

STAFF REPORT

THE

DESIGNATED LEVEL

METHODOLOGY

FOR

WASTE CLASSIFICATION

AND

CLEANUP LEVEL DETERMINATION

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CALIFORNIA REGIONAL
WATER QUALITY CONTROL BOARD
CENTRAL VALLEY REGION

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THE DESIGNATED LEVEL METHODOLOGY FOR WASTE CLASSIFICATION AND CLEANUP LEVEL DETERMINATION

EXECUTIVE SUMMARY

Improper waste disposal practices and sites which have been contaminated with toxic substances pose significant threats to the quality of California's useable ground and surface water resources. This report shows, from a water quality perspective, 1) how to classify various wastes so that appropriate disposal practices may be selected, and 2) how to determine the degree to which a contaminated site should be cleaned or to which remedial action is necessary ("how clean is clean"), and 3) how these two decision-making processes are related.

In California, the classification of wastes and the establishment of cleanup levels for sites which have been contaminated with toxic chemicals are performed by two separate State agencies with separate regulatory authority. The Department of Health Services (DHS) classifies wastes as 'hazardous' or 'restricted hazardous' and sets site cleanup/mitigation criteria based on a direct threat of these wastes or sites to public health. The State Water Resources Control Board together with the nine Regional Water Quality Control Boards classify wastes as 'designated', 'nonhazardous solid' or 'inert' and determine cleanup levels based on the threat that wastes and contaminated sites pose to the beneficial uses of waters of the State, as required by the Porter-Cologne Water Quality Control Act (contained in Division 7 of the California Water Code).

Regulations administered by these agencies clearly state, using detailed criteria, how wastes are to be classified with the exception of the 'designated waste' category. The lower boundary of this category is described only as the limit above which a waste could impair water quality at the site of discharge. This boundary can be more clearly defined by establishing "Designated Levels" for specific constituents of a waste which provide a site-specific indication of the water quality impairment potential of the waste. This report provides a methodology for calculating such levels. Designated Levels are calculated by first determining the bodies of water that may be affected by a waste and the present and probable future beneficial uses of these waters. Next, site-specific "water quality goals" are selected, based on background water quality or accepted criteria and standards, to protect those beneficial uses. Finally, these water quality goals are multiplied by factors which account for environmental attenuation and leachability. The result is a set of Soluble and Total Designated Levels which are applicable to a particular waste and disposal site and which, if not exceeded, should protect the beneficial uses of waters of the State. Wastes having constituent concentrations in excess of these Designated Levels are assumed to pose a threat to water quality and are, therefore, classified as 'designated wastes' and directed to waste management units which isolate these wastes from the environment.

In 1986, DHS released a document entitled The California Site Mitigation Decision Tree Manual²⁵ which presents a detailed methodology for determining cleanup/mitigation levels for sites contaminated with toxic substances. The object of this methodology is to

prevent toxicologic impacts on humans and other potential “biological receptors of concern”. While sufficient to cover DHS’s interests in site cleanups, this methodology is not designed to protect all present and probable future beneficial uses of waters that may be adversely impacted by the contaminants. It can be shown that the threat posed to water quality by contaminated soils is closely related to that posed by wastes in an unlined landfill. As such, the Designated Level Methodology can be used to select cleanup levels which will protect the quality of nearby ground and surface waters. As always, the background concentrations of contaminants must be factored into the cleanup level setting process.

When combined with the waste classification and cleanup level setting processes of DHS and the State Water Board’s Subchapter 15 regulations, the Designated Level Methodology can provide a complimentary set of procedures to ensure the protection of both the public health and the quality of useable waters of California.

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Chapter 1 PURPOSE

This report is intended to provide information and suggested procedures to be used in addressing the complex issues of waste classification and cleanup level determination from a purely water quality-based point of view. Currently available procedures of State and Federal regulatory agencies are insufficient to protect all present and probable future beneficial uses of waters of California from waste disposal and contaminated site cleanup / mitigation activities, as required by the Porter-Cologne Water Quality Control Act and policies and regulations of the State Water Resources Control Board. The procedures presented herein are not intended to supersede the authority or procedures of other regulatory agencies in these areas, but should complement them in a manner consistent with beneficial use protection. The Department of Health Services, the Department of Fish & Game, and the Air Resources Board should also be consulted with respect to human health, fish and wildlife, and air quality impacts of waste disposal and site cleanup activities. Appropriate local agencies should also be contacted for concurrence with decisions made in these areas.

Our knowledge of the environmental fate and impact of chemicals on the quality of our water resources is constantly evolving. The methodology presented in this report for defining the lower boundary of the 'designated waste' classification and 'how-clean-is-clean', from a water quality perspective, reflects our current level of understanding of these complex subjects and contains sufficient flexibility to permit modifications as our knowledge increases. The Designated Level Methodology will periodically be refined and updated to account for the evolution of our understanding of environmental fate processes and the effects of chemicals on water quality.

Chapter 2 WASTE CLASSIFICATION

Two State agencies share responsibility for the classification of wastes in California: 1) the Department of Health Services and 2) the State Water Resources Control Board together with the nine Regional Water Quality Control Boards. These agencies classify wastes according to regulations contained in Title 22 of the California Code of Regulations (CCR), Division 4, Chapter 30, "Minimum Standards for Management of Hazardous and Extremely Hazardous Wastes" ¹ and Title 23, CCR, Chapter 3, Subchapter 15, "Discharges of Waste to Land", ² respectively. Classifications used by DHS reflect that agency's mandate to protect public health, while classifications used by the Water Boards are designed to implement their mandate to protect present and probable future beneficial uses of water. Based on these two classification schemes, the State determines proper methods for disposal for each type of waste generated in California. Figure 1 summarizes the two waste classification schemes and the resulting selections of appropriate waste management units for the classified wastes.

Under the waste management regulations contained in Titles 22 and 23, DHS determines whether a waste is 'restricted hazardous' or 'hazardous', while classification of a waste as 'designated', 'nonhazardous solid', or 'inert' is performed by the Water Boards. The relationships between regulatory decisions, waste classifications, and disposal options are shown in Figure 2.

Figure 1
WASTE AND UNIT CLASSIFICATIONS USED IN CALIFORNIA

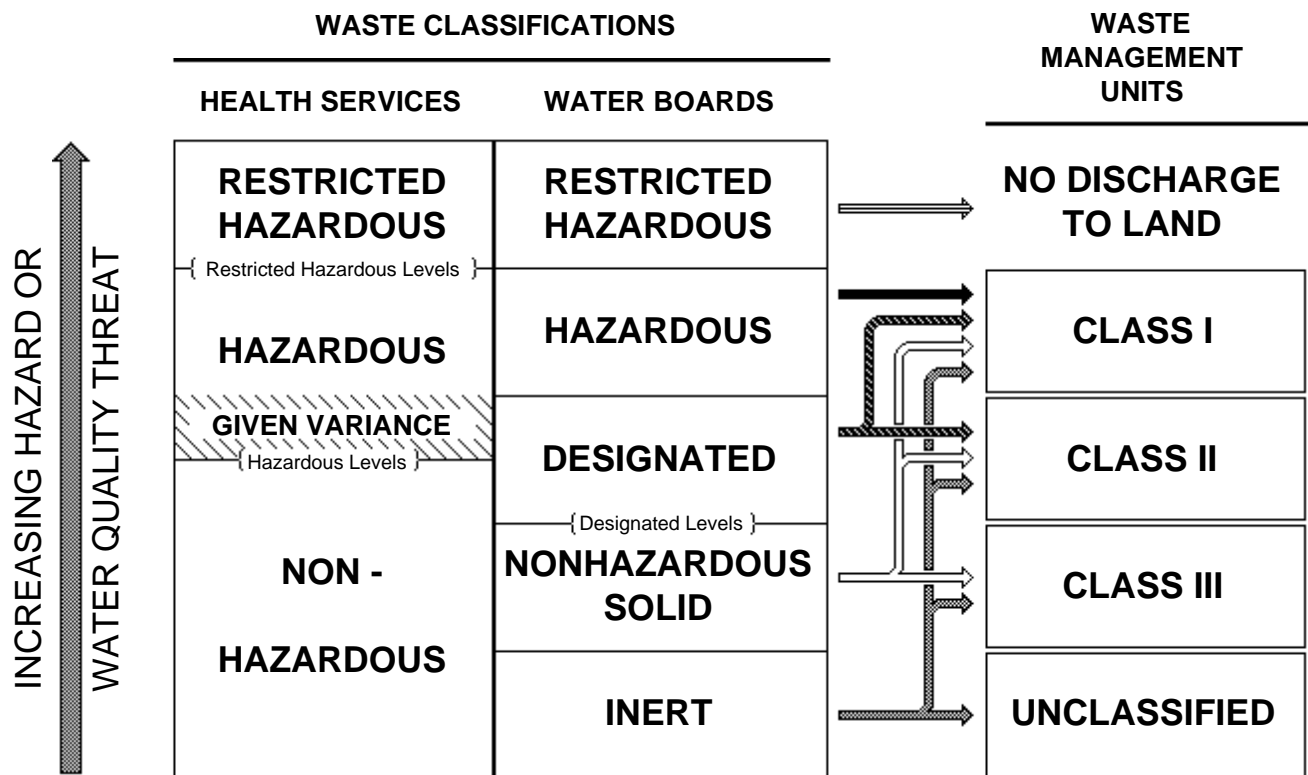


Figure 2

WASTE CLASSIFICATIONS AND DISPOSAL OPTIONS UNDER TITLE 23, CCR, CHAPTER 3, SUBCHAPTER 15

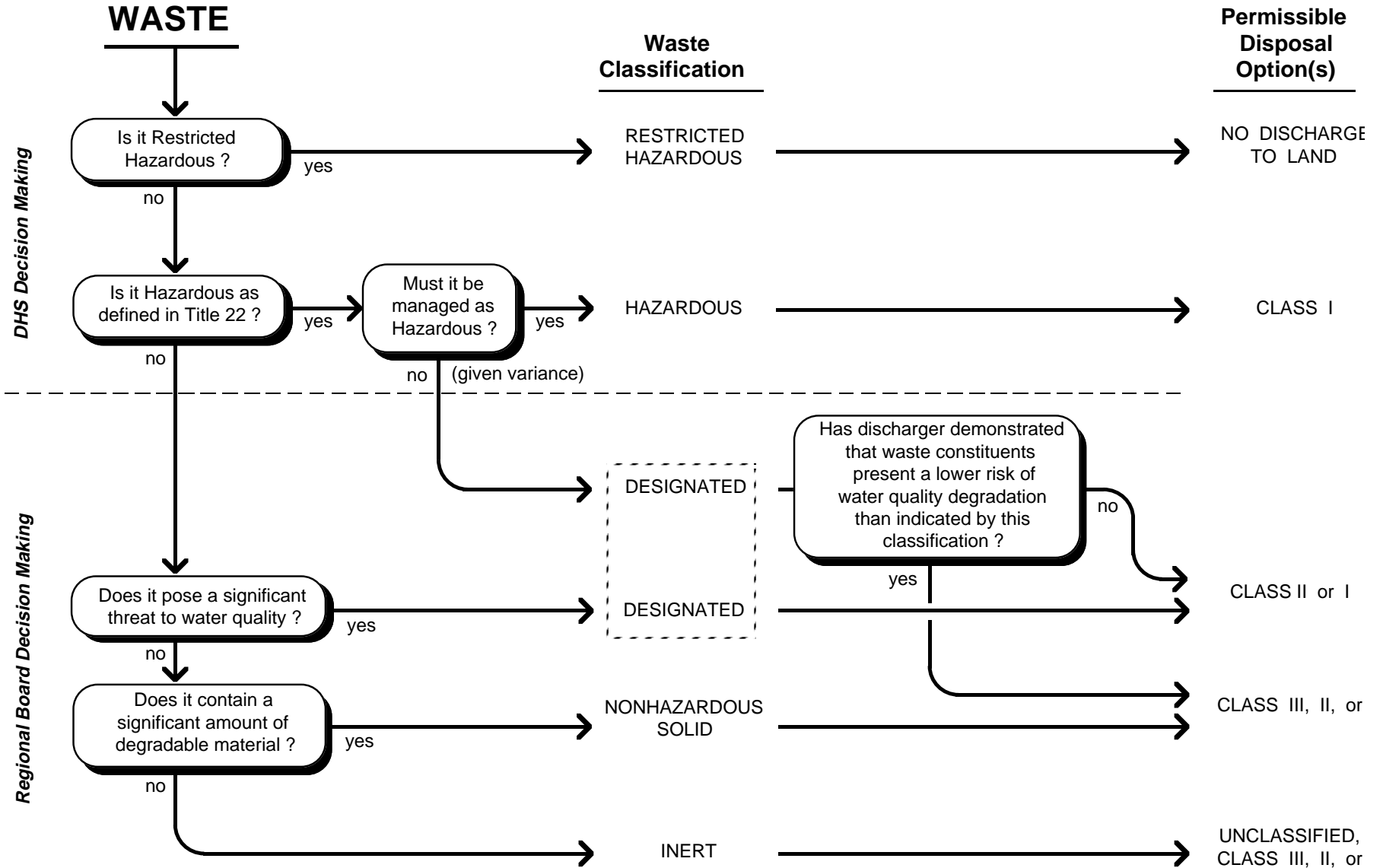


Figure 3

CALIFORNIA LAND DISPOSAL RESTRICTIONS

<u>RESTRICTED HAZARDOUS WASTES</u>	<u>RESTRICTION DATE</u>
<ul style="list-style-type: none"> • Liquids containing Free Cyanides <ul style="list-style-type: none"> ≥ 1000 mg/l 	1 June 1983
<ul style="list-style-type: none"> • Liquids containing Dissolved Metals <ul style="list-style-type: none"> ≥ the following limits : <li style="padding-left: 40px;">Arsenic 500 mg/l <li style="padding-left: 40px;">Cadmium 100 mg/l <li style="padding-left: 40px;">Chromium (VI) 500 mg/l <li style="padding-left: 40px;">Lead 500 mg/l <li style="padding-left: 40px;">Mercury 20 mg/l <li style="padding-left: 40px;">Nickel 134 mg/l <li style="padding-left: 40px;">Selenium 100 mg/l <li style="padding-left: 40px;">Thallium 130 mg/l 	1 January 1984
<ul style="list-style-type: none"> • Liquids having a pH ≤ 2.0 (acidic) 	1 January 1984
<ul style="list-style-type: none"> • Liquids containing PCBs ≥ 50 mg/l 	1 January 1984
<ul style="list-style-type: none"> • The following wastes containing Halogenated Organics <ul style="list-style-type: none"> ≥ 1000 mg/kg (total) : <li style="padding-left: 40px;">Liquids <li style="padding-left: 40px;">Organic Sludges and Solids 	1 January 1985 8 July 1989

2.1 'Restricted Hazardous Wastes'

Wastes which pose the greatest threat to human health and the environment fall into the category of 'restricted hazardous wastes' and may not be discharged to any landfill, waste pile, surface impoundment, or land treatment unit after the restriction dates shown in Figure 3.¹ Article 15 of the hazardous waste management regulations, beginning with §66900 of Title 22, CCR, defines these wastes by listing specific chemical concentrations (Restricted Hazardous Levels) above which a waste is 'restricted hazardous' (see Figures 1 and 3). Any 'restricted hazardous waste' must be treated to below Restricted Hazardous Levels prior to discharge to a waste management unit.

2.2 'Hazardous Wastes'

A waste may be classified as 'hazardous' by any of several means. Article 9, §66680(d) and (e), of the hazardous waste management regulations¹ provides lists of wastes and waste constituents (List of Common Names and List of Chemical Names). Any waste listed in the List of Common Names or any waste containing constituents listed in the List of Chemical Names is presumed to be a 'hazardous waste' unless shown to be otherwise by means of criteria contained in Article 11. ['Restricted hazardous wastes' and 'extremely hazardous wastes' are subsets of 'hazardous wastes' under these regulations. 'Extremely hazardous wastes' are not discussed further in this report.]

Article 11 of the hazardous waste management regulations, beginning with §66693, establishes criteria in four areas — toxicity, ignitability, reactivity, and corrosivity. A waste meeting any of these criteria is considered to be 'hazardous' by DHS. The toxicity criteria, summarized in Figure 4, include acute oral, dermal, inhalation and fish toxicity, carcinogenicity, and compound specific toxicity. The carcinogenicity criteria include a list of compounds for which the combined concentration in a waste exceeding 0.001 percent by weight (10 mg/kg or 10 ppm) makes the waste 'hazardous'. These compounds are:

2-Acetylaminofluorene (2-AAF)	4-Dimethylaminoazobenzene (DAB)
Acrylonitrile	Ethyleneimine (EL)
4-Aminodiphenyl	a-Naphthylamine (1-NA)
Benzidine and its salts	b-Naphthylamine (2-NA)
bis (Chloromethyl) ether (BCME)	4-Nitrobiphenyl (4-NBP)
Methyl chloromethyl ether	N-Nitrosodimethylamine (DMN)
1,2-Dibromo-3-chloropropane (DBCP)	b-Propiolactone (BPL)
3,3'-Dichlorobenzidine and its salts (DCB)	Vinyl Chloride (VCM)

The regulations include other carcinogenicity criteria in addition to this list of compounds.

The compound-specific toxicity criteria include concentration limits for several "persistent and bioaccumulative" toxic substances. The limits are called Soluble Threshold Limit Concentrations (STLCs) and Total Threshold Limit Concentrations (TTLCs) shown in Figures 5 and 6. A **solid** waste is 'hazardous' if any of the **extractable** concentrations of its toxic constituents (in mg/l of extract) equals or exceeds the STLC and/or any of the **total** concentrations of its toxic constituents (in mg/kg of waste) equals or exceeds the TTLC. The Waste Extraction Test (WET) is used to determine extractable concentrations of toxic constituents in a waste, expressed in milligrams per liter (mg/l) of extract. The full WET procedure (§66700 of Title 22, CCR) may be found in Appendix I to this report. A **liquid** waste is hazardous if any of the **total** concentrations of its toxic constituents (in mg/l of waste) exceeds the STLC. All concentrations are expressed on a wet-weight basis (as the waste is to be discharged).

Once a waste is classified as 'hazardous' under the Title 22 regulations, it must be managed as a 'hazardous waste' — discharged only to a Class I waste management unit — unless the waste generator or handler is able to demonstrate to DHS that Class I containment is not necessary to protect public health from the particular waste. The Alternative Technology

Figure 4

HAZARDOUS WASTE TOXICITY CRITERIA

ACUTE ORAL TOXICITY CRITERION:

acute oral LD50 < 5,000 mg/kg body weight

ACUTE DERMAL TOXICITY CRITERION:

acute dermal LD50 < 4,300 mg/kg body weight

ACUTE INHALATION TOXICITY CRITERION:

acute inhalation LD50 < 10,000 ppm in air

ACUTE FISH TOXICITY TEST:

aquatic 96-hour LC50 < 500 mg/l of water

CARCINOGENICITY:

sum of listed carcinogens > 10 ppm

COMPOUND SPECIFIC TOXICITY:

extractable concentrations >

Soluble Threshold Limit Concentrations (STLCs)

and/or

total concentrations >

Total Threshold Limit Concentrations (TTLCs)

Section of DHS (916/322-2822 or ATSS 492-2822) determines whether variances may be granted for these wastes. If not granted such a variance, the waste is also classified as a 'hazardous waste' under the Water Boards' Subchapter 15 regulations² which permit discharge only to a Class I waste management unit (see Figures 1 and 2). Such units are required by the regulations to isolate the waste from the surrounding environment through both natural and engineered controls.

