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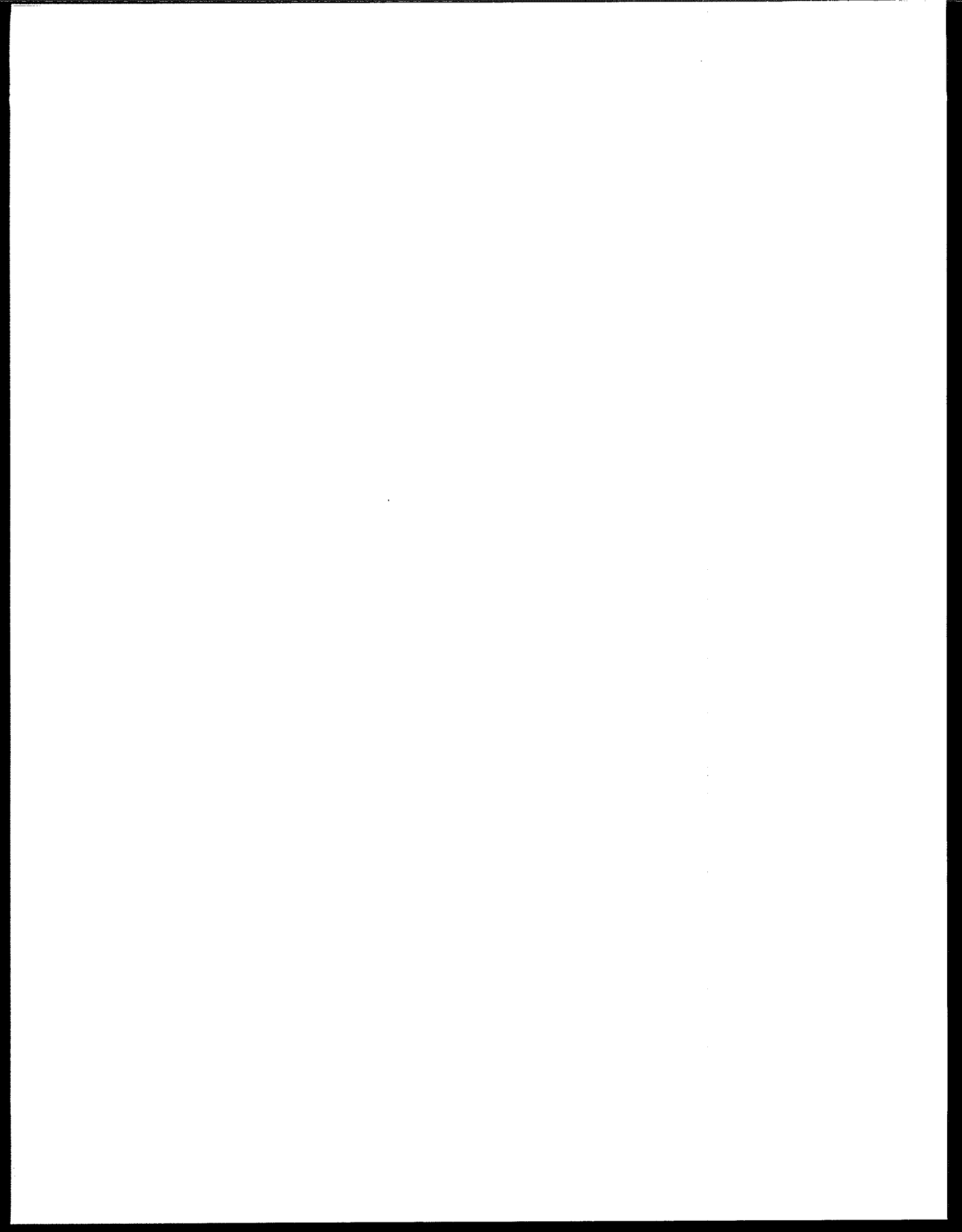# Approaches for Remediation of Uncontrolled Wood Preserving Sites

Approaches for Remediation of Uncontrolled Wood Preserving Sites

Center for Environmental Research Information
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

CONTENTS

ACKNOWLEDGMENTS

INTRODUCTION

This document provides an overview of the process of remediation of uncontrolled wood preserving sites. It is, in part, a distillation of discussions which took place at a Forum on Wood Preserving Waste held in San Francisco, California in October, 1988. Information from this workshop has been updated to reflect more recent technological advances. The audience is comprised of individuals with a scientific or an engineering background who are involved with remediation at these sites.

