamine	C_2H_7NO	--	-1.31	--
Ethylene cyanohydrin	C_3H_5NO	--	$-\tilde{1}.19$	--
Monoisopropanolamine	C_3H_9NO	--	-0.96	--
Acetone cyanohydrin	C_4H_7NO	--	--	--
Diethanolamine	$C_4H_{11}NO_2$	--	-1.43	--
Aminoethanolamine	$C_4H_{12}N_2O$	--	--	--
Diisopropanolamine	$C_6H_{15}NO_2$	--	-0.82	--
Triethanolamine	$C_6H_{15}NO_3$	--	$-\tilde{1}.53^B$	--
B. DIOLS AND POLYOLS				
Ethylene glycol	$C_2H_6O_2$	-3.31	-1.93	--
1,4-Butanediol	$C_3H_8O_2$	-2.68	$-\tilde{1}.30^A$	--
Propylene glycol	$C_3H_8O_2$	-2.77	$-\tilde{1}.35^A$	--
Glycerine	$C_3H_8O_3$	-4.15	$-\tilde{2}.56$	--
1,4-Butynediol	$C_4H_6O_2$	--	--	--
1,4-Butenediol	$C_4H_8O_2$	--	--	--
Dextrose solution	$C_6H_{12}O_6$	--	-3.29^C	--
Hexylene glycol	$C_6H_{14}O_2$	--	$-.14^A$	--
Sorbitol	$C_6H_{14}O_6$	--	-3.10^C	--
Corn Syrup	*	--	--	--
C. ALCOHOL-ETHERS				
Ethylene glycol monomethyl ether	$C_3H_8O_2$	-2.25	$-.\tilde{7}1^A$	--
Ethylene glycol monoethyl ether	$C_4H_{10}O_2$	$-\tilde{1}.43$	-.54	--
Propylene glycol methyl ether	$C_4H_{10}O_2$	--	--	--
Diethylene glycol	$C_4H_{10}O_3$	--	-1.98^A	--

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*Water solution of dextrose, maltose, and other chemicals

TABLE D-2 (continued)

CLASS II

(continued)

	EMPIRICAL FORMULA	LOG P VEGETABLE OILS	 OCTANOL	 OLEYL ALCOHOL
C. ALCOHOL-ETHERS (continued)				
Ethylene glycol monomethyl ether acetate	$C_5H_{12}O_3$	--	--	--
Diethylene glycol monomethyl ether	$C_5H_{12}O_3$	-2.38	-1.04^A	--
Triethylene glycol	$C_6H_{10}O_4$	--	$-.\tilde{1}7^A$	--
Dipropylene glycol	$C_6H_{12}O_3$	-2.70	$-\tilde{1}.20^A$	--
Ethylene glycol monobutyl ether	$C_6H_{14}O_2$	--	--	--
Diethylene glycol dimethylether	$C_6H_{14}O_3$	--	--	--
Diethylene glycol monoethylether	$C_6H_{14}O_3$	-2.22	$-.\tilde{8}6^A$	--
Ethoxytriglycol	$C_8H_{20}O_4$	--	--	--
Ethoxylated tridecanol	$C_{25}H_{52}O_7$ (typical)	--	--	--
Ethoxylated dodecanol	$C_{30}H_{62}O_{10}$ (typical)	--	--	--
Ethoxylated tetradecanol	$C_{36}H_{74}O_{12}$ (typical)	--	--	--
Ethoxylated pentadecanol	$C_{37}H_{76}O_{12}$ (typical)	--	--	--
Polypropylene glycol methyl ether	$C_{3n+1}H_{6n+4}O_{n+1}$	--	--	--
D. DI-TRI-POLY AMINES				
Urea	CH_4N_2O	-3.82	$-\tilde{2}.85^A$	--
1,1-Dimethylhydrazine	$C_2H_8N_2$	--	--	--
Ethylenediamine	$C_2H_8N_2$	--	--	--
Diethylenetriamine	$C_4H_{13}N_3$	--	--	--
Hexamethylenetetramine	$C_6H_{12}N_4$	-3.86	$-\tilde{2}.20$	--
Hexamethylenediamine	$C_6H_{16}N_3$	--	--	--
Tiethylenetetramine	$C_6H_{18}N_4$	--	-1.66^C	--

TABLE D-2 (continued)

CLASS II

(continued)

	EMPIRICAL FORMULA	LOG P VEGETABLE OILS	 OCTANOL	 OLEYL ALCOHOL
E. DIACIDS				
Oxalic acid	$C_2H_2O_4$	--	$-.66^{A}$	--
Maleic acid	$C_4H_4O_4$	--	$-.57^{A}$	-0.89
F. OTHER CHEMICALS CONTAINING 2 OR MORE HYDROPHYLIC GROUPS				
Dimethylformamide	C_3H_7NO	-2.31	$-.59^{B}$	--
1,4 Dioxane	$C_4H_8O_2$	--	- .42	--
Morpholine	C_4H_9NO	--	-1.08	--
Furfural	$C_5H_4O_2$	--	--	--
Diacetone alcohol	$C_6H_{12}O_2$	--	--	--
Paraformaldehyde	$C_nH_{2n+2}O_{n+1}$ $n \cong 30$	--	--	--

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