If DHS grants a Title 22 'hazardous waste' a variance from being managed as 'hazardous', Subchapter 15 defines that waste as a 'designated waste'. Thus, the same waste may be classified as 'hazardous' under Title 22 and as 'designated' under Title 23.

Figure 5

**DEPARTMENT OF HEALTH SERVICES CRITERIA
FOR INORGANIC CONSTITUENTS OF HAZARDOUS WASTES**

SUBSTANCE	THRESHOLD LIMIT CONCENTRATION	
	SOLUBLE (STLC) mg/l in extract	TOTAL (TTLC) wet wt. mg/kg
Antimony and/or Antimony Compounds	15	500
Arsenic and/or Arsenic Compounds	5.0	500
Asbestos	—	1.0%
Barium and/or Ba Compounds (excl. Barite)	100	10,000
Beryllium and/or Beryllium Compounds	0.75	75
Cadmium and/or Cadmium Compounds	1.0	100
Chromium (VI) Compounds	5	500
Chromium and/or Chromium (III) Compounds	560	2,500
Cobalt and/or Cobalt Compounds	80	8,000
Copper and/or Copper Compounds	25	2,500
Fluoride Salts	180	18,000
Lead and/or Lead Compounds (inorganic)	5.0	1,000
Mercury and/or Mercury Compounds	0.2	20
Molybdenum and or Molybdenum Compounds	350	3,500
Nickel and/or Nickel Compounds	20	2,000
Selenium and/or Selenium Compounds	1.0	100
Silver and/or Silver Compounds	5	500
Thallium and/or Thallium Compounds	7.0	700
Vanadium and/or Vanadium Compounds	24	2,400
Zinc and/or Zinc Compounds	250	5,000

2.3 'Designated Wastes'

As defined in §2522 of the Subchapter 15 regulations, 'designated waste' is either of the following:

- "1) nonhazardous waste which consists of or contains pollutants which, under ambient environmental conditions at the waste management unit, could be released at concentrations in excess of applicable water quality objectives, or could cause degradation of waters of the state.

Figure 6

**DEPARTMENT OF HEALTH SERVICES CRITERIA
FOR ORGANIC CONSTITUENTS OF HAZARDOUS WASTES**

SUBSTANCE	THRESHOLD LIMIT CONCENTRATION	
	SOLUBLE (STLC) mg/l in extract	TOTAL (TTLC) wet wt. mg/kg
Aldrin	0.14	1.4
Chlordane	0.25	2.5
DDT, DDE, DDD	0.1	1.0
2,4-Dichlorophenoxyacetic Acid (2,4-D)	10	100
Dieldrin	0.8	8.0
Dioxin (2,3,7,8-TCDD)	0.001	0.01
Endrin	0.02	0.2
Heptachlor	0.47	4.7
Kepone	2.1	21
Lead Compounds, Organic	—	13
Lindane	0.4	4.0
Methoxychlor	10	100
Mirex	2.1	21
Pentachlorophenol	1.7	17
Polychlorinated Biphenyls (PCBs)	5.0	50
Toxaphene	0.5	5
Trichloroethylene (TCE)	204	2,040
2,4,5-Trichlorophenoxypropionic Acid	1.0	10

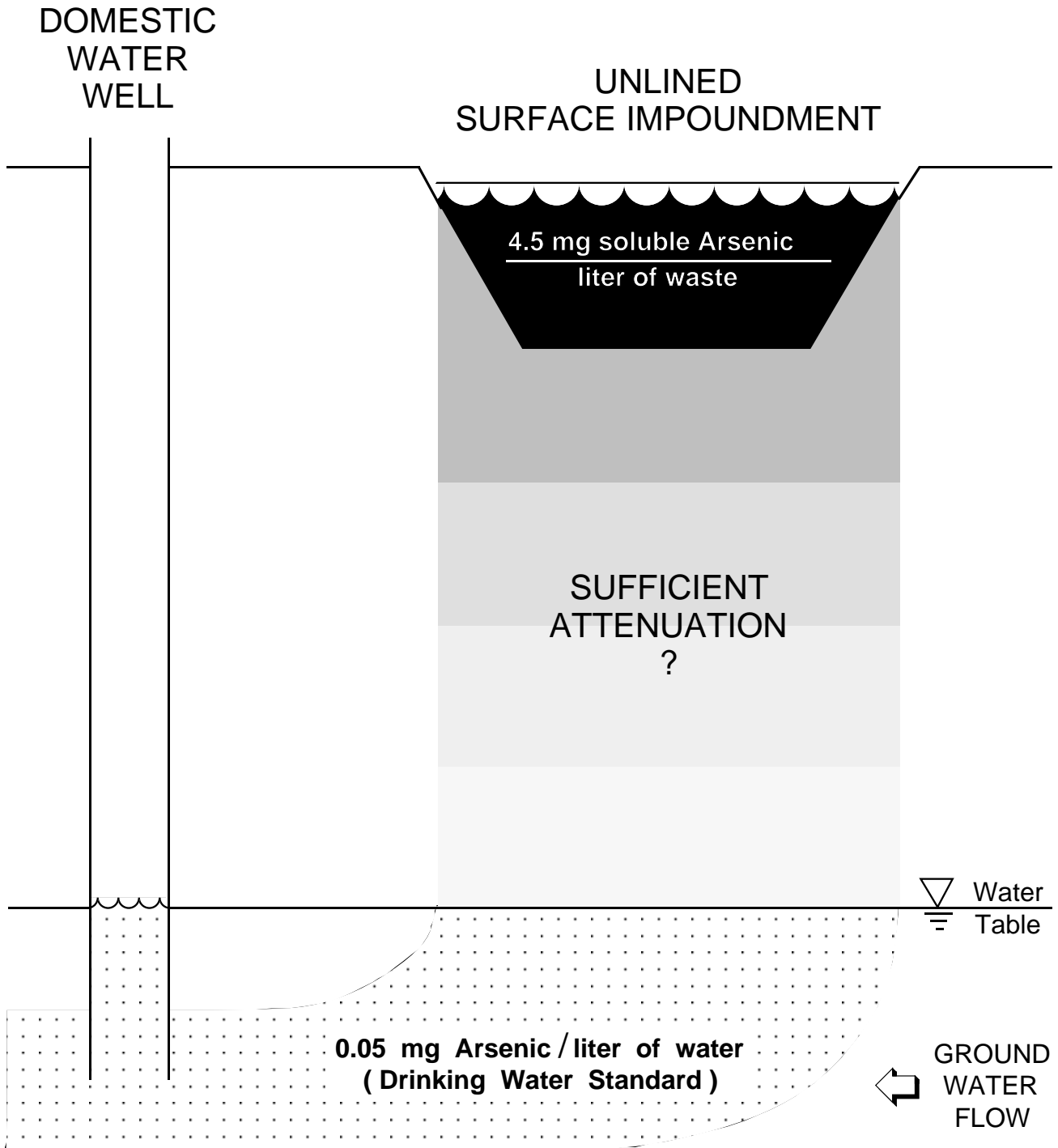
“2) hazardous waste which has been granted a variance from hazardous waste management requirements pursuant to Section 66310 of Title 22 of this code.”

The granting of variances for hazardous wastes was discussed in Section 1.2 above. However, a waste also becomes ‘designated’ is if it is not ‘hazardous’ but still poses a threat to water quality at the site of disposal. An example will clarify this point.

Figure 7 shows a situation in which a liquid waste containing 4.5 mg/l of arsenic is discharged to an unlined surface impoundment over ground water that may be used for domestic supply. The hazardous STLC for arsenic is 5 mg/l, so the waste is not ‘hazardous’ under Title 22. The drinking water standard for arsenic is 0.05 mg/l. Ground water above that level could cause adverse health effects if consumed over a prolonged

Figure 7

THE NEED FOR SITE-SPECIFIC 'DESIGNATED WASTE' CLASSIFICATION



period of time. As the liquid waste percolates through the soil, its arsenic concentration will be reduced by various attenuative mechanisms, such as adsorption and precipitation. If these mechanisms are not capable of reducing the arsenic concentration sufficiently (high permeability soils and/or insufficient separation between the waste and ground water), enough arsenic will enter ground water to cause the drinking water standard to be exceeded. Its beneficial use for domestic supply would be impaired. In this situation the waste would be classified as a 'designated waste'.

It can be seen from the example above that: 1) the classification of a waste as 'hazardous' is made purely on waste-specific factors, while the classification of a waste as 'designated' must be based on both waste- and site-specific factors; and 2) the 'hazardous waste' classification system is insufficient to protect all waters of the State from the discharge of wastes to land. Subchapter 15 provides no guidance to the Regional Boards on how to determine whether a non-'hazardous' waste should be classified as 'designated' other than the language in §2522, quoted above. A methodology for making these decisions is provided in Chapter 3 of this report.

Subchapter 15 requires 'designated wastes' to be discharged to Class I or Class II waste management units. These units are to be designed to isolate the wastes from the surrounding environment through natural and/or engineered controls. Under §2520(a)(1) of Subchapter 15, a Title 22 'hazardous waste' that is given a variance by DHS may be discharged to a Class III waste management unit if the discharger demonstrates to the appropriate Regional Board that the waste does not pose a significant threat to water quality (see Figure 2). Only rarely will the discharger be able to make this demonstration. An example of a waste for which this demonstration is appropriate is asbestos. Wastes containing over 1.0 % asbestos are 'hazardous' under Title 22; however, DHS has granted asbestos a variance from hazardous waste management if these wastes are double-bagged and covered immediately after discharge. If discharged to a Class III landfill, the asbestos does not pose a threat to ground water quality, since asbestos fibers are unable to migrate through soils. The Regional Boards, therefore, frequently grant a §2520(a)(1) variance from Class II disposal for these 'designated wastes'.

2.4 'Nonhazardous Solid Wastes' and 'Inert' Wastes

Wastes in the remaining two classifications of Subchapter 15 are not required to be discharged to waste management units which provide isolation from the surrounding environment. 'Nonhazardous solid waste' is more commonly referred to as "municipal solid waste" or "refuse". It contains a significant quantity of degradable materials, but cannot contain 'designated waste'. Examples of 'nonhazardous solid waste' include solid refuse from food processing and handling, paper products, cardboard, wood, rubber, tree prunings, and dead animals. Subchapter 15 allows 'nonhazardous solid waste' to be discharged to Class III waste management units which are located and/or designed to prevent impairment of beneficial uses of nearby ground and surface waters. Thus, limited or controlled leakage of leachate from the waste to the surrounding environment is permitted.

'Inert waste' does not contain 'designated waste' nor a significant amount of degradable material. The only water quality threat posed by these wastes is siltation. Examples of 'inert waste' include construction and demolition wastes such as clean earth, rock, concrete and inert plastics, vehicle tires, uncontaminated clay products, and glass. 'Inert wastes' may be discharged to unclassified waste management units as long as they are prevented from entering surface waters. [Unclassified waste management units may have Waste Discharge Requirements from the appropriate Regional Board.] Again the emphasis is on beneficial use protection, rather than isolation of the waste from the surrounding environment.

Chapter 3 THE DESIGNATED LEVEL METHODOLOGY

Existing California regulations clearly define how wastes are to be classified; and detailed guidance is provided for the implementing agencies to set all but one of the boundaries between the five major waste classes (see Figure 1). The one significant boundary not clearly delineated is the lower end of the ‘designated waste’ classification. Wastes above this boundary — ‘designated wastes’ and ‘hazardous wastes’ — have the potential to significantly degrade water quality and must be discharged to waste management units (Class II and Class I) which isolate them from the surrounding environment (see Figure 2). Wastes below this boundary — ‘nonhazardous solid wastes’ and ‘inert wastes’ — may be discharged to units (Class III and unclassified) that do not provide this isolation. Thus, failure to classify a waste as ‘designated’ or ‘hazardous’ permits its discharge to waste management units that have little or no natural or engineered controls to prevent the release of waste constituents to the environment (most Class III and unclassified units are not required to have liners nor leachate collection and removal systems).

How are the regulatory agencies and the regulated community to determine whether a waste discharged to one of these waste management units poses a threat to beneficial uses of water? The following discussion presents a methodology which may be used to determine whether a waste has the potential to degrade water quality if discharged to a waste management unit that provides less than Class II containment. The methodology defines the lower boundary of the ‘designated waste’ classification (as well as the criteria which may be used to grant §2520(a)(1) variances under Subchapter 15) by establishing “Designated Levels” (see Figure 1). These levels are concentrations of waste constituents above which a waste is presumed to pose a threat to water quality at the site being considered. Designated Levels are derived from numerical “water quality goals”, limits or levels of water quality constituents which are established to protect the beneficial uses of water. Wastes whose constituent concentrations exceed the site-specific Designated Levels should be classified as ‘designated wastes’ with respect to that site, and the site should be required to provide Class II containment under Subchapter 15.

[The Designated Level Methodology is adapted from a procedure used by DHS to calculate ‘hazardous’ STLCs and TTLCS from drinking water standards, which is presented in the document “Final Statement of Reasons for Proposed Regulations, ‘Criteria for Identification of Hazardous and Extremely Hazardous Wastes’” in Title 22 (CAM SOR), adopted by DHS in February 1984.³]

3.1 Determining Available Concentrations of Waste Constituents

In order to determine the threat posed to water quality by a particular waste it is first necessary to ascertain the quantity of each constituent of concern in the waste that is available to migrate to waters of the State.

3.1.1 Liquid Wastes

The quantity of chemical constituents that is available to migrate from liquid wastes is dependent on the expected migration route. Only the **dissolved** concentrations of waste

constituents are available to migrate through soils to ground or surface waters. In cases where a waste may only threaten ground water, filtered samples should be subjected to analysis.

Note: Caution should be exercised in the decision to filter samples for analysis. Increased exposure of a sample to air that may occur during the filtration process can increase the dissolution of carbon dioxide and result in changes of chemical equilibria that, in turn, can alter the solubilities of many constituents. Erroneous analytical data may be the final result.

If overland flow to surface waters is possible, the **total** constituent concentrations may be available for movement and analyses should be conducted on unfiltered samples.

3.1.2 Solid Wastes

Since it is the soluble fraction of a constituent of a solid waste which actually has the potential to migrate to waters of the State, the **extractable** concentration is a more accurate measure (than the total concentration) of the ability of a particular solid waste constituent to degrade water quality. Therefore, it is recommended that whenever possible, extractable concentrations be determined for use in classifying solid wastes for purposes of water quality protection.

Determining Extractable Concentrations

For consistency with the hazardous waste identification procedures in Title 22 of CCR, extractable waste constituent concentrations should be determined using the Waste Extraction Test (WET) procedure from §66700 of those regulations, as indicated in Figures 8 and 9. The full WET procedure is contained in Appendix I to this report. In many cases, waste generators or dischargers must perform this test on their wastes to comply with the hazardous waste identification regulations of Title 22 of CCR, Division 4, Chapter 30, Article 11. Thus, much of the data needed to determine whether the waste is a 'designated waste' will be generated by that process. Further justification for use of the WET over other extraction procedures is presented in the CAM SOR.³

Note: Users are cautioned to ignore the phrase in part (b) of the WET procedure which permits the elimination of analyses for constituents whose total concentrations in the waste fall below hazardous STLC criteria (see Appendix I below). This exemption was developed for determinations of whether a waste is 'hazardous' under Title 22 of CCR. The determination of whether a waste is 'designated' under Subchapter 15 often involves more stringent criteria and these eliminated analytical results may be critical to this determination.

As shown in Figure 9, the WET requires a 10-fold dilution (wt./vol.) of waste into the extract solution. The results of the extraction in terms of milligrams of soluble constituent **per liter of extract solution** (mg/l) is, therefore, equal to one tenth (1/10) of the concentration expressed in milligrams of soluble constituent **per kilogram of solid waste**. This fact will be used in the calculation of Designated Levels in Section 3.3.3 of this report.

Figure 8

**DETERMINING SOLUBLE/EXTRACTABLE CONCENTRATIONS
OF CONSTITUENTS OF WASTES OR SOILS**

Extraction Procedure

Waste Extraction Test (WET) from Title 22, CCR, §66700 with the following modifications :

Selecting the Extractant

Especially important for metallic constituents.

- 1) Are the wastes/soils in a potentially acidic environment ?**
- 2) Are the wastes/soils capable of generating acid ?**

Determine Acid-Base Account

**If *either* answer is “yes” . . .
extract with the standard Citrate Buffer.**

**If *both* answers are “no” . . .
extract with Deionized Water.
May need to adjust to the acidity of local rainfall.**

Select Extraction Vessel

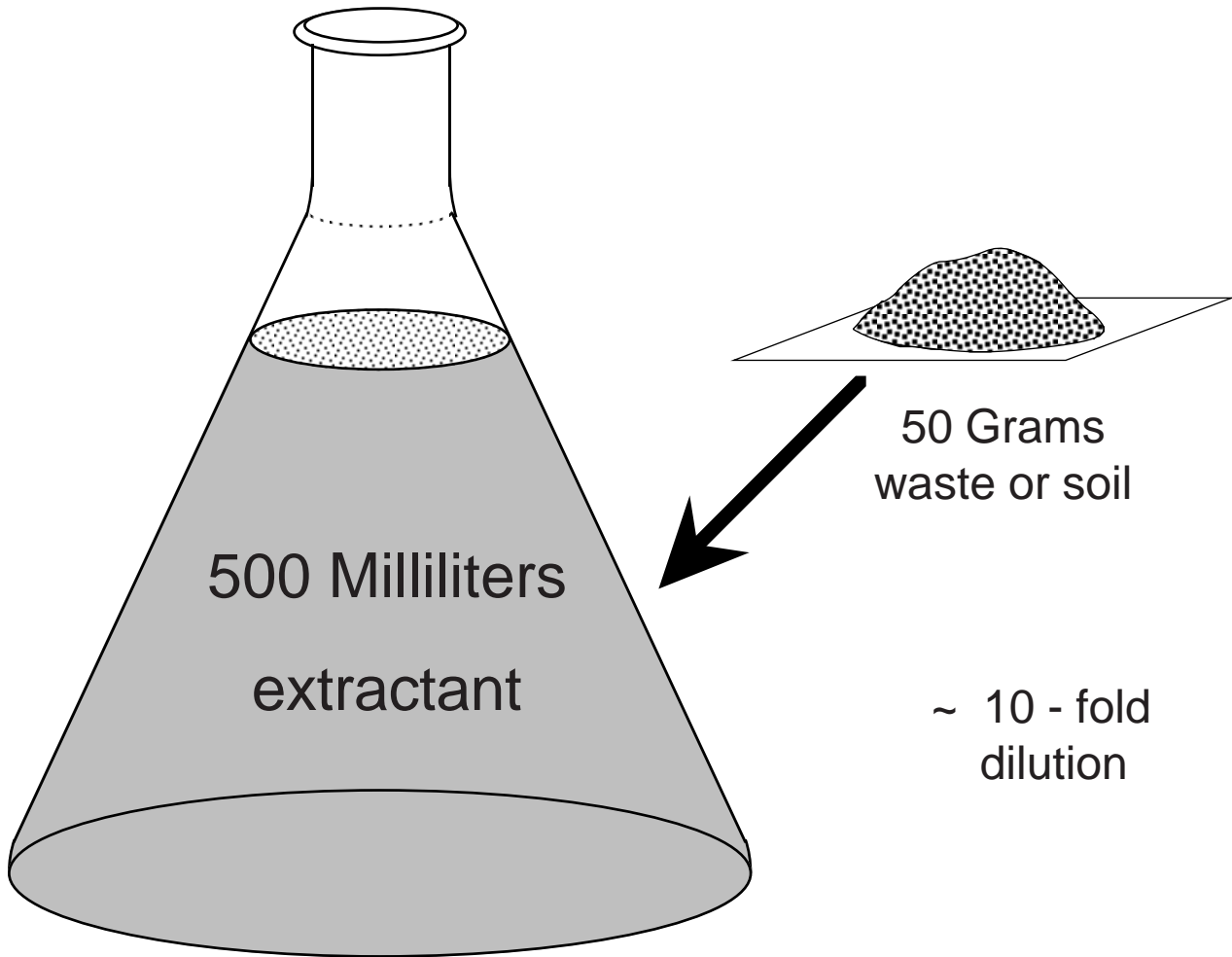
For volatile constituents . . .