This document emphasizes two important elements of the wood preserving remediation process: 1) site specific factors and 2) multiple technology utilization. Greater emphasis is placed on the treatment of soils rather than ground water treatment and containment mechanisms. The reader is cautioned that some of the soil treatment data presented may be from only a limited number of studies and may not have universal application.

More detailed technical documents regarding the investigation and evaluation of wood preserving sites are being developed. (USEPA, 1990; NETAC, 1990)

References

USEPA, Planning Guide for Selection of Control Technologies for Wood Preserving Sites (Draft), Cincinnati, OH (1990).

NETAC, A Technology Overview of Existing and Emerging Environmental Solutions for Wood Treating Chemicals, Pittsburgh, Pennsylvania (1990).
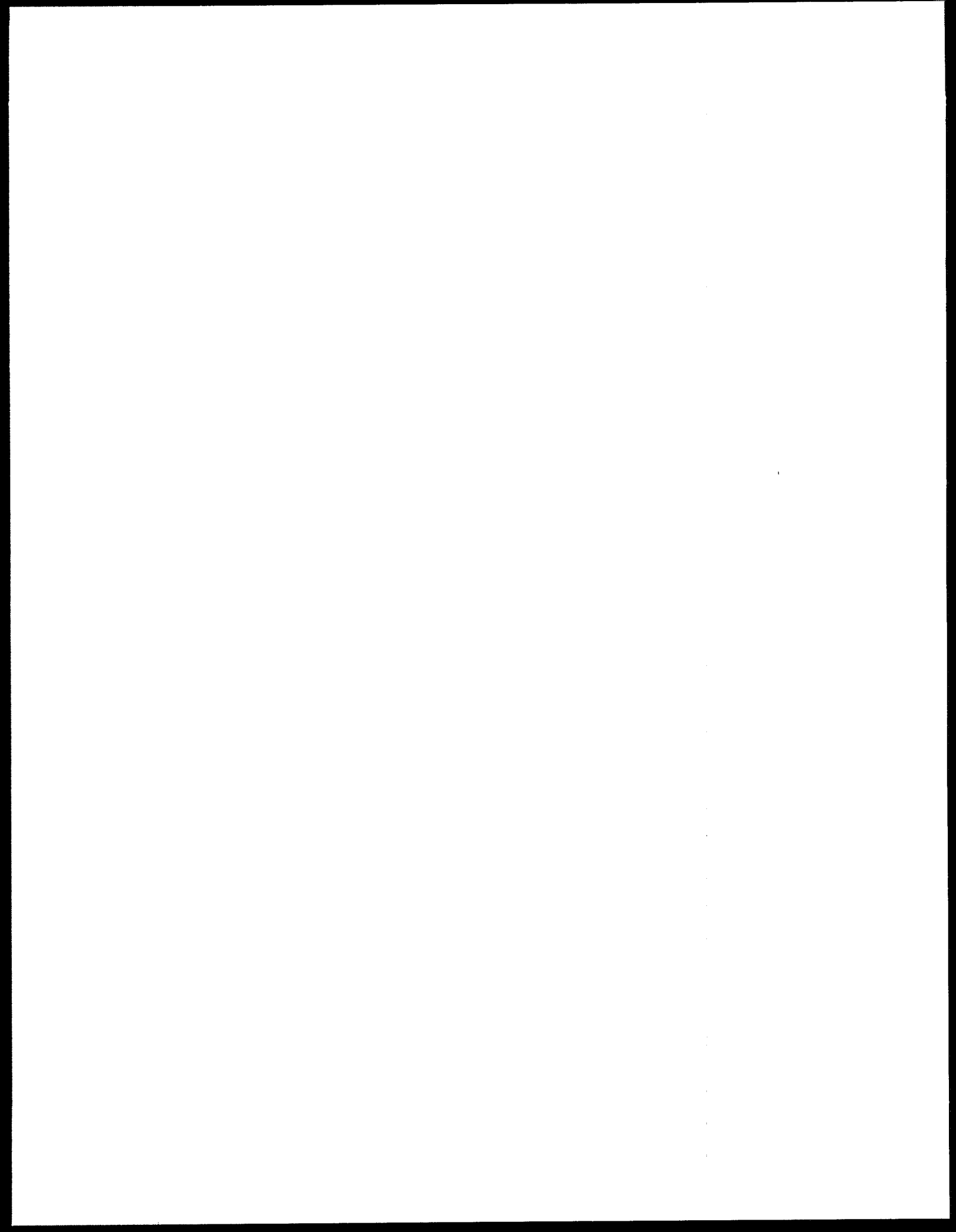
Physical and Chemical Nature of Wood Preserving Compounds

Wood preserving compounds are generally of the following three types:

> Organic based - creosote
> Organic based - pentachlorophenol (PCP)
> Inorganic based (Metallic salt) - primarily copper/chromium/arsenic (CCA)

The physical and chemical characteristics of these waste types differ and these differences will influence the sampling, monitoring, and migration of the wastes as well as the choices of remediation technologies. In addition, an uncontrolled waste site may contain wastes from one, two, or all three of the above waste types.