- 1) perform WET using Zero Headspace Extraction Vessel and procedures outlined in draft of EPA “Toxicity Characteristic Leaching Procedure” (TCLP), or**
- 2) calculate Total Designated Levels for comparison with total constituent concentrations.**

The Department of Health Services developed the WET procedure for use in determining whether sufficient amounts of extractable constituents are available to leach to ground water, and thereby impact human health, if the waste is discharged to a Class III (sanitary) landfill. The WET uses a citrate buffer solution with a pH of 5.0 to mimic the extraction capability of ‘nonhazardous solid waste’ leachate, which is often acidic. Acidic solutions are more capable than deionized water or some other neutral solution of extracting metallic and other constituents from a waste. If the proposed waste management scheme is co-

Figure 9

**CALIFORNIA WASTE EXTRACTION TEST (WET)
TITLE 22, CCR, §66700**



CONVERTING EXTRACTABLE CONCENTRATIONS FROM mg/kg TO mg/l:

Because of the dilution in the Waste Extraction Test,
 Z milligrams per liter of extract is approximately equivalent
to $Z \times 10$ milligrams per kilogram of waste or soil.

disposed with 'nonhazardous solid waste' in a Class III landfill, if the waste is to be discharged to some other potentially acidic environment, or if the waste itself is capable of generating acidic leachate (see "*Acid-Base Account*" below), the standard citrate buffer should be used in the WET. If the waste is not to be discharged to a Class III landfill with 'nonhazardous solid waste' or to some other potentially acidic environment and if the waste is not capable of generating acidic leachate, deionized water could be substituted for the citrate buffer extract solution in the WET to more accurately assess the leachability of waste constituents.

Another reason for choosing to perform a deionized water extraction on a solid waste is to determine the extractable concentrations of constituents or parameters for which the citrate buffer would interfere in the analysis. Common examples are hexavalent chromium (Cr VI), total dissolved solids (TDS), specific conductivity (EC), and pH. As mentioned in Subsection (e) of the WET procedure (see Appendix I), a deionized water extraction must be performed to determine extractable Cr VI concentrations in wastes. In the presence of the acidic citrate buffer, Cr VI is reduced to trivalent chromium (Cr III), thereby making analysis for Cr VI invalid. The citrate buffer contains dissolved solids and has a fixed pH of 5.0 that can prevent the assessment of TDS, EC, or pH contributed by the waste itself. Deionized water extraction should not replace citrate buffer extraction if the waste is to be discharged to a Class III landfill or some other acidic environment or if the waste itself is capable of generating acidic leachate. Deionized water extraction should be performed in addition to the citrate buffer extraction in these cases where information on extractable Cr VI, TDS, EC, or pH is desired.

Acid-Base Account

Even if the waste is not to be discharged to a Class III landfill with 'nonhazardous solid waste' or to some other potentially acidic environment, acidic leachate could be generated by the waste itself. This is particularly true of some mining wastes which contain pyritic minerals.⁴ These sulfur containing minerals become oxidized when the waste materials are exposed to air for the first time. The oxidation process produces sulfurous acid (H_2SO_3), a major component of acid mine drainage. The acidic leachate so formed can readily mobilize toxic heavy metals in the mining waste. However, minerals such as calcium carbonate ($CaCO_3$) may also be present in the mining waste which have sufficient capacity to neutralize acid formed from pyrite oxidation. [Mining wastes will be discussed further in Chapter 5 below.] In order for the waste to be able to produce acid, the ability of the waste to generate acid must exceed its ability to neutralize acid over the life of the waste management unit in which the waste is to be placed.

The potential of a waste to produce acid is termed the "acid generation potential" (AGP), while the ability of a waste to neutralize acid is called the "neutralization potential" (NP). AGP may be expressed in pounds of $CaCO_3$ required to neutralize the acid formed by 1,000 pounds of waste; while NP may be expressed in pounds of $CaCO_3$ equivalents per 1,000 pounds of waste. When expressed in these terms, the ratio of NP to AGP is a measure of the overall ability of the waste to produce acid. Analytical procedures exist for determining AGP and NP, and thereby determining the overall acid-base account, of a waste.^{5,6} Appendix II of this report contains procedures for determining the acid-base

account of a waste. A ratio of NP to AGP of less than 3:1 indicates that an acidic leachate may be formed, while a ratio of NP to AGP of 3:1 or greater indicates that an acidic leachate will probably not be formed by the waste. The selection of the 3:1 ratio, in which NP exceeds AGP, accounts for the greater leachability of many of the minerals responsible for NP (mainly carbonates) as compared with those responsible for AGP (mainly sulfides), and accounts for the uneven distribution of these minerals within a waste which may cause localized pockets of acid generation.

The results of the acid-base account would indicate which extraction solution should be used in the WET. The citrate buffer is appropriate for any waste which has a NP to AGP ratio of less than 3:1. Deionized water could be substituted for the citrate buffer for wastes having a NP to AGP ratio of 3:1 or greater. (In some cases, it may be appropriate to adjust the deionized water to the pH of local rainwater to be able to assess the resulting leachability of waste constituents from this increasingly important environmental factor.) The appropriateness of choosing deionized water may cross checked by performing other analytical procedures such as the use of the humidity cell method, which attempts to demonstrate acid generation in accelerated bench scale oxidation test.⁶

Analysis for Volatile Constituents

The current WET procedure cannot be used to accurately determine extractable concentrations of purgeable (volatile) constituents of a solid waste. Examples of these constituents include trichloroethylene, vinyl chloride and other volatile organic contaminants (VOCs) and organic lead compounds. Due to their high vapor pressures and relatively low solubilities in water, significant fractions of the concentrations of these constituents would be lost to the air space (head space) in the extraction vessel during the extraction procedure. Losses to the atmosphere would also occur during other portions of the waste and extract handling phases of the WET. For these reasons, soluble or extractable concentrations may not be used as an accurate measure of the potential threat to water quality posed by most volatile components of wastes. Total concentrations must be used.

However, recognizing the need for an extraction procedure for volatiles, the U.S. EPA has proposed a new test called the "Toxicity Characteristic Leaching Procedure" or TCLP.⁷ This procedure includes a "Zero Headspace Extraction Vessel" in which extractions for volatile constituents could be performed without appreciable loss to the atmosphere. If these or other similar vessels become available for general use, they could be substituted for the standard vessel in the WET, making extraction for volatiles possible.

3.2 Water Quality Goals

The basis of the Designated Level Methodology is the assessment of concentrations of waste constituents which, if equalled or exceeded, could be mobilized and transported to ground and/or surface waters in amounts which would cause degradation of the quality of those waters. The assessment must, therefore, begin with the identification of the bodies of water which could be affected by a particular waste disposal and of numerical parameters indicative of existing water quality at the proposed site of waste disposal. These parameters will be called "water quality goals" in this report.

In most cases, background water quality — the concentrations of substances in natural waters which are unaffected by waste management practices — are appropriate for use as water quality goals. This is consistent with the establishment of “water quality protection standards” for indicator parameters and waste constituents which are reasonably expected to be in or derived from wastes discharged to waste management units, under §2552 of Subchapter 15, which also states:

“The background concentrations of applicable indicator parameters and waste constituents at or near the new waste management unit before wastes are discharged shall be established as the water quality protection standards for the unit... For existing waste management units, the background concentration shall be determined from nearby wells beyond the influence of the unit or facility.”

This Section of Subchapter 15 also cautions that the selection of background concentrations should take into consideration significant seasonal or long term water quality fluctuations and trends that are unrelated to the discharge of waste.

The non-degradation ideal is also the focal point of the State Water Resources Control Board’s Resolution No. 68-16 “Statement of Policy With Respect to Maintaining High Quality of Waters in California”. This resolution states that existing high water quality is to be protected even if some degradation in that water quality would not impair beneficial uses. Deviation from the non-degradation ideal is permitted if it can be demonstrated to the State that:

- 1) some degradation is in the best interest of the citizens of California; and
- 2) beneficial uses of the waters are not impaired.

If it is determined that some water quality degradation is in the best interest of the State, water quality goals may be selected by identifying 1) the present and probable future beneficial uses of waters which may be affected by the particular waste disposal and 2) numerical concentrations of waste constituents and indicator parameters allowable in the waters so that those uses are protected. The Water Quality Control Plan Reports (“Basin Plans”) of the nine Regional Water Quality Control Boards or the California Ocean Plan⁸ should be consulted to determine beneficial uses. Also cited in these plans are “water quality objectives” for several constituents of concern which, if not exceeded, will protect those uses. These “Basin Plan objectives” and several other numerical criteria and standards may be used as water quality goals for deriving Designated Levels. Water quality criteria and standards that are designed to protect a number of beneficial uses such as human health and welfare, aquatic life, agricultural use, and aesthetics may be found in the literature and are summarized below:

Human Health

- Primary Drinking Water Standards or Maximum Contaminant Levels (MCLs) in Title 22 of CCR, Division 4, Chapter 15, “Domestic Water Quality and Monitoring” which have

been adopted by DHS for use in California;

Note: These values are derived in conjunction with technologic and economic factors and are, therefore, not purely health-based.

- State “Action Levels” published by the Sanitary Engineering Branch of DHS¹⁰;
- Recommended Maximum Contaminant Levels (RMCLs)¹¹ promulgated by the U.S. EPA under the National Primary Drinking Water Regulations as the first step in establishing MCLs;
Note: By law, these are purely health based values, and are set at “zero” for carcinogens.
- Quality Criteria for Water, 1986 (“Gold Book”)¹² and the Ambient Water Quality Criteria volumes¹³ (1980) published by EPA for the priority pollutants which contain No-Adverse-Effect Levels for non-carcinogens, 10^{-6} incremental cancer risk estimates for carcinogens, and other toxicity-based criteria;
- Quality Criteria for Water (“Red Book”)¹⁶ published by EPA in 1976 [superseded by Quality Criteria for Water, 1986 (“Gold Book”)¹² and the Ambient Water Quality Criteria volumes¹³ for the priority pollutants];
- Water Quality Criteria, 1972 (“Blue Book”)¹⁷ published by EPA in 1973 [superseded by Quality Criteria for Water (“Red Book”)¹⁶];
- “Health Effects Advisories” published by the U.S. EPA, Office of Drinking Water¹⁴ which include Suggested No Adverse Response Levels (SNARLs) for non-carcinogens and 10^{-6} incremental cancer risk estimates for carcinogens;
- Drinking Water and Health volumes 1, 3, 4, 5, 6, and 7¹⁵ published by the National Academy of Sciences which include Suggested No-Adverse-Response Levels or SNARLs [values are presented for some carcinogens which do not include consideration of the cancer risk posed by those chemicals] and 10^{-6} incremental cancer risk estimates;
- Proposition 65 No-Significant-Risk Levels (NSRLs) established by the Health and Welfare Agency in CCR Title 22 for known human carcinogens and reproductive toxins which may be converted into concentrations in water;
- Estimated Permissible Ambient Goals¹⁸ published by EPA in 1977 as informal criteria;
Note: These are estimated from occupational exposure to airborne pollutants and are, therefore, not very reliable. They should only be used if no other criteria are available.

Human Welfare

- Secondary MCLs (Drinking Water Standards) in Title 22 of CCR, Division 4, Chapter 15, “Domestic Water Quality and Monitoring”⁹ which have been adopted by DHS;
- State “Action Levels” published by the Sanitary Engineering Branch of DHS¹⁰ which contain taste and odor thresholds for some chemicals;

-
- Ambient Water Quality Criteria volumes¹³ published by EPA in 1980 for the priority pollutants which contain taste and odor-based criteria for some chemicals;

Aquatic Life and Wildlife

- Quality Criteria for Water, 1986 (“Gold Book”)¹² and the Ambient Water Quality Criteria volumes for the priority pollutants¹³ (1980) published by EPA with updates for some chemicals published in 1985¹⁹;

Note: 4-day average, 24-hour average, or chronic criteria should be used as water quality goals whenever available to protect the surface water resource for the long term.

- Quality Criteria for Water (“Red Book”)¹⁶ published by EPA in 1976 [superseded by Quality Criteria for Water, 1986 (“Gold Book”)¹² and the Ambient Water Quality Criteria volumes¹³ for the priority pollutants];
- Water Quality Criteria, 1972 (“Blue Book”)¹⁷ published by EPA in 1973 [superseded by Quality Criteria for Water (“Red Book”)¹⁶];
- Estimated Permissible Ambient Goals¹⁸ published by EPA in 1977 as informal criteria;
Note: These are estimated criteria and should only be used if no other criteria are available.

Agricultural Use

- Water Quality for Agriculture¹⁶ published by the Food and Agriculture Organization of the United Nations in 1985;

Other Uses

- Water Quality Criteria²¹ written by McKee and Wolf and published by the State Water Resources Control Board in 1963 which contains criteria for human health and welfare, aquatic life, agricultural use, industrial use, and various other uses.

A list of these water quality goals may be found in the staff report *A Compilation of Water Quality Goals*.

To protect the maximum number of beneficial uses, the most restrictive (lowest), applicable, and justifiable water quality goals should be selected for deriving Designated Levels. Due to the rapidly changing data base on the health and environmental effects of chemicals, caution should be observed in selecting among the various water quality criteria and standards to be sure that the most recent information is utilized. The original literature should be consulted whenever possible to determine the applicability and limitations of the criteria and standards being selected. Other government agencies, such as the California Department of Health Services, the California Department of Fish and Game, and the U.S. Environmental Protection Agency may be consulted for up-to-the-minute information.

It is common practice to rely on Primary MCLs as “enforceable standards”. However, care should be taken in the application of Primary MCLs to the protection of **sources** of

drinking water. A common example of incorrect application is the use of the total trihalomethane (TTHM) MCL for the protection of ground water from chloroform. Chloroform is one of the four chemicals covered by the term “trihalomethanes”. The TTHM standard of 100 µg/l is over 500-times greater than the 10^{-6} incremental cancer risk estimate for chloroform. EPA has stated that the MCL for TTHMs was based mainly on technology and economics.²² Therefore, this standard does not clearly protect the beneficial use for domestic supply of waters of the State. The MCL for TTHMs was derived, for application to drinking water as it is delivered to consumers after disinfection by chlorination, by balancing the benefit provided by the chlorination process (elimination of pathogens in drinking water) with the health threat posed by the trihalomethane by-products of this process. In the case of contaminated ground water this type of cost/benefit balancing is not germane, and so the MCL does not apply to the protection of the ambient quality of domestic water supply sources. The 10^{-6} cancer risk estimate of 0.19 µg/l should be used as the measure of potential impairment by chloroform of the beneficial use of ground water for domestic supply. Staff of EPA, Region 9 has stated that the application of the 10^{-6} cancer risk estimate, instead of the TTHM MCL, as a water quality goal for chloroform in ground water appears to be consistent with the federal Clean Water Act and the recently adopted Safe Drinking Water Act.²³ and that the TTHM standard is not appropriate for protection of ambient water quality.²⁴

In fact, virtually all primary MCLs are derived by balancing the technologic and economic concerns that are directly related to the use of water for domestic supply with the health effects information developed under the RMCL process. Thus primary MCLs are not necessarily reliable indicators of protection of beneficial uses of an ambient water resource and should not necessarily be relied upon as water quality goals in these situations. There are other instances where water quality criteria more stringent than MCLs are applied to protect the beneficial uses of a water resource. For example, it is common practice to require compliance with aquatic life criteria for heavy metal contaminants in surface waters that are often much lower than MCLs for the same contaminants.

Once it has been decided that some degradation in water quality will be permitted (i.e., background water quality is not used for water quality goals), other factors may require water quality goals to be set below water quality-related standards and criteria. Care should be taken to consider other dischargers in the area and the contribution to the degradation of water quality that each imposes. If one discharger is permitted through the disposal of his waste to degrade the water resource to just below the point where beneficial uses are impaired, then no additional capacity exists for further degradation by other discharges of waste. In addition, the knowledge of the health and environmental effects of chemicals or combinations of chemicals is constantly evolving. What is considered to be safe at or below 10 µg/l today may be found to be harmful at 1 µg/l tomorrow.

3.3 Calculating Designated Levels

Designated Levels are measures of the minimum concentrations of waste constituents which, upon accounting for environmental attenuation at the proposed site of discharge, have the potential to cause the water quality goals for the constituents to be equalled or exceeded in ground and/or surface waters. Designated Levels fall into two main types,

Soluble and Total. Soluble Designated Levels represent concentrations of **soluble** or **extractable** constituents in a solid waste (represented by the concentration of the constituent in the extract from the Waste Extraction Test) which threaten to degrade water quality if equalled or exceeded. Total Designated Levels represent **total** concentrations of constituents in a solid waste or **total** or **dissolved** concentrations of constituents in a liquid waste which threaten to degrade water quality if equalled or exceeded. The calculation of site-specific Soluble and Total Designated Levels for solid and liquid wastes is also discussed below.

Since their values are based upon site-specific environmental attenuation, the calculation of Designated Levels from water quality goals must include factors which account for the environmental processes that can alter a constituent's ability to reach waters of the State in sufficient amounts to cause an adverse impact.

3.3.1 Environmental Attenuation Factors

As constituents in a liquid waste or in leachate from a solid waste migrate through the environment from the place of waste discharge to surface or ground waters the opportunity exists for attenuation or reduction of the concentrations of these constituents. The degree of expected attenuation under reasonable worst-case conditions at the site of discharge may be approximated with "environmental attenuation factors" — the greater the degree of expected attenuation, the larger the factor. These factors may be used to transform water quality goals into site-specific Designated Levels, that is, concentrations of constituents **in the waste** that have the potential to degrade water quality at the site of discharge.

The degree to which waste constituent concentrations become attenuated as they migrate toward ground and/or surface waters is governed by a set of processes collectively termed "environmental fate". Environmental fate processes include adsorption of constituents to clay particles and organic matter in the soil, ionic or covalent binding of the constituents to soil components, filtration of larger constituents by fine-grained soils, chemical or biochemical degradation, volatilization to the atmosphere or to air spaces within the unsaturated or vadose zone, and dispersion and dilution with vadose zone waters, surface waters or ground water. The total quantity of a waste constituent applied to a site (i.e., mass loading) may be sufficient to saturate some of the key environmental fate processes at a site, rendering them unavailable to further attenuate waste constituent concentrations. Other constituents in the waste, such as organic solvents, may increase the expected mobility of the constituent being considered.

Some of the key **characteristics** that influence the environmental fate of waste constituents are shown in Figure 10. Several of these characteristics involve hydrogeologic information on the site of waste discharge, while others involve the environmental chemistry of the waste constituents themselves — how the constituents are expected to chemically interact with environmental characteristics.

Also shown in Figure 10 is how increases in the environmental characteristics effects the selection of an environmental attenuation factor. If **ground water** is threatened by waste

Figure 10

EXAMPLES OF ENVIRONMENTAL FATE CHARACTERISTICS WHICH INFLUENCE THE SELECTION OF ATTENUATION FACTORS

As the following characteristics increase...	Effect on	
	↑	↓
For the Protection of Ground Water —		
• Depth to Highest Ground Water (including capillary fringe)	✓	
• Net Recharge (i.e., [rainfall] — [evaporation])		✓
• Characteristics of the Vadose Zone:		
Permeability and Porosity		✓
Clay Content	✓	
Organic Matter Content (for organics)	✓	
Ion Exchange Capacity and pH (for inorganics)	✓	
• Pollutant Characteristics:		
Polarity		✓
Ionic Strength (more positive)	✓	
Volatility (potential for vapor transport)		✓
Viscosity	✓	
Degradability / Biologic Activity	✓	
Octanol/Water Partition Coefficient (K_{ow})	✓	
• Other Constituents that Could Increase Mobility		✓
• Topography (Steepness of Terrain)	✓	
• Total Pollutant Load (Mass Loading)		✓
• Volumetric Ground Water Flow Rate	✓	
• Uncertainty of the Data and Assumptions		✓
For the Protection of Surface Waters —		
• Distance from Drainage Courses	✓	
• Topography (Steepness of Terrain)		✓
• Pollutant Characteristics:		
Volatility (loss to atmosphere)	✓	
Reactivity / Degradability	✓	
Polarity		✓
Octanol/Water Partition Coefficient (K_{ow})	✓	
• Other Constituents That Could Increase Mobility		✓
• Initial Dilution Upon Reaching Surface Waters (minimum surface water flow vs. maximum pollutant flow)	✓	
• Interconnection of Ground and Surface Waters		✓
• Total Pollutant Load (Mass Loading)		✓
• Uncertainty of the Data and Assumptions		✓

constituents, increases in the depth to ground water (thickness of the vadose zone), in the clay content, organic matter content, ion exchange capacity or pH of vadose zone materials, in the ionic strength, viscosity, degradability or octanol/water partition coefficient (the affinity of the chemical for octanol or soil organic matter versus its affinity for water) of the waste constituent, in the concentrations of solvents or other chemicals that can increase the permeability of soils or act as carriers for the constituent, in the steepness of the terrain, and in the rate of flow of ground water will cause the attenuation factor to be larger (greater attenuation). Increases in the net recharge rate (a driving force for movement of waste constituents), in the permeability or porosity of vadose zone materials, in the polarity or volatility of the waste constituent, and in the mass loading of waste constituents will cause the attenuation factor to be smaller (less attenuation as the constituent migrates to ground water). If **surface waters** are threatened by constituents in a waste, increases in the distance of travel from the site of waste discharge to surface water, in the volatility, reactivity, degradability or octanol/water partition coefficient of the waste constituent, in the concentrations of solvents or other chemicals that can increase the permeability of soils or act as carriers for the constituent, and in the amount of initial dilution that the waste or leachate would receive upon entering surface waters will cause the attenuation factor to be larger. Increases in the steepness of the terrain, in the polarity of the constituent, in the amount of interconnection of ground and surface waters, and in the total constituent loading will lower the attenuation factor.

Undoubtedly the most important characteristic that must be evaluated in the derivation of environmental attenuation factors is the relative uncertainty of the data and assumptions used to describe environmental fate processes. The more uncertainty involved in the estimation of environmental attenuation factors, the more the assumptions being used in their derivation should lean in the direction of underestimating the amount of attenuation expected to occur. In this way, a greater assurance of water quality protection is provided. The degree of uncertainty in the estimation of environmental attenuation should also be reflected in the amount of vadose zone and ground water monitoring that is required for a waste management unit. Greater uncertainty necessitates a greater monitoring effort to assure that the environmental fate analysis was protective of water quality.

Note: Because of the great uncertainty in environmental fate analysis, some regulators favor an approach for setting Designated Levels that does not consider any attenuation between the initial leachate or liquid waste and waters of the State. While this approach is surely protective of water quality, it does not appear to be feasible from an economic nor logistic point of view at the present time, since many more wastes would be found to be 'designated' and would require Class II or Class I disposal.

Site- and constituent-specific information regarding key environmental fate characteristics under reasonable worst-case conditions may be used to derive attenuation factors for specific waste constituents at the site. The DHS publication The California Site Mitigation Decision Tree Manual,²⁵ the EPA document Water Related Environmental Fate of the 129 Priority Pollutants,²⁶ The Soil Chemistry of Hazardous Materials by James Dragun,³⁵ Handbook of Environmental Data on Organic Chemicals by Karel Verschueren,²⁷ and the EPA publication DRASTIC: A Standardized System for Evaluating Ground Water Pollution Potential Using Hydrogeologic Settings²⁸ contain useful information and

procedures that can be used to assess the fate of chemicals in the environment and estimate environmental attenuation factors for specific waste constituents and site conditions.

Detailed information on many environmental fate characteristics may prove difficult or impractical to obtain. Therefore, the analysis may be approached initially in a simplified manner, by using more easily obtainable information on some of the key characteristics and conservative assumptions about the remaining characteristics to approximate the minimum expected attenuation. For example, in the analysis of the threat posed to surface waters the lowest anticipated initial dilution of the waste or leachate into surface waters can be used as a measure of attenuation. If this type of simplistic analysis can clearly demonstrate that waste constituents cannot adversely impact water quality, then further and more detailed analysis may be unnecessary. If a simplified analysis gives inconclusive results or shows that the potential for water quality degradation may exist, the waste discharger may wish to obtain detailed information on heretofore undetermined environmental fate characteristics in order to refine the analysis.

In many cases, resources may not permit a detailed environmental fate analysis for the selection of attenuation factors. This is especially true where a discharger requires a preliminary idea of how a waste will be classified. For these cases it is proposed that a “generic” environmental attenuation factor be chosen in a manner similar to that used by DHS in the setting of hazardous STLCS. The CAM SOR³ justifies the use of a 100-fold attenuation factor, based on studies conducted by Batelle Laboratories and EPA.^{29,30} Both studies stress that the degree of attenuation of waste constituents depends on waste- and site-specific conditions, as discussed above. It is, therefore, impossible to select an attenuation factor that will be appropriate for all wastes constituents or all disposal sites and situations. Expected landfill-to-useable ground water attenuations cited by EPA range from one to 1,000-fold, based on mathematical models and actual field data. Both the Batelle and EPA documents selected a 100-fold attenuation factor to conservatively represent average attenuation of waste constituents as leachate moves to an underground source of drinking water; however, neither study provides detailed descriptions of which waste- and site-specific conditions are best approximated by the 100-fold factor.

In selecting a “generic” environmental attenuation factor for purposes of deriving designated levels, the 100-fold factor should be used in those disposal situations which provide an “average” degree of natural protection for water quality from the discharge of wastes under reasonable worst-case conditions. An example of such an average disposal situation would be a landfill in the alluvium of the Central Valley with a significant depth (i.e., greater than 30 feet) of soil containing appreciable and continuous clay or silty-clay strata between the base of the landfill and ground water. For sites that provide less than this “average” amount of water quality protection (e.g., high ground water or more highly permeable geologic materials—sandy soils or fractured rock), a lower environmental attenuation factor, such as one (1) or ten (10) should be chosen. Where a very low degree of natural water quality protection may exist or for situations in which the mass loading of waste constituents is likely to saturate environmental attenuation processes (e.g., the discharge of large volumes of a liquid waste to a surface impoundment continuously over many years in an area with moderately permeable soils), a factor of one (1) should be used. A factor of 1,000 may be appropriate in areas that provide a very high degree of water

quality protection or for constituents that are known to have a much greater than average degree of environmental attenuation. [Examples of such constituents are free cyanide in surface waters, copper, zinc, and DDT under common environmental conditions ^{3,26}.]

Whenever sufficient site- and waste-specific data can be obtained, a more thorough analysis of environmental fate should be substituted for this “generic” attenuation factor approach. It is the responsibility of the waste discharger to provide this analysis.

3.3.2 Designated Levels for Liquid Wastes

The Total Designated Level for a constituent of a liquid waste is calculated by multiplying the water quality goal by the environmental attenuation factor that takes into account reasonable worst-case site- and waste-specific conditions at the proposed place of waste discharge.

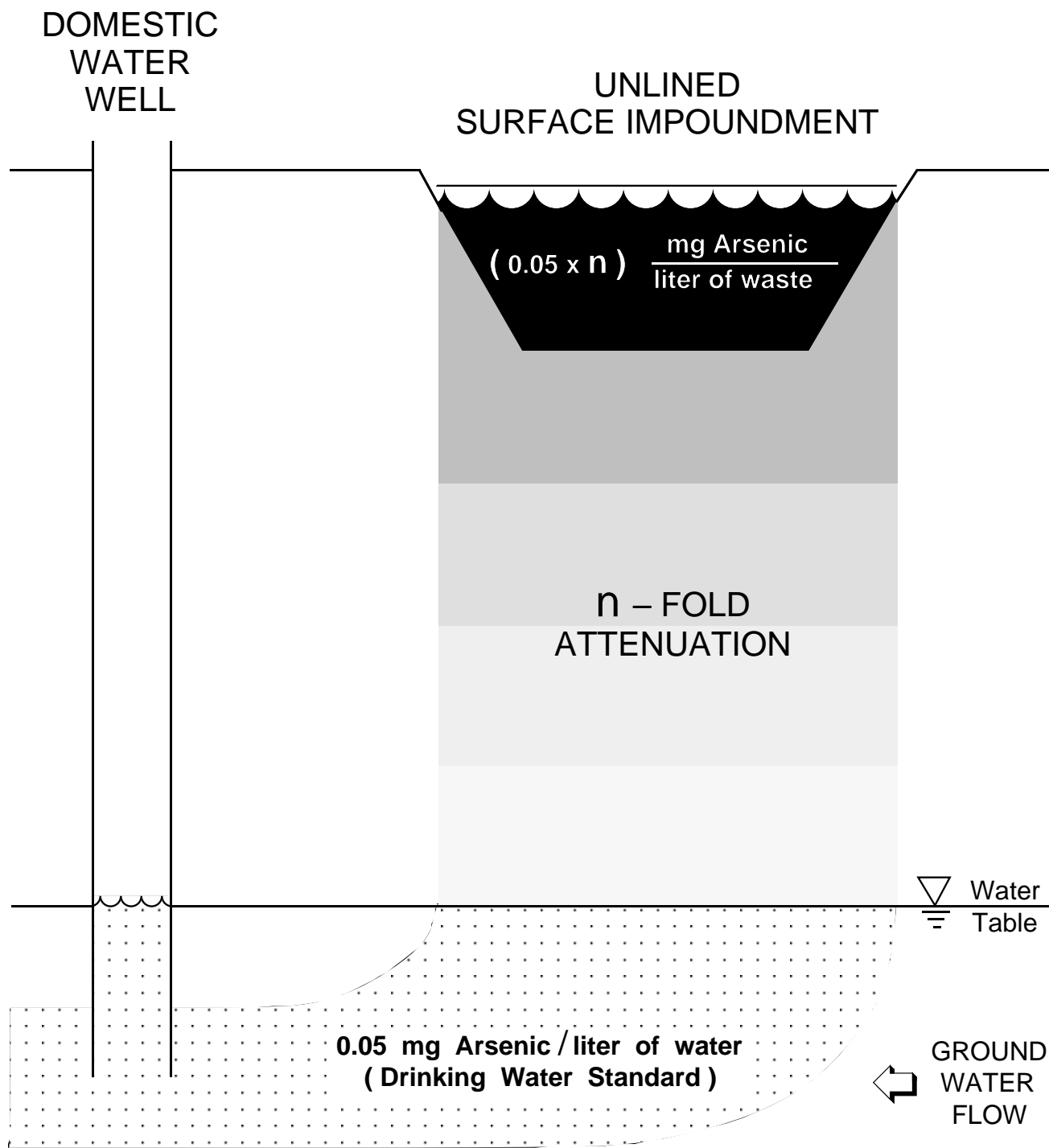
$$\begin{array}{l} \text{Total Designated Level} \\ \text{for constituent of a} \\ \text{liquid waste (mg/l of waste)} \end{array} = \begin{array}{l} \text{Water} \\ \text{Quality} \\ \text{Goal (mg/l)} \end{array} \times \begin{array}{l} \text{Environmental} \\ \text{Attenuation} \\ \text{Factor} \end{array} \quad [1]$$

Figure 11 presents an example of the disposal of a hypothetical liquid waste to an unlined surface impoundment. In this example, the constituent of concern in the waste is arsenic and the potential threat to ground water is being considered. Ground water at this site has the potential for use as domestic supply. The Primary MCL for arsenic of 50 µg/l (0.05 mg/l) has been chosen as the water quality goal, protective of this beneficial use. By environmental fate analysis, the soils between the base of the impoundment and the highest anticipated elevation of ground water have been estimated to provide a minimum of “n”-fold attenuation for arsenic. The environmental attenuation factor is, therefore, equal to “n”. The disposal of this waste is proposed to occur over a two year period; thus, the attenuative processes for arsenic in the soil are not expected to become saturated. The Total Designated Level for arsenic in the liquid waste discharged to this hypothetical impoundment is, therefore, equal to $(0.05 \times n)$ mg/l. If analysis of the waste shows that its dissolved arsenic concentration is equal to or greater than $(0.05 \times n)$ mg/l, the waste will not receive sufficient attenuation as it migrates from the impoundment to ground water and the resulting concentration of arsenic in ground water may exceed the Primary MCL, thus impairing the beneficial use of the water for domestic supply. This waste should, therefore, be classified as a ‘designated waste’ and the impoundment should be required to meet Class II surface impoundment construction standards. If the arsenic concentration in the waste is below $(0.05 \times n)$ mg/l, the waste does not have the potential to degrade ground water quality and would be classified as an ‘inert waste’ for this site. (Obviously, a liquid waste may not be classified as a ‘nonhazardous solid waste’.)

If the arsenic concentration in the waste is close to but does not exceed $(0.05 \times n)$ mg/l, some impoundment construction requirements, such as a single clay liner, may be prudent to ensure that sufficient attenuation exists. This would be especially important if questions exist about the representativeness of the waste sampling and analysis or if the waste characteristics are expected to vary significantly over the period of time that the discharge will occur.

Figure 11

TOTAL DESIGNATED LEVEL FOR A CONSTITUENT OF A LIQUID WASTE



3.3.3 Designated Levels for Solid Wastes

The goal in calculating Designated Levels for a solid waste is to determine concentrations of **soluble** constituents **in the waste** above which leachate would be able to carry them to ground or surface waters in amounts that would cause water quality goals to be exceeded in those waters. Figure 12 illustrates a scenario of how soluble/extractable constituents of

solid waste in an unlined landfill or waste pile could impair water quality. As moisture from infiltrating rainfall or from the waste itself percolates through the solid waste, soluble constituents are dissolved in the liquid phase. In this way leachate accumulates soluble waste constituents until it reaches the base of the landfill or waste pile. At that point, this “initial leachate” poses a water quality threat that is similar to that posed by the liquid waste considered in Section 3.3.2 above. The same environmental fate processes and attenuation factors that govern the potential impact of constituents of a liquid waste apply to constituents of the “initial leachate” from a solid waste. Therefore, the concentrations of constituents in the “initial leachate” which have the potential to degrade water quality are equal to the Total Designated Levels for constituents of a liquid waste. Therefore, from equation [1],

$$\begin{array}{l} \text{Concentration of Constituent} \\ \text{in "Initial Leachate" (mg/l)} \\ \text{that could degrade water quality} \end{array} = \begin{array}{l} \text{Water} \\ \text{Quality} \\ \text{Goal (mg/l)} \end{array} \times \begin{array}{l} \text{Environmental} \\ \text{Attenuation} \\ \text{Factor} \end{array} \quad [2]$$

At this point, an assumption is made that the concentrations of **soluble** constituents in the waste itself (in mg/kg of waste) prior to leaching are numerically equivalent to their concentrations in the “initial leachate” (in mg/l of leachate) formed from the waste. Therefore, from equation [2],

$$\begin{array}{l} \text{Soluble Concentration of} \\ \text{Constituent in Waste (mg/kg of waste)} \\ \text{that could degrade water quality} \end{array} = \begin{array}{l} \text{Water} \\ \text{Quality} \\ \text{Goal (mg/l)} \end{array} \times \begin{array}{l} \text{Environmental} \\ \text{Attenuation} \\ \text{Factor} \end{array} \quad [3]$$

As explained in the CAM SOR,³ concentrations in the “initial leachate” (in mg/l of leachate) could be lower, but could also exceed the soluble concentrations in the waste itself (in mg/kg of waste).

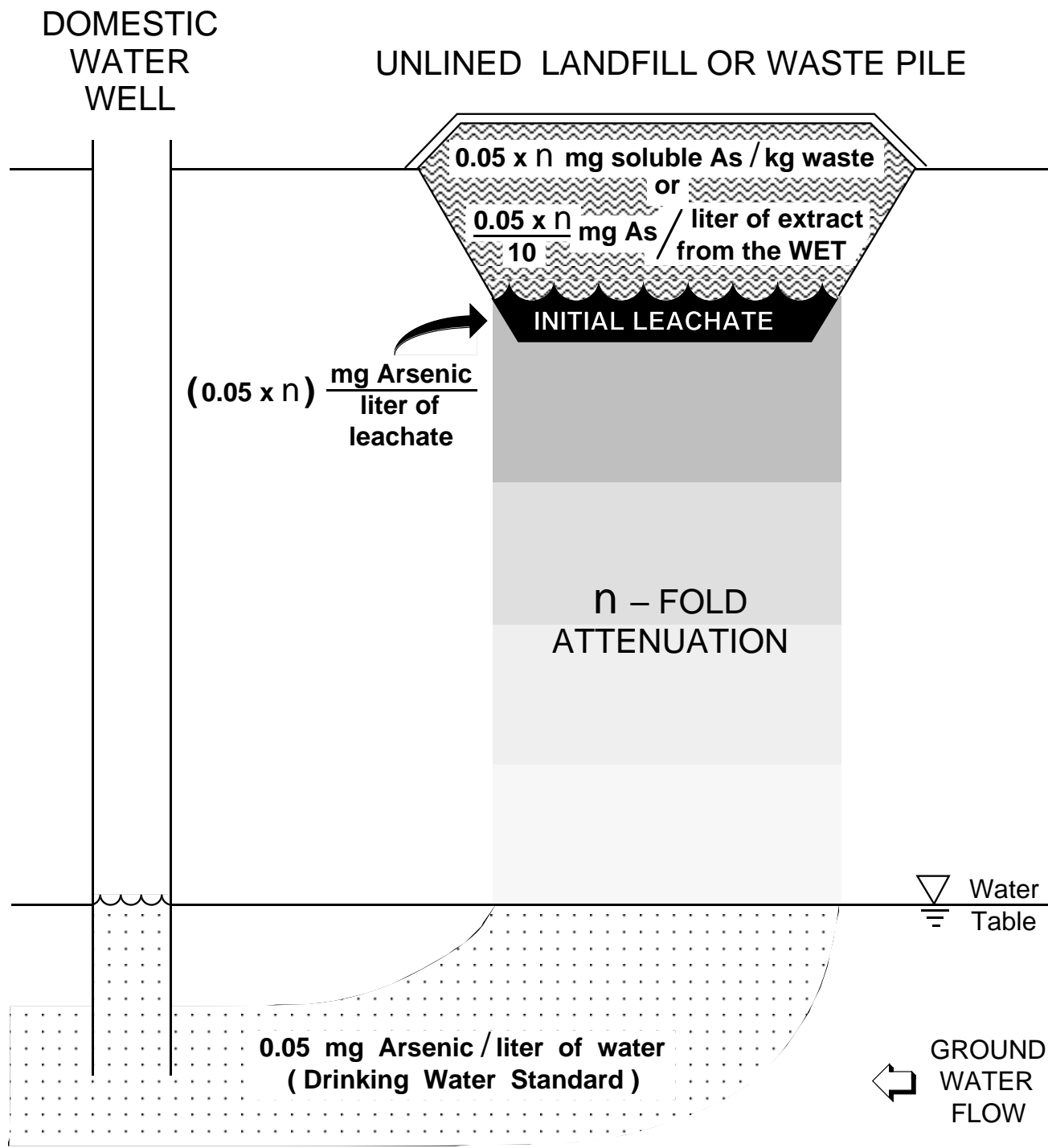
*Note: Concentrations of constituents in the “initial leachate” should not be confused with concentrations of constituents in **extract** from the Waste Extraction Test. They are not the same. Concentrations of constituents in the “initial leachate” are the result of the **accumulation** of constituents from the waste as moisture migrates through a landfill or waste pile. Concentrations of constituents in the extract from the WET are the result of a specific laboratory procedure where waste constituents are extracted from a solid waste by an extract solution under a controlled set of circumstances. The extract from the WET is, therefore, not a simulation of the “initial leachate”, but a measure of the **amount of waste constituents** that may be leached from the waste in a landfill.*