The following information is a listing of the compounds that could generally be found in each class. Even within each chemical class, the exact physical and chemical characteristics will vary depending on intended use and supplier (vendor). The reader is referred to material safety data sheets (MSDS) for more accurate information about commercial products.

Organic Based

A. Creosote - coal tar distillate mixture of over 250 individual compounds

> 35% by weight aliphatic hydrocarbon (oil)
> 65% by weight polynuclear aromatic
> hydrocarbons (PAHs)--including:
> > naphthalene
> > acenapthene
> > fluoranthene
> > pyrene
> > chrysene
> > carbozole
> minor compounds may include:
> > nitroquinolenes

Table 1 lists the major components of commercial grade creosote and Figure 1 shows the structure of the most prevalent polynuclear aromatic hydrocarbons in this type of waste.

Table 2 presents some of the most important physical properties of creosote compounds for evaluating waste distribution and treatment options.

Figure 2 shows the general relationship between the number of six membered condensed rings and physical and chemical properties.

B. Pentachlorophenol (4-8% weight) in heavy oil carrier mixture also includes tetrachlorophenol used to make PCP soluble, and "higher" chlorophenols.

Benzene, toluene, and xylene may be present in the carrier oil. Mixtures exposed to sunlight may also contain dioxin.

Figure 3 shows the structure and composition of pentachlorophenol and several related compounds.

Inorganic Based (Metallic Salt)

A. Copper, chromium, arsenic (CCA)--major group
B. Zinc, copper, arsenic
C. Ammonia and metal salts
D. Dinitrophenol, zinc, and other metal salts

References

Verschueren, K., Handbook of Environmental Data on Organic Chemicals, Von Nostrand-Reinhold, New York (1977)
Occupational Health Services, Material Safety Data Sheets Database.
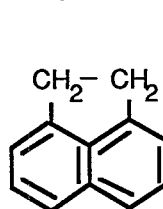
Table 1. Major Components of Creosote

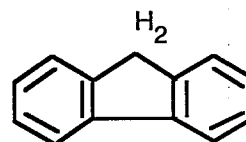| Creosote component	Composition
Naphthalene	17.0
2-Methylnaphthalene	6.5
1-Methylnaphthalene	3.5
Biphenyl	1.9
Acenaphthylene	0.5
Acenaphthene	7.8
Dibenzofuran	5.2
Fluorene	6.0
Phenanthrene	19.4
Anthracene	2.5
Carbazole	5.1
Fluoranthene	11.8
Pyrene	8.4
1,2-Benzanthracene/Chrysene	4.2
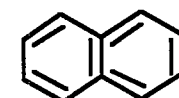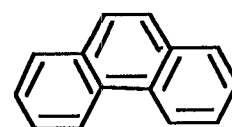
Naphthalene   Phenanthrene

Acenaphthene   Fluorene   Pyrene
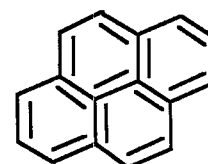
Figure 1. Structure of the Major Components of Creosote

Table 2. Physical Properties of Creosote Compounds

Compound	Molecular Weight	Solubility	Specific Gravity	Vapor Pressure	Boiling Point (Condition Unspecified)
benzene	78.11	1780 mg/l at 20°C	0.88	76.0 mm @ 20°C	176°F
naphthalene	128.00	insol	1.10	0.5 mm@20°C	424°F
pyrene	202.26	0.16 @ 26°C	1.27	1.0 mm @ 20°C	739°F
chrysene	228.20	0.06 mg/l @ 25°C	1.27	not available	488°C
benzo(a)anthracene	252.30	.003 mg/l	1.35	1.0 mm @ 20°C	590-594°F

Source of data (Verschueren, 1977) (Occupational Health Services)

Number of Condensed Rings ↑   Molecular Weight ↑   Solubility ↓   Photo-chemical Degradation ↑   Microbial Degradation ↓   Genetic Toxicity ↑

Figure 2. General Relationship Between the Number of Six Membered Condensed Rings and Physical and Chemical Properties as Number of Rings Increase