Soluble Designated Levels

Extractable concentrations from the Waste Extraction Test are expressed in milligrams per liter (mg/l) of extract, rather than milligrams per kilogram (mg/kg) of waste. Soluble Designated Levels for constituents of a solid waste should also be expressed in mg/l of extract so that direct comparison with results from the WET may be made. However, conversion from the units of mg/kg of waste to mg/l of extract must take into account the 10-fold dilution in the WET procedure as explained in Section 3.1.2, “Determining

Figure 12

SOLUBLE DESIGNATED LEVEL FOR A CONSTITUENT OF A SOLID WASTE



Extractable Concentrations," above. Therefore, an expression for the Soluble Designated Level for a constituent of a solid waste may be derived from equation [3].

$$\text{Soluble Designated Level for a Constituent of a Solid Waste (mg/l of WET extract)} = \frac{\text{Water Quality Goal (mg/l)}}{\text{Environmental Attenuation Factor} \div 10} \quad [4]$$

Figure 12 shows these calculations for a solid waste containing soluble arsenic. The water quality goal has been chosen to be equal to the Primary MCL of 0.05 mg/l and the site-specific environmental attenuation factor has been determined to be equal to “n”. The concentration of arsenic in the “initial leachate” that has the potential to degrade ground water quality is calculated from equation [2], to be $(0.05 \times n)$ mg/l of leachate. The concentration of soluble arsenic in the waste that has the potential to degrade water quality is calculated from equation [3] to be $(0.05 \times n)$ mg/kg of waste. The Soluble Designated Level for arsenic in the solid waste at this site is calculated, from equation [4], to be $(0.05 \times n \div 10)$ mg/l of extract from the WET or $(0.005 \times n)$ mg/l. A solid waste for which the concentration of arsenic in the WET extract exceeds $(0.005 \times n)$ mg/l would be classified as a ‘designated waste’ and the landfill or waste pile would be required to provide Class II containment under Subchapter 15.

Leachability Factors and Total Designated Levels

If extractable concentrations of a solid waste cannot be determined for particular constituents, such as volatile organics, analyses for total constituent concentrations are usually possible. Under these circumstances, Total Designated Levels must be calculated for comparison with total constituent concentrations in the waste, using available information on the leachability of the constituents under worst-case conditions at the site of waste discharge. As shown in Figure 13, only a certain fraction of the total constituent concentration is available for leaching from the waste and for uptake by organisms upon which the constituent would have a toxic or deleterious effect. The remainder of the constituent concentration is immobile or unavailable for leaching due to such factors as encapsulation in the waste matrix, chemical bonding, or other molecular interactions within the waste. Information on the fraction of leachable constituent under reasonable worst-case conditions at the proposed site of discharge may be used to derive a “leachability factor”. The leachability factor is equal to the total constituent concentration (leachable plus non-leachable) divided by the leachable constituent concentration, in other words, the reciprocal of the fraction of the constituent concentration that is leachable.

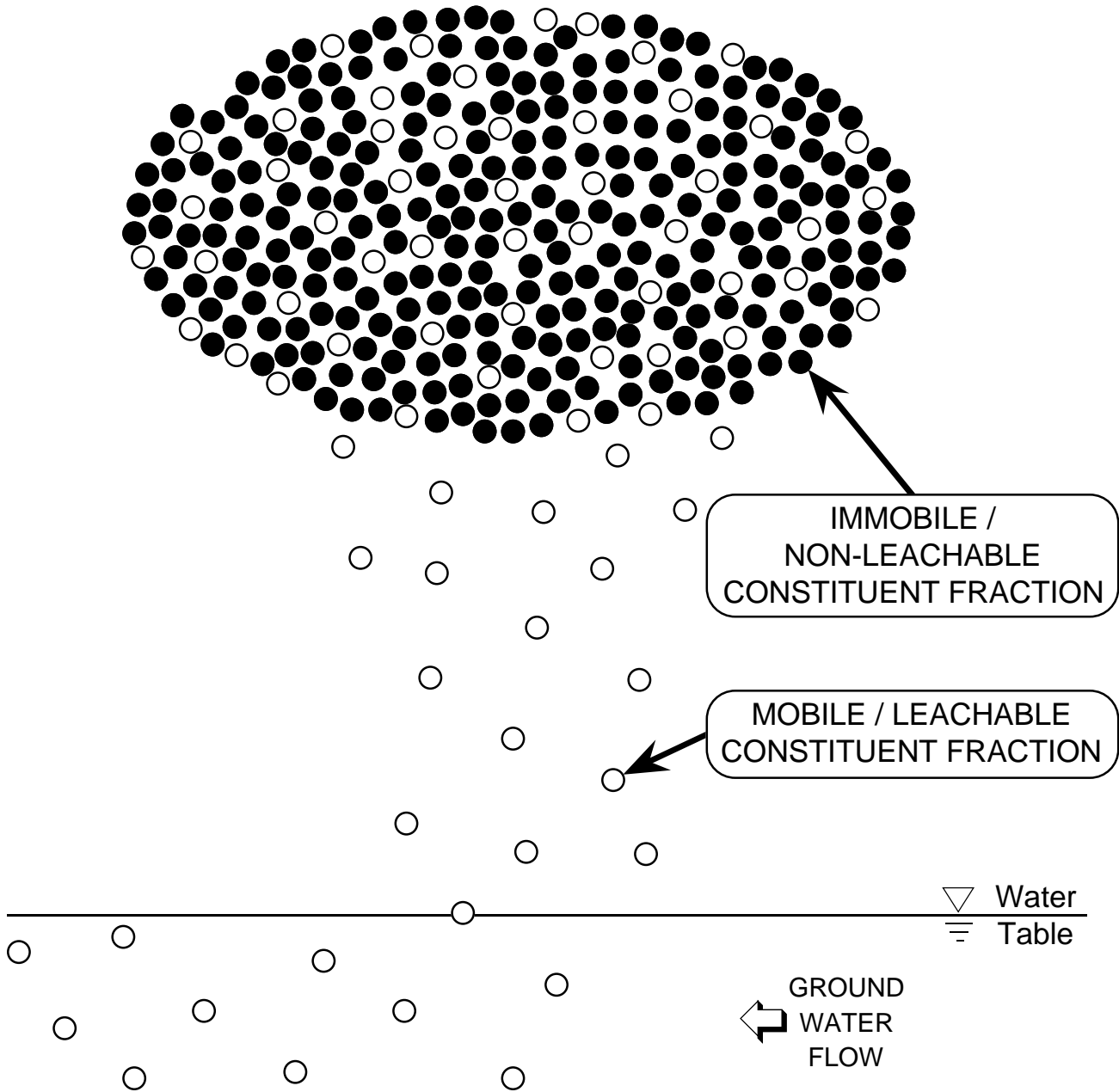
$$\begin{aligned} \text{Leachability Factor} &= \frac{\text{Total Constituent Concentration}}{\text{Leachable Constituent Concentration}} \\ &= 1 / (\text{Leachable Constituent Fraction}) \end{aligned} \quad [5]$$

For example, if it is known that for a particular constituent in a waste, reasonable worst-case conditions at the proposed site of discharge are able to mobilize one tenth (1/10) of the total concentration of the constituent, the leachability factor would be equal to ten (10).

Usually, when extractable concentrations of solid waste constituents cannot be determined, information on the leachable fraction is also unavailable. In these cases, the leachability factor must be approximated. The CAM SOR, in deriving TTLCs from STLCs for “persistent and bioaccumulative toxic substances”, uses a leachability factor [called the “bioavailability factor” in that document] of 100 for toxic inorganic constituents and 10 for toxic organic constituents. The reason for this difference is explained as follows:

Figure 13

A SIMPLE VIEW OF THE LEACHABILITY FACTOR



“The organic substances...are generally artificial. Their occurrence in nature is negligible. None are essential nutrients to humans or animals. Accordingly, humans and animals have developed few natural defenses to these substances. Most are much more bioaccumulative and more toxic than the inorganic substances...”³

The “persistent and bioaccumulative toxic substances” for which TTLCs were derived fall into several chemical classes, including heavy metals (e.g., arsenic and mercury), organometallics (lead compounds, organic) base/neutral extractable compounds (e.g., chlordane, lindane and toxaphene), acid extractable compounds (pentachlorophenol), phenoxy acids (2,4,5-trichlorophenoxyacetic acid), and volatile organic compounds (trichloroethylene). Most of the waste constituents that have the potential to degrade water quality (and will, therefore, be considered in the classification of wastes) fall into one or more of these chemical classes. For this reason, it is recommended that the “generic” 10-fold leachability factor for organics and 100-fold leachability factor for inorganics be used in situations where information on the leachable constituent fraction is unavailable.

The Total Designated Level for a constituent of a solid waste may be calculated by multiplying the Soluble Designated Level by the leachability factor. However, since the Total Designated Level is to be expressed in units of milligrams of constituent per kilogram of waste (mg/kg), the Soluble Designated Level from which it is calculated must also be expressed in these units. Due to the 10-fold dilution in the WET,

$$\begin{array}{l} \text{Soluble Designated Level} \\ \text{for a Constituent of a Solid} \\ \text{Waste (mg/kg of waste)} \end{array} = \begin{array}{l} \text{Soluble Designated Level} \\ \text{for a Constituent of a Solid} \\ \text{Waste (mg/l of WET extract)} \end{array} \times 10 \quad [6]$$

The Total Designated Level for a constituent of a solid waste is, therefore, calculated as follows:

$$\begin{array}{l} \text{Total Designated Level} \\ \text{for a Constituent} \\ \text{of a Solid Waste} \\ \text{(mg/kg of waste)} \end{array} = \begin{array}{l} \text{Soluble Designated Level} \\ \text{for a Constituent} \\ \text{of a Solid Waste} \\ \text{(mg/l of WET extract)} \end{array} \times \begin{array}{l} \text{Leachability} \\ \text{Factor} \end{array} \times 10 \quad [7]$$

By combining equations [4] and [7], the Total Designated Level for a constituent of a solid waste may be expressed in terms of the water quality goal.

$$\begin{array}{l} \text{Total Designated Level} \\ \text{for a Constituent} \\ \text{of a Solid Waste} \\ \text{(mg/kg of waste)} \end{array} = \begin{array}{l} \text{Water} \\ \text{Quality} \\ \text{Goal} \\ \text{(mg/l)} \end{array} \times \begin{array}{l} \text{Environmental} \\ \text{Attenuation} \\ \text{Factor} \end{array} \times \begin{array}{l} \text{Leachability} \\ \text{Factor} \end{array} \quad [8]$$

A solid waste with total constituent concentrations greater than their Total Designated Levels would be classified as ‘designated wastes’ and would be required to have Class II containment at the site of waste discharge.

3.3.4 Summary of Designated Level Calculations

The **Total Designated Level** for a constituent of a **liquid waste**, expressed in milligrams of total or dissolved constituent per liter of waste (mg/l of waste), is equal to:

$$\text{Water Quality Goal (mg/l)} \times \text{Environmental Attenuation Factor}$$

The **Soluble Designated Level** for a constituent of a **solid waste**, expressed in milligrams of constituent per liter of extract from the Waste Extraction Test (mg/l of WET extract), is equal to:

$$\text{Water Quality Goal (mg/l)} \times \text{Environmental Attenuation Factor} \div 10$$

The **Total Designated Level** for a constituent of a **solid waste**, expressed in total milligrams of constituent per kilogram of waste (mg/kg of waste) is equal to:

$$\text{Soluble Designated Level} \times \text{Leachability Factor} \times 10 \quad \text{or}$$

$$\frac{\text{Water Quality Goal (mg/l)}}{\text{Environmental Attenuation Factor}} \times \frac{\text{Leachability Factor}}{\text{Factor}}$$

If the total concentration of a constituent of a solid waste equals or exceeds the Total Designated Level but the extractable concentration of the constituent does not exceed the Soluble Designated Level, the waste should **not** be classified as a 'designated waste', since it is the extractable or soluble constituent concentration that has the potential to adversely impact water quality.

If the **total** concentration of a constituent in a solid waste is less than ten (10) times the Soluble Designated Level for the constituent, it would be impossible for the extractable constituent concentration from the WET to equal or exceed the Soluble Designated Level; therefore, extraction testing would be unnecessary and the waste would not be considered a 'designated waste'. This is true because if all of the constituent was soluble, its concentration would be diluted by ten-fold in performing the WET and the resulting extractable concentration (in mg/l of extract) would be one-tenth (1/10) of the total concentration (in mg/kg of waste) prior to extraction.

Note: Because the calculation of Total Designated Levels for solid wastes introduces an additional degree of uncertainty in the form of the leachability factor, extractable concentrations of solid waste constituents from the WET should be determined and compared with Soluble Designated Levels whenever possible.

Note: In certain situations, a calculated Designated Level may fall below the concentration that is detectable using currently available analytical methods. In such cases, the Designated Level should be set at the "limit of detection" (i.e., if the constituent is detected, it is assumed to exceed the Designated Level). Care should be taken to specify that the lowest acceptable method detection limit must be achieved by the laboratory.

Chapter 4 CUMULATIVE EFFECTS OF COMBINATIONS OF CONSTITUENTS

When several chemicals of concern are present in a particular waste, their interactive environmental/health effects—either additive, antagonistic, or synergistic—should be considered. However, data on the cumulative effects of chemicals is generally not available in the literature. As a conservative rule, the potential water quality impact of several constituents that manifest their effects in the same or similar manner should be assumed to be additive. Constituent groups for which this rule would likely apply include primary carcinogens, organophosphate and carbamate pesticides, halogenated organic pesticides, organic solvents, petroleum hydrocarbons, and heavy metals.

Under the additivity assumption, the waste would be considered to be a ‘designated waste’ if the sum of the quotients obtained by dividing the concentration of each constituent by its Designated Level is greater than 1.0.³¹

$$\text{if } \sum_{i=1}^n \frac{(\text{Concentration of Constituent})_i}{(\text{Designated Level for Constituent})_i} > 1.0, \quad \text{then the waste is a 'designated waste'} \quad [9]$$

This criterion could require the classification of a waste as ‘designated’ even if the concentrations of individual constituents are all below their respective Designated Levels. This indicates that even if no potentially adverse water quality impact is posed by individual constituents, the combination of constituents does have the potential to impair beneficial uses of waters of the State.

For example, consider a liquid waste that contains four carcinogenic volatile organic constituents in the following concentrations:

	Measured Concentration in the Waste	Hypothetical Designated Level
1,2-Dichloroethane	50 µg/l	100 µg/l
Tetrachloroethylene	250 µg/l	400 µg/l
Trichloroethylene	400 µg/l	500 µg/l
Vinyl chloride	120 µg/l	200 µg/l

Each constituent is below its individual Designated Level, however...

$$\frac{50}{100} + \frac{250}{400} + \frac{400}{500} + \frac{120}{200} = 2.5 \quad [10]$$

On the basis of cumulative carcinogenic risk ($\Sigma > 1.0$), this waste should be classified as a ‘designated waste’.

Chapter 5 MINING WASTES

Because mining wastes are usually not discharged together with other wastes and because the location of disposal often must be close to the area being mined, Subchapter 15 uses different terms to classify these wastes. However, because of similar properties and class definitions, they can be compared to the classifications of other wastes as follows:

<u>Mining Waste</u>	=	<u>Other Wastes</u>
Group A	=	'hazardous'
Group B	=	'designated'
Group C	=	'inert'

Mining wastes are to be discharged to mining waste management units classified as Class A, Class B, and Class C, respectively.

The hazardous waste management regulations of Title 22 of CAC determine the boundary between Group A and Group B mining wastes. The Designated Level Methodology may be used to define the boundary between Group B and Group C mining wastes. For determining whether a mining waste is Group B or Group C, deionized water (in some cases, adjusted to the pH of local rainfall) may be substituted for the citrate buffer in the WET only where mining wastes have been shown not to be capable of generating acidic leachate **and** where the disposal environment will be neutral or basic, pH ≥ 7.0 (see "*Determining Extractable Concentrations*" and "*Acid-Base Account*" in Section 3.1.2 above).

Chapter 6 SLUDGE AND ASH

§2523(c) and (d) of the “Discharges of Waste to Land” regulations in Subchapter 15² indicate that dewatered sewage and water treatment sludges and incinerator ashes “may be” discharged to a Class III landfill if the Department of Health Services determines that the waste need not be managed as ‘hazardous waste’ and, for sludges, if certain moisture controlling conditions are met in the landfill. This wording appears to preclude the classification of these wastes as ‘designated wastes’. However, legal staff of the State Water Resources Control Board has stated that Regional Boards may classify these wastes as ‘designated’ if they determine that it is necessary to protect water quality.³² Concurrence is found in §2510(a) of Subchapter 15, which states:

“Requirements of this subchapter are minimum standards for proper management of each waste category. Regional boards may impose more stringent requirements to accommodate regional and site-specific conditions.”

Concurrence is also found in recent correspondence from the Executive Office of the State Water Resources Control Board³³, which states:

“...the Regional Boards may, on a case-by-case basis, determine that certain nonhazardous sewage sludges must be discharged to a Class II landfill. Such sludges must meet the criteria of a designated waste as stated in Section 2522(a) of the regulations on waste discharge to land.”

A memorandum from the Executive Director of State Board to the Regional Board Executive Officers³⁴ states:

“Until we more thoroughly understand what occurs in waste management units as a result of...ongoing studies and monitoring, we should continue to allow disposal of municipal wastewater sludge in those Class III waste management units where problems are not evident or evidence does not exist that a particular problem is likely to occur. Exceptions must be justified on the basis of specific technical evaluations of the site and the waste in accordance with the present language of Subchapter 15.”

The Designated Level Methodology can provide this technical waste- and site-specific evaluation. Where the evaluation indicates that waste constituents have the potential to cause water quality degradation, non-hazardous ashes and sludges should be classified as ‘designated wastes’. As explained in Chapter 3 of this report, the classification would apply specifically to a particular waste and a particular site. Thus, not all sludges and ashes are expected to be classified as ‘designated wastes’ under this methodology and what is classified as ‘designated’ may not be so classified at a different disposal site that is more protective of water quality. As shown in Chapter 7 below, disposal in a Class I or Class II unit is not the only option for the discharge of a sludge or ash waste that is classified as ‘designated’.

Chapter 7 RE-USE OF 'DESIGNATED WASTES'

Under the Subchapter 15 regulations,² disposal at a Class I or Class II waste management unit is not the only option for the discharge of a waste which has been classified as 'designated'. Exemptions listed in §2511 of the regulations permit the re-use of a 'designated waste', provided that the use does not threaten to degrade water quality. A waste-, use-, and site-specific evaluation must be made to determine whether waste constituents would be available in concentrations that could cause water quality goals to be exceeded and beneficial uses to be impaired.

7.1 Soil Amendments

§2511(f) permits the re-use of a waste as a soil amendment under certain conditions. Re-use as a soil amendment may provide a lower cost alternative to Class I or Class II disposal for such wastes as sewage treatment sludges and incinerator ashes. A waste that contains constituents in excess of Designated Levels may still be used for this purpose provided that the following conditions are met:

- 1) the waste is not 'hazardous';
- 2) loading rates of the waste to the soil are such that constituent concentrations in soils remain below Designated Levels for the site (i.e., the resulting concentrations in soil will not pose a threat to ground or surface water quality) and below levels which would be injurious to plants or crops or, through plant uptake, to consumers of crops from the site;
- 3) waste application is controlled to prevent direct constituent release to surface waters via tail water from the field; and
- 4) the waste is shown to provide a benefit for the soil on which it is applied, such that the re-use does not simply constitute disposal.

A site monitoring program should be implemented to ascertain compliance with points (2) and (3) above.

7.2 Recycling

Recycling of 'designated wastes' is permissible under §2511(h) of Subchapter 15. A similar site-, waste-, and use-specific analysis would be necessary to demonstrate that water quality is protected and that the recycling is not just disposal. The party proposing the recycling should provide this analysis to the appropriate Regional Water Quality Control Board for review and approval.

Chapter 8 CLEANUP LEVEL DETERMINATION AND CONTAMINATED SITE MITIGATION

One of the most crucial determinations made in the cleanup of a contaminated site is what concentrations of contaminants can safely remain without the need for further remedial action; in other words, “how clean is clean?”. These concentrations are often called “cleanup levels”. Ideally, all contaminants should be removed and the site returned to “background” conditions; however, removing every molecule of a contaminant is often technologically infeasible and may not be the best use of economic resources. A method for determining what is safe to leave at a site is, therefore, necessary.

It is important at the outset of cleanup to establish goals for the mitigation effort. Ground water should be cleaned to the level where beneficial uses are restored (i.e., water quality goals are not exceeded). Soils should be removed or mitigation provided such that the remaining contaminants do not pose a threat to water quality, or to human health or the environment through direct or indirect pathways. If naturally occurring concentrations of constituents in waters or soils at the site (“background”) exceed these cleanup criteria, the background levels should guide the cleanup effort. If background levels are lower than cleanup criteria, cleanup to background levels may also be appropriate if technologically and economically feasible (see the discussion of the State Water Resources Control Board Resolution No. 68-16, “Statement of Policy With Respect to Maintaining High Quality of Waters in California” in Section 3.2 above).

Under the Health and Safety Code, §25356.1, DHS and the Regional Water Boards share the responsibility for remedial action at sites contaminated with toxic and hazardous substances. Subsection (c) of that section lists six factors that must be considered in the development of a remedial action plan (RAP) for such sites. These factors are:

- 1) health and safety risks at the site;
- 2) the effect of contamination or pollution levels upon present, future and probable beneficial uses of contaminated, polluted, or threatened resources;
- 3) the effect of alternative remedial action measures on the reasonable availability of ground water resources for present, future, and probable beneficial uses;
- 4) site specific characteristics;
- 5) cost effectiveness; and
- 6) potential environmental impacts.

The terms “present, future, and probable beneficial uses” clearly reflect wording of the Porter-Cologne Water Quality Control Act (Water Code, Division 7) and mandate the direct involvement of the Regional Water Boards in the cleanup and /or prevention of water quality impacts from contaminated sites.

The Department of Health Services has recently developed extensive technical guidance on cleanup level determination for the prevention of toxicologic impacts on humans and other “biological receptors of concern”. The procedures in this guidance, entitled The California Site Mitigation Decision Tree Manual,²⁵ reflect the legislative mandates that govern the site mitigation activities of DHS and, to a large extent, those of the U.S. EPA. However, the legislative mandate to protect all present and probable future beneficial uses of waters of the State, contained in the Porter-Cologne Water Quality Control Act and policies promulgated thereunder, require the State and Regional Water Boards to approach site mitigation from a somewhat different position. The three main areas of difference between the DHS and Water Board approaches to the cleanup question are summarized in Figure 14. The State and Regional Boards must prevent even non-toxicologic endpoints of contamination (e.g., taste and odor, recreation impairment) and endpoints that do not involve biological receptors (e.g., industrial use). The State and Regional Boards may require cleanup to levels below those that appear to protect all beneficial uses of water in order to account for the incompleteness of our current knowledge of environmental fate processes and the effects of contaminants as well as to address the allocation of water resources among potential users (i.e. if an individual is permitted to contaminate a body of water up to the water quality goal, there exists no room for additional contamination). Finally, the mandate to protect **probable future** uses of water require the State and Regional Boards to seek cleanup of even on-site waters to levels that will permit their future use.

For the reasons stated above, it is necessary for the State and Regional Boards to have a methodology to determine cleanup levels from a perspective of beneficial use protection. The Designated Level Methodology can fill this need. The threat to water quality posed by constituents of a contaminated soil is similar to the threat posed by constituents of a solid waste in an unlined landfill or waste pile, as seen by comparing Figures 12 and 15. These two situations share the same environmental fate processes that govern constituent attenuation and the same goal of beneficial use protection. By applying analytical procedures relevant to reasonable worst-case conditions at the site to determine the concentrations of constituents that are potentially available for migration to water (see Section 3.1 above) and by deriving site-specific Designated Levels for constituents of contaminated soils, the necessity for cleanup or mitigative measures for water quality protection should be apparent.

In many cases, the exceedance of Designated Levels by constituents of contaminated soils does not necessitate soil removal and re-disposal. It does indicate that mitigation measures are necessary to prevent potential water quality impacts.

As in waste classification, Designated Levels derived for use as cleanup levels should reflect site- and constituent-specific characteristics whenever possible. The water quality goals used in the assessment must be applicable to the present and probable future beneficial uses of the water resource being protected or cleaned-up (see Section 3.2 above). To reduce the level of uncertainty, extractable constituent concentrations from the soils should be compared with Soluble Designated Levels whenever practicable. The selection of extractant (citrate buffer or deionized water) should reflect the potential for acidic conditions at the site. Finally, care should be taken to account for the combined effects of

Figure 14

**MAJOR DIFFERENCES BETWEEN
THE DHS AND WATER BOARD APPROACHES TO CLEANUP
WITH RESPECT TO WATER QUALITY PROTECTION**

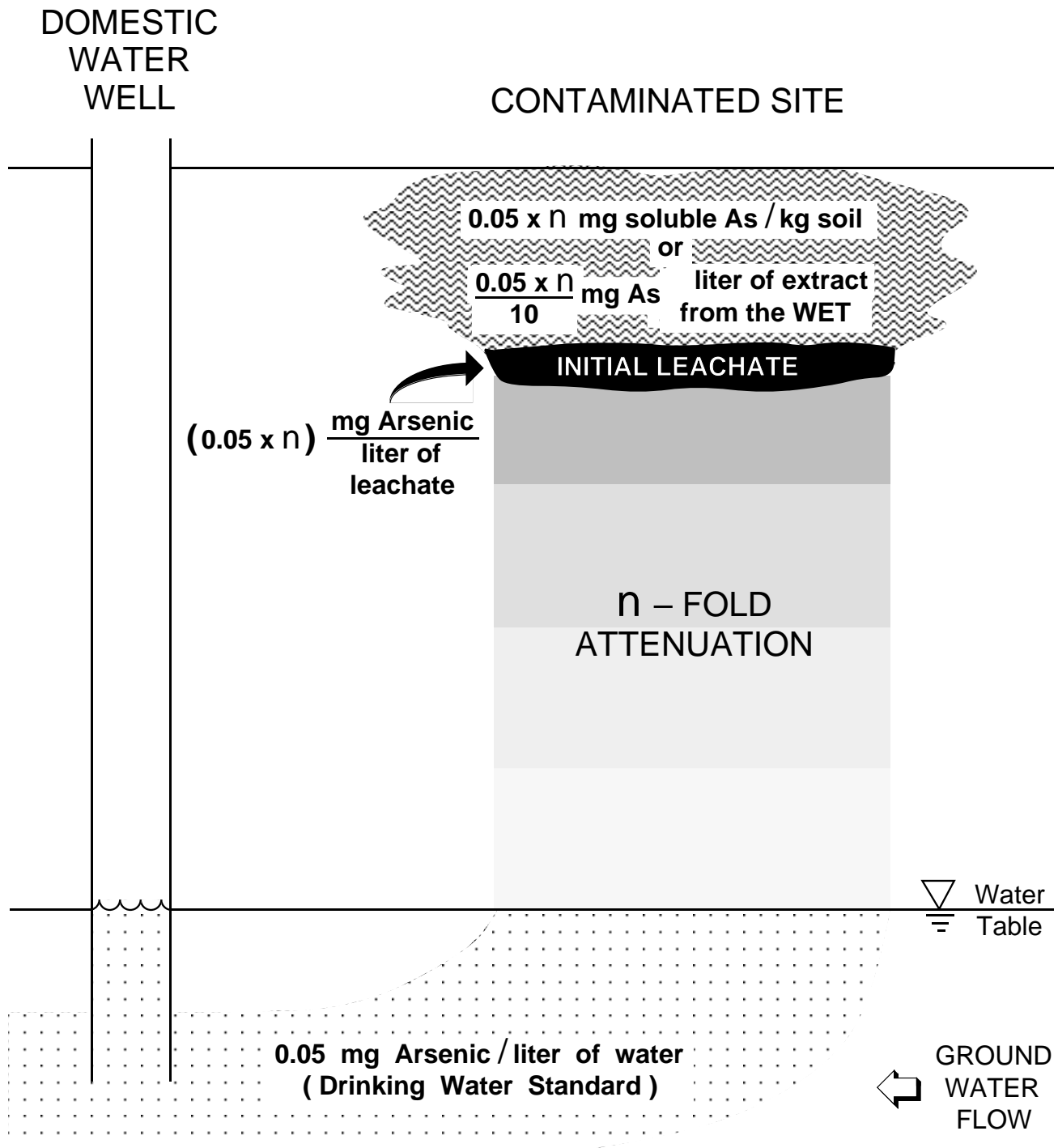
	DEPARTMENT OF HEALTH SERVICES	STATE & REGIONAL WATER BOARDS
End points addressed:	Toxicologic effects on humans and other biological receptors.	Any impact on present or probable future beneficial uses of water, including non-toxicologic effects on biological receptors and effects on non-biological endpoints .
What criteria are applied:	Threshold effect level for non-genotoxic (non-mutagenic, carcinogenic or teratogenic) agents. 10^{-6} risk level for genotoxic agents.	In the initial assessment, background . Relaxed under certain demonstrations of responsible party, but in no case shall beneficial uses be impaired.
Where criteria & standards are applied:	At the boundary of the site or the nearest point of current use.	Any and all waters of the State, even on-site or directly under the source of contamination, due to the probability for future beneficial use.

combinations of constituents at the site, either on constituent mobility or on toxicologic endpoints (see Chapter 4 of this report).

The Designated Level Methodology is not designed to account for all potential impacts of a contaminated site (e.g., airborne migration of toxic constituents). Therefore other agencies, such as DHS and the Air Resources Board must be involved in site investigation and decision making processes. The Designated Level Methodology is intended to complement

Figure 15

**SOLUBLE DESIGNATED LEVEL FOR A CONSTITUENT OF SOIL
AT A CONTAMINATED SITE**



the procedures of these and other agencies to assure the protection of human and environmental health and water quality. Where one agency's cleanup levels differ from those of another for the same site, the more restrictive levels will protect both agencies concerns and it is these levels that should guide the site mitigation effort. It is, therefore, imperative that all agencies with potential concerns be brought into the decision making process as early as possible.

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Appendix I

CALIFORNIA WASTE EXTRACTION TEST (WET)

Title 22 of the California Code of Regulations,
Division 4, Chapter 30, §66700.

California Register 85, No. 2
12 January 1985

NOTE: The underlined phrase below should be ignored if WET results are to be compared with Soluble Designated Levels or water quality based cleanup criteria.

66700. Waste Extraction Test (WET).

(a) The WET described in this section shall be used to determine the amount of extractable substance in a waste or other material as set forth in Section 66699(a).

(b) Except as provided in Section 66700(d), the WET shall be carried out if the total concentration in the waste, or other material, of any substance listed in Section 66699 equals or exceeds the STLC value, but does not exceed the TLIC value, given for that substance. The total concentrations of substances listed in Section 66699 shall be determined by analysis of samples of wastes, or other materials, which have been prepared, or meet the conditions, for analysis as set forth in subsections (c) and (d) of this section. Methods used for analysis for total concentrations of substances listed in Section 66699 shall be those given in the following documents or alternate methods that have been approved by the Department pursuant to Section 66310(e):

(1) For metal elements and their compounds, the waste shall be digested according to the indicated methods described in "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", SW-846, 2nd edition, U.S. Environmental Protection Agency, 1982:

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§ 66700

(Register 85, No. 3—1-12-85)

(p. 1800.79)

(A) All listed metal elements and their compounds, except hexavalent chromium: Method 3050.

(B) Hexavalent chromium: Method 3060.

(2) For the following substances, the indicated methods as described in "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", SW-846, 2nd edition, U.S. Environmental Protection Agency, 1982 shall be utilized:

(A) Antimony: Method 7040 or Method 7041.

(B) Arsenic: Method 7060 or Method 7061.

(C) Barium: Method 7080 or Method 7081.

(D) Cadmium: Method 7131.

(E) Total chromium: Method 7190.

(F) Hexavalent chromium: Method 7195, Method 7196 or Method 7197.

(G) Lead: Method 7421.

(H) Mercury: Method 7470 or Method 7471.

(I) Nickel: Method 7520 or Method 7521.

(J) Selenium: Method 7740 or Method 7741.

(K) Silver: Method 7760 or Method 7761.

(L) Trichloroethylene: Method 8010 or Method 8240.

(M) Pentachlorophenol: Method 8040, Method 8250 or Method 8270.

(N) Aldrin, Lindane, Chlordane, DDD, DDE, DDT, Dieldrin, Heptachlor, Toxaphene and PCBS: Method 8080, Method 8250 or Method 8270.

(O) 2,4-Dichlorophenoxyacetic acid and 2,4,5-trichlorophenoxypropionic acid: Method 8150.

(3) For the following substances, the indicated methods as described in "Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-020, U.S. Environmental Protection Agency, 1979 shall be utilized:

(A) Beryllium: Method 210.1 or Method 210.2.

(B) Cobalt: Method 219.1 or Method 219.2.

(C) Copper: Method 220.1 or Method 220.2.

(D) Molybdenum: Method 246.1 or Method 246.2.

(E) Thallium: Method 279.1 or Method 279.2.

(F) Vanadium: Method 286.1 or Method 286.2.

(G) Zinc: Method 289.1 or Method 289.2.

(H) Fluoride: Method 340.1, Method 340.2 or Method 340.3.

(4) For the following substances, the indicated methods as described in "Manual of Analytical Methods for the Analysis of Pesticides in Humans and Environmental Samples", EPA-600/8-80-038, U.S. Environmental Protection Agency, 1980 shall be utilized:

(A) Kepone: Section 5,A,(5),(a).

(B) 2,3,7,8-Tetrachlorodibenzo-p-dioxin: Section 9,G.

(5) For asbestos, the indicated method as described in the Federal Register, Volume 47, Number 103, Appendix A, pages 23376-23389, May 7, 1982 shall be utilized.

(c) Samples shall be prepared for analysis for total and extractable content of substances listed in Section 66699 (b) and (c) as follows:

(1) Type i: If the waste or other material is a millable solid, the sample shall be passed directly, or shall be milled to pass, through a No. 10 (two millimeter) standard sieve before it is analyzed. If the sample contains non-friable solid particles which do not pass directly through a No. 10 sieve and which are extraneous and irrelevant as hazardous constituents to the waste or other material, they shall be removed to the extent feasible by mechanical means and discarded. Solids which remain in the waste or other material after removal of the aforesaid extraneous particles shall be milled to pass through a No. 10 sieve and shall then be combined and mixed well with the solids which passed through the sieve without milling. The reconstituted sample shall then be analyzed as prescribed in this section.

(2) Type ii: If the waste or other material is a filterable mixture of liquid and solids in which the solids constitute five-tenths (0.5) percent by weight or greater of the sample, the liquid and solids shall be separated by filtration through a 0.45 micron membrane filter. The filtrate so obtained is to be designated as Initial Filtrate. Its volume is determined, and it is retained. The separated solids shall be sieved in a No. 10 sieve and any nonfriable extraneous particles of the kinds described in subsection (c) (1) which do not pass through the sieve shall be removed to the extent feasible by mechanical means and discarded. The solids which remain after removal of the extraneous particles shall be milled to pass through a No. 10 sieve and shall be recombined with solids which passed through the sieve without milling. This recombined solid material shall be extracted following the procedure in subsection (f). A ratio of 10 milliliters of extraction solution per gram of solid shall be utilized with appropriate modifications for extraction vessel size. After completion of solids extraction, the filtered extractant is combined with Initial Filtrate mixed thoroughly and analyzed as described in subsection (f) (3).

(3) Type iii: If the waste or other material is a nonfilterable and nonmillable sludge, slurry, or oily, tarry or resinous material, it shall be analyzed as received unless it contains non-friable extraneous and irrelevant solid particles of the kinds described in paragraph (c) (1) of this section. If it contains such solid particles and they are of such size as not to pass through a No. 10 sieve, they shall be removed to the extent feasible by mechanical means and discarded. The remainder of the sample shall be analyzed as prescribed in this section.

(4) If it is necessary to dry a solid sample or the solids fraction of a sample before sieving, milling or removal of extraneous solids, or if a sample is dried prior to analysis, all weight losses due to drying shall be determined, and these losses and the conditions of drying shall be reported.

(d) If the waste or other material is a liquid containing less than five-tenths (0.5) percent by weight of undissolved solids, it shall not be subject to the WET procedure, but shall be analyzed directly for the substances listed in Section 66699. The waste shall be classified as a hazardous waste if the total concentration in the waste of any substances listed in Section 66699 exceeds the TTLC value given for that substance. If, however, the total concentration is less than the TTLC but exceeds the STLC when expressed on a milligrams per liter basis, the waste or other material shall be filtered through a 0.45 micron membrane filter, the solids discarded and the filtrate shall be analyzed directly for the substances listed in Section 66699. The waste shall be classified as a hazardous waste if the concentration in the filtrate of any of the substances listed in Section 66699 exceeds the STLC value given for that substance.

(e) The WET extraction solution shall consist of 0.2 M sodium citrate at pH 5.0 ± 0.1 , which is prepared by titrating an appropriate amount of analytical grade citric acid in deionized water with 4.0 N NaOH, except that the extraction solution for the determination of chromium (VI) shall consist of deionized water.

(f) The extraction procedure shall be as follows:

(1) Fifty grams of sample, or less if it is a type ii sample prepared pursuant to subsection (c) (2), obtained pursuant to subsection (c) or (d) of this section shall be placed in a clean polyethylene or glass container designated the Treatment, capable of physically withstanding the extraction procedure and which was rinsed previously with, in succession, an aqueous 1:1 ratio by volume nitric acid solution and deionized water. If the extract will be analyzed for any of the organic substances listed in Section 66699 (c), a glass container shall be used. Furthermore, a container of the same size, shape and material shall be used for an extraction designated as the Blank, which shall be carried through the same procedure as the Treatment, but without addition of the sample.

(2) Five hundred milliliters of extraction solution, or less if the waste sample is a type ii sample prepared pursuant to subsection (c) (2) shall be added to the Treatment and Blank containers, which shall be then fitted with covered air scrubbers extended well into the extraction solutions and flushed vigorously with nitrogen gas for 15 minutes so as to remove and exclude atmospheric oxygen from the extraction medium. If the sample is to be analyzed for any volatile substance, such as trichloroethylene, the sample shall be added after deaeration with nitrogen to avoid volatilization loss. After deaeration the containers shall be quickly sealed with tightly fitting caps and agitated, using a table shaker, an overhead stirrer or a rotary extractor, operated at a speed which shall maintain the sample in a state of vigorously agitated suspension. Required equipment is described in test method 1310 in "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", SW-846, 2nd edition, U.S. Environmental Protection Agency, 1982. The temperature during the extraction shall be maintained between 20 and 40 degrees centigrade. After 48 hours of extracting, the contents of the Treatment and Blank containers shall be either filtered directly or centrifuged and then filtered. Filtering shall be through a medium porosity prefilter and then through a 0.45 micron membrane filter, using a clean, thick-walled suction flask. For coarser solids, prefiltration shall not be necessary. Pressure filtration shall be an optional alternative to vacuum filtration. If the extracts are first centrifuged, glass or polyethylene bottles shall be used as prescribed for extraction. For very fine solids, centrifuging at as high as $10,000 \times G$ may be necessary. After centrifugation, the liquids shall be decanted, prefiltered if necessary, and then passed through a 0.45 micron membrane filter. All filters shall be of low and identified extractable heavy metals, fluoride and organic chemicals content.

(3) If the filtered extracts are to be analyzed only for the metal elements listed in Section 66699 (b), the filtered extracts from the Treatment and Blank shall be transferred to clean polyethylene bottles and acidified with nitric acid to five percent by volume acid content soon after each extract is filtered. For those wastes or waste materials classified under subsection (c) (2), the Treatment shall be the Initial Filtrate combined with the extract generated by the WET extraction of the initially separated solids. Similarly the Blank in this instance shall be the filtrate generated by the WET Blank accompanying the initially separated solids, to which is subsequently added a volume of deionized

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(p. 1800.82)

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water equivalent to that of the Initial Filtrate. These procedures shall be followed prior to acidification of Treatment and Blank solutions with nitric acid to five percent (by volume) acid content. The bottle shall then be stored at room temperature or frozen. If the extracts are also to be analyzed for the organic substances listed in Section 66699 (c), or for the organic substances only, the filtered extracts shall be transferred to clean glass bottles. If the extracts are to be analyzed for fluoride, they shall be transferred to clean polyethylene bottles. These extracts, containing organic substances or fluoride, shall not be acidified, but shall be frozen soon after each extract is obtained and held frozen until the day of analysis, unless the extracts are analyzed within 24 hours.

(g) Sample analysis and data treatment shall be as follows:

(1) Each of the filtered extracts from the Treatment and Blank extractions shall have been acidified to five percent by volume nitric acid, and stored at room temperature or frozen in polyethylene bottles or kept frozen without addition of acid in glass bottles until the day of analysis, as prescribed. Each of the extracts shall be thoroughly mixed just prior to being individually analyzed for the substances listed in Section 66699 in order to determine whether the extractable concentration (EC) in the waste or other material exceeds the STLC for any of the substances listed. The extracts shall be analyzed according to the procedures identified in Sections 66700(b) (2), (b) (3) and (b) (4).

(2) The net EC of a substance in the Treatment sample which is listed in Section 66699 shall be calculated and reported as milligrams per liter of sample (mg/l). This value is derived after subtracting the concentration of the substance in the appropriate Blank extract from that concentration determined in the Treatment extract.

NOTE: Authority cited: Sections 208, 25141 and 25150, Health and Safety Code. Reference: Section 25141, Health and Safety Code.

HISTORY:

1. Editorial correction filed 10-5-84; designated effective 10-27-84 (Register 84, No. 41).

Appendix II

ACID-BASE ACCOUNT

Selected sections from:

Field and Laboratory Methods Applicable
to Overburdens and Minesoils

by Andrew A. Sobek, *et al*, West Virginia University

Produced under contract
with the U. S. Environmental Protection Agency.

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FIELD AND LABORATORY METHODS APPLICABLE
TO OVERBURDENS AND MINESOILS

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1.3 PREPLANNING TOTAL MINING OPERATION

1.3.1 Acid-Base Account

In the humid areas of the United States, the toxicity associated with acid results largely from the oxidation of iron disulfides. This process takes place when earth disturbance activities such as mining (Temple and Koehler, 1954; Hill, 1970) and highway construction (Miller et al., 1976) expose iron disulfides to the atmosphere. Since the public in the United States has supported legislation that acid-toxic or potentially toxic materials (a source of pollution) will not be left exposed, the need for a basis to evaluate overburden materials arose.

Acid-base accounting is a dependable criterion by which overburden materials can be evaluated. An acid-base account consists of two measurements: (1) total or pyritic sulfur and (2) neutralization potential. The accounting balances maximum potential acidity (from immediately titratable sources plus sulfuric acid equivalent calculated from total sulfur) against total neutralizers (from alkaline carbonates, exchangeable bases, weatherable silicates or other rock sources capable of neutralizing strong acids as measured by the neutralization potentials).

The total or pyritic sulfur content (see 3.2.4) accurately quantifies potential acidity of materials when all sulfur is present as a pyritic mineral. When gypsum is found in an overburden sample or the materials are weathered, sulfur occurs in the form of sulfates. Samples high in organic carbon usually contain organic sulfur. When part of the sulfur occurs in nonacid-producing forms, the maximum potential acidity as calculated will be too high. It is for this reason that such calculations are referred to as maximums and that in doubtful cases appropriate acid and water leachings should be made to rule out those forms of sulfur which do not produce acid (see 3.2.6). Then from the stoichiometric equation of pyrite oxidation, the maximum potential acidity can be calculated in terms of calcium carbonate equivalent. Overburden material containing 0.1% sulfur (all as pyrite) yields an amount of sulfuric acid that requires 3.125 tons of calcium carbonate to neutralize one thousand tons of the material. The neutralization potential (see 3.2.3) of overburden materials, the second component of a net acid-base account, measures the amount of neutralizers present in the overburden materials. This measurement is found by treating a sample with a known amount of standardized hydrochloric acid, heating to assure complete reaction, and titrating with a standardized base. The result is then expressed in calcium carbonate equivalents. When balanced against acidity from the total sulfur measurement, a net acid-base account can be made.

From the acid-base account, potentially toxic material is defined as any rock or earth material having a net potential deficiency of 5.0 tons of calcium carbonate equivalent or more per 1000 tons of material. The 1000 tons is based on the assumption that an acre plow-layer contains 2 million pounds of soil. Regardless of the acid-base account, materials which have a pH of less than 4.0 in a pulverized rock slurry in distilled water are defined as being acid-toxic.

The choice of the deficiency of 5 tons of calcium carbonate equivalent per 1000 tons of material as the division between toxic and non-toxic material obviously is arbitrary. However, when applied to the large number of samples studied during the past several years of minesoil research at West Virginia University, it corresponds to other supporting laboratory information about these samples as well as to extensive field experiences with minesoils developing in the different rock types. If rock or soil samples were defined to be toxic at much lower calcium carbonate equivalent deficiencies than 5 tons per 1000 tons, we would be declaring many of our native soils to be toxic. On the other hand, with deficiencies much greater than 5 tons per 1000 tons, toxic concentrations of plant-available aluminum and pH values below 4.0 often develop rapidly.

Rock type is incorporated with the acid-base account because it is useful to categorize the materials which comprise coal overburdens. Knowledge of the rock types can provide an estimate of the texture and base status of a future minesoil, as well as stability of rock fragments. For example, sandstones containing moderate amounts of pyrite and lacking sufficient neutralizers become active acid producers when exposed to the atmosphere.

The properties previously discussed are represented graphically in Figure 1. There are two zones of acid-toxic materials (the 16.2 to 17.1 m and the 20.7 to 21.6 m depths) indicated by pH values of less than 4.0. Both zones contain enough sulfur to continue to overwhelm the small amount of neutralizers present. Thus, these materials have the potential for remaining acid-toxic unless large amounts of neutralizers (50 and 80 tons calcium carbonate equivalent per 1000 tons of material, respectively) are added. In addition, there is a zone of potentially toxic material at a depth of 13.4 to 16.2 m and two zones below the 23 m depth (underlying the first coal and overlying the bottom coal), which are defined by a calcium carbonate deficiency of more than 5 tons per 1000 tons of material even though the pH is above 4.0.

Non-toxic zones, which exhibit varying amounts of excess neutralizers, exist from the surface to a depth of 13.4 m, from the 17.1 to 21 m depth, and from the 24.4 to 25.4 m depth. These materials can be removed and replaced in sequential order, selectively blended before replacement, or totally blended before replacement. Other methods of handling the overburden materials would include utilization of the limestone, after crushing, as a source of neutralizers to be blended with the potentially toxic materials.

The acid-base accounting method provides a useful tool for evaluating overburdens in the humid areas of the United States, since it is useless to look for plant toxicities from elements such as aluminum, boron, etc., until the acid problem is eliminated.

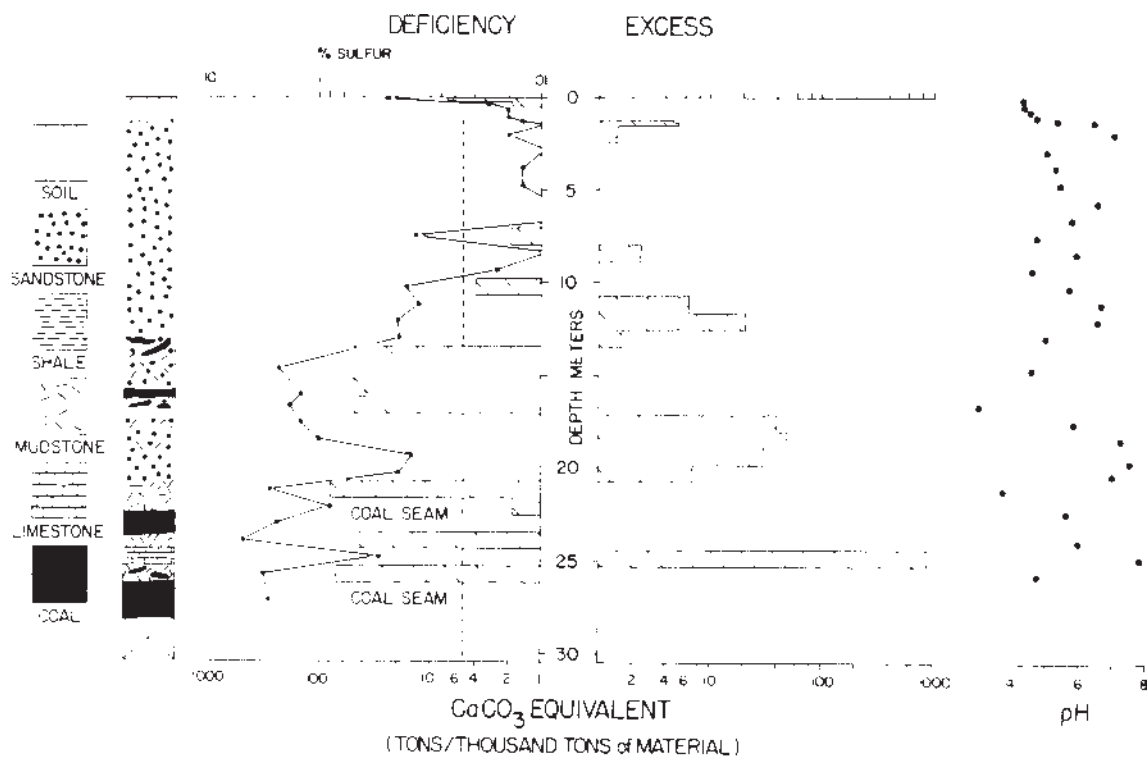


Figure 1. Acid-base account of the Kentucky no. 11 and no. 12 coal overburden.

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10. Label vial with the sample identification shown on the field container.
 11. Mix sample thoroughly by tumbling the vial end-over-end before subsampling for laboratory procedures (primarily chemical analyses).

3.2 CHEMICAL METHODS

3.2.1 Summary

Chemical methods for characterizing overburdens and minesoils are given. For a particular parameter, more than one method may be listed. This will allow the user of the manual some freedom of choice.

The determination of toxic or nontoxic materials due to acidity is overriding in importance in the Appalachian and Eastern and Western Interior Coal Provinces. The methods for determining toxic or potentially toxic materials are given high priority and are listed at the very front of the chapter. Methods 3.2.2, 3.2.3, 3.2.4, and 3.2.6 are used to determine the acid-base balance of minesoils and overburdens.

Next in importance is the nutrient status of the overburden materials. Nutrient status can be measured by using methods 3.2.5, 3.2.6, and 3.2.15. These methods give a measure of plant nutrients such as phosphorus, potassium, calcium, magnesium, and nitrogen. A knowledge of what plant nutrients are contained in an overburden material enables the mine operator to efficiently plan the mining operation so that full advantage can be taken of these nutrients in the resulting minesoil.

For more intensive study of minesoils and overburden materials, procedures for determining the cation exchange capacity (3.2.16 and 3.2.17) are given. Ways of estimating the lime requirement in minesoils are presented in methods 3.2.7 through 3.2.10. Also, methods applicable to arid and semi-arid regions have been included.

3.2.2 Paste pH

3.2.2.1 Principle--

Perhaps the most commonly measured soil characteristic is pH. Soil pH was defined by Sorensen (1909) as the negative logarithm of the hydrogen-ion concentration. However, in actuality, hydrogen-ion activity is measured instead of hydrogen-ion concentration.

Soil pH is measured by a glass electrode incorporated with a pH meter for this procedure. Water is added to the sample forming a paste. The electrode is placed in the paste with pH being read directly from the meter.

3.2.2.2 Comments--

Six factors affecting the measurement of pH are: (1) drying the soil sample during preparation; (2) soil:water ratio used; (3) soluble salts content;

(4) seasonally influenced carbon dioxide content; (5) amount of grinding given the soil; and (6) electrode junction potential (Jackson, 1958; Peech, 1965).

Care must be taken to insure electrode life and accurate pH measurements: (1) Electrode should not remain in the sample longer than necessary for a reading, especially if more alkaline than pH 9.0. (2) Electrode should be washed with a jet of distilled water from a wash bottle after every measurement (sample or buffer solution). (3) Electrode should be dipped in dilute (1 part acid to 3 parts water) hydrochloric acid for a few seconds and washed with distilled water to remove any calcium carbonate film which may form, especially from alkaline samples. (4) Drying out of the electrode should be avoided. Electrode is cleaned and suspended in distilled water (which is protected from evaporation) for storage. (6) Place pH meter in standby position when electrode is not in a solution (Jackson, 1958; Peech, 1965).

The pH meter and electrode should be standardized with buffers differing by 3 or 4 pH units, such as 4.0 and 7.0, before beginning a series of measurements. After every tenth measurement, recheck the standardization with both buffers. Care should be taken not to contaminate one buffer with the other buffer or with the test solution. Never return used standard buffers to their stock bottles. The procedure describes the technique for measuring pH with a glass electrode and meter. If pH is taken in the field using color paper strips or indicator solutions, modification will have to be made by qualified personnel to the procedure.

3.2.2.3 Chemicals--

1. Standard buffer solutions, pH 4.00 and pH 7.00.
2. Distilled water (H₂O).

3.2.2.4 Materials--

1. pH meter (Corning model 12 or equivalent) equipped with combination electrode.
2. Paper cups, 30 ml (1 oz) capacity.
3. Plastic cups.
4. Stirring rod.
5. Wash bottle containing distilled water.
6. Balance, can be read to 0.1 g.

3.2.2.5 Procedure--

1. Turn on, adjust temperature setting, and "zero" pH meter per instruction manual.

-
2. Place pH 4.0 and pH 7.0 standard buffers in two plastic cups (one buffer in each cup). NOTE: NEVER return used buffers to stock bottles.
 3. Place electrode in the pH 7.0 buffer.
 4. Adjust pH meter to read pH 7.0.
 5. Remove electrode from buffer solution and wash with a jet of distilled water from a wash bottle.
 6. Place electrode in the pH 4.0 buffer and check the pH reading. NOTE: If pH meter varies more than ± 0.1 pH units from 4.0, something is wrong with the pH meter, electrode, or buffers.
 7. Weigh 10 g of less than 60 mesh material into a paper cup.
 8. Add 5 ml of distilled water to sample. NOTE: Do not stir! Allow water to wet sample by capillary action without stirring. With most overburden and minesoils materials, the 2:1 (soil:water) ratio provides a satisfactory paste for pH measurements; however, for the very coarse textured and the very fine textured material, more material or water can be added to bring the soil near saturation. At near saturation conditions, water should not be puddled nor dry soil appear at the surface.
 9. Stir sample with a spatula until a thin paste is formed adding more water or soil as required to keep soil at saturation point. NOTE: At saturation, the soil paste glistens as it reflects light and the mixture slides off the spatula easily. Wash the spatula with a jet of distilled water before stirring another sample.
 10. Place electrode in paste and move carefully about to insure removal of water film around the electrode. CAUTION: Do not trap particles between electrode and inside surface of the sample container. Electrodes are easily scratched. Contact between paste and electrode should be gentle to avoid both impact and scratching damage, especially in sandy samples.
 11. When reading remains constant, record pH and remove electrode from paste. Carefully wash electrode with distilled water to insure removal of all paste. If all pH measurements are completed, the electrode should be stored in a beaker of distilled water. NOTE: After every 10 samples, check meter calibration with standard buffers.

3.2.3 Neutralization Potential

3.2.3.1 Principles--

The amount of neutralizing bases, including carbonates, present in overburden materials is found by treating a sample with a known excess of standardized hydrochloric acid. The sample and acid are heated to insure that the reaction between the acid and the neutralizers goes to completion.

The calcium carbonate equivalent of the sample is obtained by determining the amount of unconsumed acid by titration with standardized sodium hydroxide (Jackson, 1958).

3.2.3.2 Comments--

A fizz rating of the neutralization potential is made for each sample to insure the addition of sufficient acid to react all the calcium carbonate present.

During digestion, do not boil samples. If boiling occurs, discard sample and rerun. Before titrating with acid, fill buret with acid and drain completely. Before titrating with base, fill buret with base and drain completely to assure that free titrant is being added to the sample.

3.2.3.3 Chemicals--

1. Carbon dioxide-free water: Heat distilled water just to boiling in a beaker. Allow to cool slightly and pour into a container equipped with ascarite tube. Cool to room temperature before using.
2. Hydrochloric acid (HCl) solution, 0.1 N, certified grade (Fisher So-A-54 or equivalent).
3. Sodium hydroxide (NaOH), approximately 0.5 N: Dissolve 20.0 g of NaOH pellets in carbon dioxide-free water and dilute to 1 liter. Protect from CO₂ in the air with ascarite tube. Standardize solution by placing 50 ml of certified 0.1 N HCl in a beaker and titrating with the prepared 0.5 N NaOH until a pH of 7.00 is obtained. Calculate the Normality of the NaOH using the following equation:

$$N_2 = (N_1V_1)/V_2, \text{ where:}$$

V_1 = Volume of HCl used.

N_1 = Normality of HCl used.

V_2 = Volume of NaOH used.

N_2 = Calculated Normality of NaOH.

4. Sodium hydroxide (NaOH) approximately 0.1 N: Dilute 200 ml of 0.5 N NaOH with carbon dioxide-free water to a volume of 1 liter. Protect from CO₂ in air with ascarite tube. Standardize solution by placing 20 ml of certified 0.1 N HCl in a beaker and titrating with the prepared 0.1 N NaOH until a pH of 7.00 is obtained. Calculate the Normality of the NaOH using the equation in 3.2.3.3 No. 3.

5. Hydrochloric acid (HCl), approximately 0.5 N: Dilute 42 ml of concentrated HCl to a volume of 1 liter with distilled water. Standardize solution by placing 20 ml of the known Normality NaOH prepared in 3.2.3.3 No. 3 in a beaker and titrating with the prepared HCl until a pH of 7.00 is obtained.

Calculate the Normality of the HCl using the following equation:

$$N_1 = (N_2V_2)/V_1, \text{ where:}$$

V_2 = Volume of NaOH used.

N_2 = Normality of NaOH used.

V_1 = Volume of HCl used.

N_1 = Calculated Normality of HCl.

6. Hydrochloric acid (HCl), approximately 0.1 N: Dilute 200 ml of 0.5 N HCl to a volume of 1 liter with distilled water. Standardize solution as in 3.2.3.3.5, but use 20 ml of the known Normality NaOH prepared in 3.2.3.3 No. 4.

7. Hydrochloric acid (HCl), 1 part acid to 3 parts water: Dilute 250 ml of concentrated HCl with 750 ml of distilled water.

3.2.3.4. Materials--

1. Flasks, Erlenmeyer, 250 ml.
2. Buret, 100 ml (one required for each acid and one for each base).
3. Hotplate, steam bath can be substituted.
4. pH meter (Corning Model 12 or equivalent) equipped with combination electrode.
5. Balance, can be read to 0.01 g.

3.2.3.5 Procedure (revised and updated from Smith et al., 1974)--

1. Place approximately 0.5 g of sample (less than 60 mesh) on a piece of aluminum foil.
2. Add one or two drops of 1:3 HCl to the sample. The presence of CaCO_3 is indicated by a bubbling or audible "fizz."
3. Rate the bubbling or "fizz" in step 2 as indicated in Table 1.
4. Weigh 2.00 g of sample (less than 60 mesh) into a 250 ml Erlenmeyer flask.
5. Carefully add HCl indicated by Table 1 into the flask containing sample.
6. Heat nearly to boiling, swirling flask every 5 minutes, until reaction is complete. NOTE: Reaction is complete when no gas evolution is visible and particles settle evenly over the bottom of the flask.

TABLE 1. VOLUME AND NORMALITY OF HYDROCHLORIC ACID USED FOR EACH FIZZ RATING

Fizz Rating	HCl	
	(ml)	(Normality)
None	20	0.1
Slight	40	0.1
Moderate	40	0.5
Strong	80	0.5

7. Add distilled water to make a total volume of 125 ml.

8. Boil contents of flask for one minute and cool to slightly above room temperature. Cover tightly and cool to room temperature. CAUTION: Do not place rubber stopper in hot flask as it may implode upon cooling.

9. Titrate using 0.1 N NaOH or 0.5 N NaOH (concentration exactly known), to pH 7.0 using an electrometric pH meter and buret. The concentration of NaOH used in the titration should correspond to the concentration of the HCl used in step 5. NOTE: Titrate with NaOH until a constant reading of pH 7.0 remains for at least 30 seconds.

10. If less than 3 ml of the NaOH is required to obtain a pH of 7.0, it is likely that the HCl added was not sufficient to neutralize all of the base present in the 2.00 g sample. A duplicate sample should be run using the next higher volume or concentration of acid as indicated in Table 1.

11. Run a blank for each volume or normality of acid using steps 5, 7, 8, and 9.

3.2.3.6 Calculations--

1. Constant (C) = (ml acid in blank)/(ml base in blank).

2. ml acid consumed = (ml acid added) - (ml base added X C).

3. Tons CaCO₃ equivalent/thousand tons of material = (ml of acid consumed) X (25.0) X (N of acid).

3.2.4 Maximum Potential Acidity by Total Sulfur Determination

3.2.4.1 Principles--

This method measures the total sulfur in a sample. If all of the total sulfur occurs in pyritic forms, the calculation of maximum potential acidity from sulfur corresponds with actual potential acidity from sulfur. But if part of the sulfur occurs in other forms, the maximum as calculated will be too high. This is the reason that such calculations are referred to as maximums and in doubtful cases approximate determinations should be made which rule out other sulfur forms (see 3.2.6). These determinations are not necessary when the maximum acid from total sulfur is within safe limits.

A sample is heated to approximately 1600°C. A stream of oxygen is passed through the sample during the heating period. Sulfur dioxide is released from the sample and collected in a dilute hydrochloric acid solution containing potassium iodide, starch, and a small amount of potassium iodate. This solution is automatically titrated with a standard potassium iodate solution.

A trace amount of potassium iodate reacts with potassium iodide and dilute hydrochloric acid to yield free iodine, potassium chloride and water. The free iodine combines with the sulfur dioxide and water to yield sulfuric acid and hydroiodic acid. The amount of potassium iodate solution used during the titration is recorded. The calculation of the percent total sulfur is based on the potassium iodate measurement (Smith et al., 1974):

3.2.4.2 Comments--

Some samples, e.g. coal, when first placed in the furnace may change the color of the solution in the titration vessel to pink or purple (probably due to organic compounds). Some samples may contain halogens (iodine, chlorine, fluorine) which darken the solution in the titration vessel and will therefore produce results that are low. The halogen problem, if encountered, may be eliminated by the use of an antimony trap between the furnace and titration assembly. Interference may result with samples high in nitrogen; however, this does not appear to happen with rock samples. Additional information can be obtained by reading Leco Equipment Application 120 and Instructions for Analysis of Sulfur in Hydrocarbons by the Leco High Frequency Combustion Titration Procedure.

Materials with a low chroma (2 or less) may have a high (over 1.0%) sulfur content; therefore, use a 0.250 g sample when the chroma of the material is 1 or 2. If the chroma of the material is zero, a 0.100 g sample is used. If sulfur is not detectable or more accurate values are desired in this sample size, increase to next highest sample size and rerun.

Read entire manuals on both the Leco Induction Furnace and the Automatic Titrator.

Periodically clean titration chamber and associated glassware with acetone or concentrated hydrochloric acid and rinse thoroughly with distilled water.

The following procedure is for use with a LECO Induction Furnace, Model 521 with Automatic Sulfur Titrator, Model 532. Other similar or advanced models of this instrumentation may perform equally well; however, the following procedure will require detailed modifications by a qualified person for application to other instruments.

3.2.4.3 Chemicals--

1. Iron chip accelerator (Leco number 501-077).
2. Iron powder accelerator (Leco number 501-078).
3. Copper ring (Leco number 550-189).
4. Magnesium oxide (MgO).
5. Potassium iodate (KIO_3), 0.0052 N: Dissolve 1.110 g KIO_3 in distilled water and dilute to 1 liter.
6. Hydrochloric acid (HCl) solution: Dilute 15 ml of concentrated HCl to a volume of 1 liter with distilled water.
7. Arrowroot starch solution: Dissolve 4.0 g of arrowroot starch (Leco number 501-061) in 100 ml of distilled water in a 250 ml beaker. Stir on a mechanical stirrer with a stirring bar. While starch is stirring, boil 300 ml of distilled and deionized water in a 600 ml beaker. Remove from heat when boiling point is reached. Remove starch from stirrer. Place boiled water on mechanical stirrer with stirring bar. While water is continually stirring, add 5 ml of starch mixture in 20 second intervals until all starch solution has been added. Place a small amount of the solution in the 600 ml beaker back into the 250 ml beaker that contained the starch mixture. Wash beaker by hard swirling and then pour contents back into the 600 ml beaker. Continue stirring solution in the 600 ml beaker allowing solution to cool to 40°C. Add 12.0 g of potassium iodide (KI). Continue stirring for 15 to 20 minutes.
8. Potassium iodide (KI).
9. Sulfur standards (Leco number 501-502).

3.2.4.4 Materials--

1. Leco Automatic Sulfur Analyzer, package unit, number 634-700.
2. Scoops, 0.2 ml volume.
3. Ceramic crucibles with porous covers.
4. Carboys, 19 liters (5 gal).
5. Tongs.

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6. Glass wool.
 7. Oxygen regulators.
 8. Mechanical stirrer.
 9. Stirring bar.
 10. Combustion tube, hydrocarbon (Leco number 519-004).
 11. Hot plate.
 12. Balance, can be read to 0.001 g.

3.2.4.5 Procedure (revised and updated from Smith et al., 1974)--

NOTE: Read entire manuals on Leco Furnace, Automatic Titrator and this entire procedure before starting.

1. Place one level scoop of iron chips in crucible.
2. Weigh 0.500 g of sample (less than 60 mesh) into the crucible.

NOTE: For samples that are suspected to contain over 1% sulfur or have a chroma of less than 2, see 3.2.4.2.

3. Add one scoop MgO.
4. Add one copper ring and then one scoop of iron powder.
5. Gently shake the crucible to evenly cover the bottom and place one porous cover on the crucible.
6. Turn on "Filament Voltage" grid tap to medium position.
7. Wait for one minute then turn "High Voltage" switch to ON.
8. Set "Titrate-Endpoint" switch to its middle position.
9. Turn on titrator (upper left switch above "Endpoint Adjust").
10. Drain "Titration Vessel" completely.
11. Set timer switch to ON, adjust timer to 10 minutes, or a time sufficient to satisfy steps 25, 26, and 27.
12. Slosh carboys containing HCl and KIO₃ to mix the condensate on the walls of the container.
13. Fill "Iodate Buret."

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14. Fill "Titration Vessel" approximately one-third full with the HCl solution.
 15. Turn on oxygen. Set the pressure to 15 psi, and the flow rate to 1.0 liter per minute. NOTE: Oxygen flow must be started before starch is added.
 16. Raise the "Locking Mechanism Handle" WITHOUT a sample crucible on the pedestal, and lock in place. NOTE: Make sure there is an airtight contact between sample platform and combustion chamber by observing a vigorous bubbling in the "Titration Vessel" chamber.
 17. Add one measure (5 ml) of starch solution. NOTE: If solution in "Titration Vessel" chamber turns turbid or yellow after starch solution is added, turn off the instrument following steps 33 through 39 and make NEW starch solution.
 18. Set "Titrate-Endpoint" switch to "Endpoint."
 19. After a few seconds when titrant level in "Iodate Buret" has stopped falling (Buret reading should be no more than 0.004) the solution in the "Titration Vessel" chamber should be a deep blue. NOTE: If the solution is a pale blue or almost black, turn off the instrument following steps 33 through 39 and make NEW starch solution.
 20. Set "Titrate-Endpoint" switch to middle position and lower "Locking Mechanism Handle."
 21. Refill "Iodate Buret."
 22. Place sample crucible on pedestal, making sure it is centered, and carefully raise "Locking Mechanism Handle" and lock in place.

NOTE: Make sure there is an airtight contact between sample platform and combustion chamber by observing a vigorous bubbling in the "Titration Vessel" chamber.
 23. Set "Titrate-Endpoint" switch to Titrate, or if it is known that sample will evolve SO_2 slowly, set switch at Endpoint. The Endpoint setting acts as a "Fine Control" allowing buret valve to discriminate smaller increments.
 24. Push RED button on timer to start analysis.
 25. Plate current must go to 400-450 ma for at least 2 minutes during the analysis; if not, reweigh and rerun sample.
 26. Adjust rheostat to prevent plate current from exceeding 450 ma.
 27. When buret reading does not change for 2 minutes, and Plate Current has achieved 400 to 450 ma, it can be assumed that all of the sulfur has been removed from the sample. If buret reading is still changing when timer shuts off instrument, set Timer Switch to OFF, which restarts furnace, leave furnace on until buret is stable for 2 minutes, then turn Timer Switch to ON.

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28. Set "Titrator-Endpoint" to middle position. IMPORTANT: Record titration reading.
 29. Lower sample platform, remove crucible using tongs, place fresh sample crucible in place, but do not close sample chamber.
- NOTE: Slightly drain titrating chamber to maintain original level. Drain, flush, and refill titrating chamber every 3rd sample, or more often if a large quantity of titrant was used by the previous sample (steps 16-22).
30. Refill KIO_3 buret.
 31. Close sample chamber, making sure it is tight. Check endpoint (steps 18, 19 and 21).
 32. Go to step 23 and continue until all samples have been processed.
 33. Turn "Titrator-Endpoint" switch to mid position.
 34. Turn off main O_2 valve on top of tank.
 35. Turn off "High Voltage."
 36. Turn off Automatic Titrator.
 37. Drain titration chamber; flush twice with a chamber full of HCl solution or water, cover and leave chamber full of HCl solution.
 38. If O_2 has stopped bubbling in the purifying train, turn off small knurled valve on gauge outlet.
 39. Turn off "Filament Voltage."

3.2.4.6 Calculations--

1. Percent sulfur. NOTE: Percent sulfur is dependent upon the concentration of potassium iodate titrant and sample size.
 - A. Using 1.110 g KIO_3/L and 0.500 g sample (0.005 - 1.00% sulfur range)
 $\%S = \text{Buret reading} \times 5.0.$
 - B. Using 1.110 g KIO_3/L and 0.250 g sample (0.010 - 2.00% sulfur range)
 $\%S = \text{Buret reading} \times 10.0.$
 - C. Using 1.110 g KIO_3/L and 0.100 g sample (0.025 - 5.00% sulfur range)
 $\%S = \text{Buret reading} \times 25.0.$
2. To convert % sulfur to maximum CaCO_3 equivalents: Multiply % sulfur by 31.25 to get tons CaCO_3 equivalent/1000 tons of material.

3.2.6.1 Principle--

In doubtful cases, as stated in 3.2.4.1, this method should be used to rule out HCl-extractable and non-extractable forms of sulfur which are not considered to be acid formers. The HNO₃-extractable sulfur is determined by calculations. This form of sulfur will react with oxygen to produce acid.

3.2.6.2 Comments--

It is necessary to remove chlorides and nitrates by water leachings after the hydrochloric and nitric acid (respectively) extractions before running total sulfur.

Care should be taken that no sample is lost by run over, splashing or breaking through the filter paper during all leachings.

3.2.6.3 Chemicals--

1. Hydrochloric acid (HCl), 2 parts acid to 3 parts water: Mix 400 ml of concentrated HCl with 600 ml of distilled water.
2. Nitric acid (HNO₃), 1 part acid to 7 parts water: Mix 125 ml of concentrated HNO₃ with 875 ml of distilled water.
3. Silver Nitrate (AgNO₃), 10%: Dissolve 10.0 g of AgNO₃ in 90 ml of distilled water. Store in amber bottle away from light.
4. Nessler's Solution (Fisher Scientific Co. No. So-N-24 or equivalent).

3.2.6.4 Materials--

1. Leco Induction Furnace and Automatic Sulfur Titrator as in 3.2.4.4.
2. Funnels, 28 mm I.D. polyethylene.
3. Filter paper, 5.5 cm glass fiber.
4. Flasks, Erlenmeyer, 250 ml.

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5. Beakers, 100 ml.
 6. Syringe.
 7. Balance, can be read to 0.001 g.

3.2.6.5 Procedure (Revised and updated from Smith et al., 1974)--

1. Take three 0.500 g subsamples of less than 60 mesh material.
2. Take one subsample and analyze for total sulfur (see 3.2.4).
3. Taking care not to sharply crease the glass fibers, fold filter paper to fit a polyethylene funnel.
4. Place second subsample in filter. NOTE: Make sure all material is placed in the filter.
5. Place subsample and filter onto funnel holder in sink or other suitable pan which can receive outflow from funnel.
6. Using a syringe, pipette, or other graduated dispenser, add 2:3 HCl to almost the top of the filter paper. Caution: During this step and all other leaching steps, be careful not to lose any sample by runover, splashing or breaking through the filter paper.
7. Repeat step 6 until a total of 50 ml of acid has been added.
8. Place funnel holder, containing funnel and subsample, over a 100 ml beaker.
9. Leach subsample with 50 ml of distilled and deionized water. Discard leachate. NOTE: Stop here if procedure cannot be completed in one day. CAUTION: Samples must be kept moist.
10. Leach subsample with another 50 ml of distilled and deionized water.
11. Test leachate for chlorides by adding 3 drops of 10% AgNO_3 with a dropper. NOTE: The presence of chlorides will be detected by a white precipitate.
12. Discard leachate and repeat steps 10 and 11 until no precipitate forms.
13. Discard leachate.
14. Air dry subsample and filter overnight.
15. Carefully fold glass fiber filter around the sample and transfer to a ceramic crucible for total sulfur analysis (see 3.2.4).
16. Place third subsample in a 250 ml Erlenmeyer flask. NOTE: Make sure all of the subsample is placed in the flask.

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17. Add 50 ml of HNO_3 (1:7).
 18. Let stand overnight at room temperature.
 19. Taking care not to sharply crease the glass fibers, fold a filter to fit a polyethylene funnel.
 20. Place a funnel holder over a sink or other suitable pan which can receive outflow from funnel.
 21. Carefully pour subsample and acid from the Erlenmeyer flask into the funnel. NOTE: Do not get material above top of filter paper.
 22. Repeat step 21 using distilled and deionized water to wash all materials remaining in the Erlenmeyer flask into the funnel.
 23. Place funnel holder containing funnel and subsample over a 100 ml beaker. NOTE: Stop here if procedure cannot be completed in one day. CAUTION: Sample must be kept moist.
 24. Leach subsample with 50 ml of distilled and deionized water. Discard leachate.
 25. Leach subsample with another 50 ml of distilled and deionized water.
 26. Test leachate for presence of nitrates by adding 3 drops of Nessler's Solution with a dropper. NOTE: If nitrates are present, the leachate will turn yellow within 30 seconds as seen against a white background.
 27. Discard leachate and repeat steps 25 and 26 until no nitrates are detected.
 28. Discard leachate.
 29. Air dry subsample and filter overnight.
 30. Carefully fold glass fiber filter around the sample and transfer to a ceramic crucible for total sulfur analysis (see 3.2.4).

3.2.6.6 Calculations--

1. HCl -extractable sulfur (mostly sulfates) = (Total sulfur of untreated sample) minus (Total sulfur after HCl treatment).
2. HNO_3 -extractable sulfur (mostly pyritic sulfur) = (Total sulfur after HCl treatment) minus (Total sulfur after HNO_3 treatment).
3. Non-extractable sulfur (mostly organic sulfur) = Total sulfur after HNO_3 treatment.

Appendix III

A COMPILATION OF WATER QUALITY GOALS

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as of January 1990.*

CONTENTS:

Selecting Water Quality Goals

Cross Reference of Chemical Names

Inorganic Constituents

Organic Constituents

Footnotes

References

Note: The Designated Level examples presented in earlier versions of Appendix III have been deleted due to misapplication by persons who did not have access to the text of this report. Designated Levels applicable to particular waste constituents and to a particular disposal situation or site may be calculated from the Water Quality Goals presented in this Appendix. The reader is referred to the text of "The Designated Level Methodology" for a discussion of the derivation and proper use of Designated Levels.