Pentachlorophenol   85-90%

Higher Chlorophenols   2-6%

2,3,4,6-Tetrachlorophenol   4-8%

Dioxin
(octa-, traces of hepta-, and hexachlorodioxin)   ≈ 0.1%

Figure 3. Composition of Technical Grade Pentachlorophenol

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Sampling and Monitoring Methodologies
to Determine Extent of Contamination

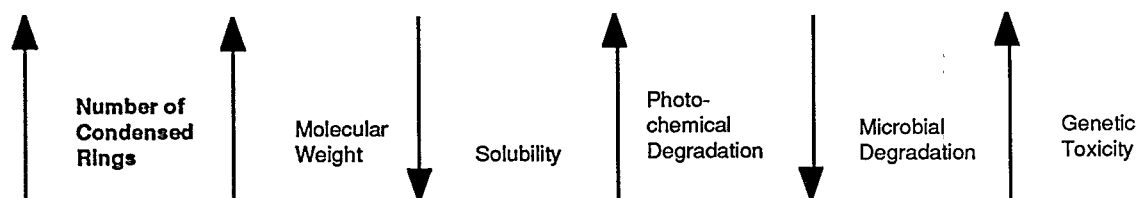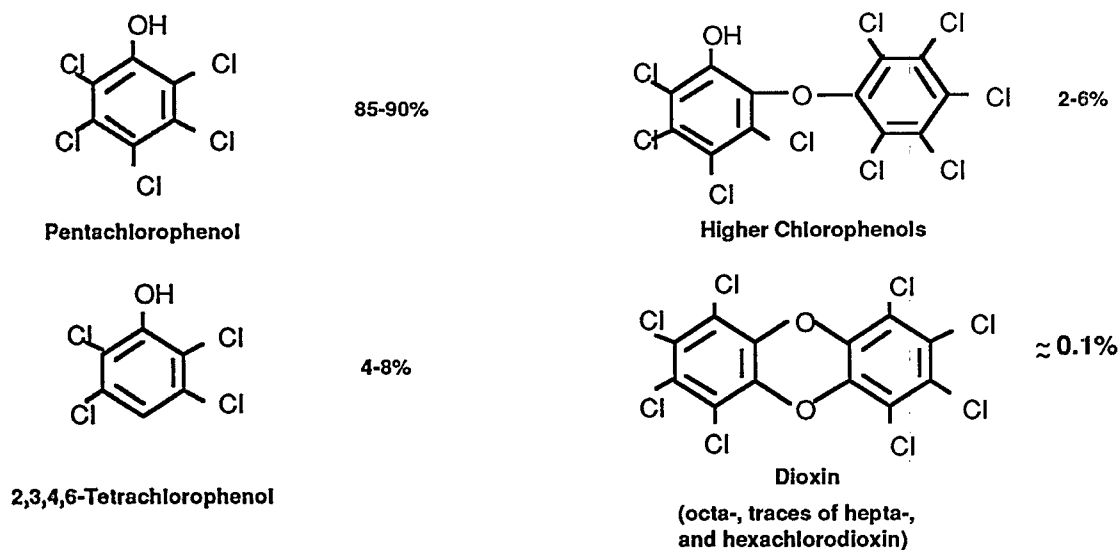The investigation and monitoring of wood preserving contamination is dependent on site specific factors such as the chemistry of the wastes at the site and the soil characteristics.

Waste Distribution/Contaminant Behavior

The migration of contaminants is influenced by factors such as density and viscosity, pore space, degree of water saturation, and organic content of the soil at the site (USEPA, 1989).

Wood preserving waste/ground water interactions may be classified into three general types depending on the preservative, carrier oil, and ground water chemistry.

Immiscible
 Sinker - dense nonaqueous phase liquid (DNAPL)
 Floater - light nonaqueous phase liquid (LNAPL)
Miscible
 Soluble

DNAPL will sink by gravity and be located on top of a less permeable zone. LNAPL will float on top of the water table. Miscible compounds will be soluble in the ground water.

Chemical Characteristics

When analyzing air, soil, or liquid for chemical constituents, one must monitor for compounds from the carrier, manufacturing by-products, and environmental by-products as well as the major wood preserving compounds.

Monitoring Well Materials and Installation

Caution must be exercised when developing a monitoring well so that distinct aqueous layers (LNAPL, DNAPL, ground water) can be identified. The material comprising the monitoring well should not chemically interact with the extracted liquid.

Reference

USEPA, Transport and Fate of Contaminants in the Subsurface (EPA/625/4-89/019) Cincinnati, OH (1989).
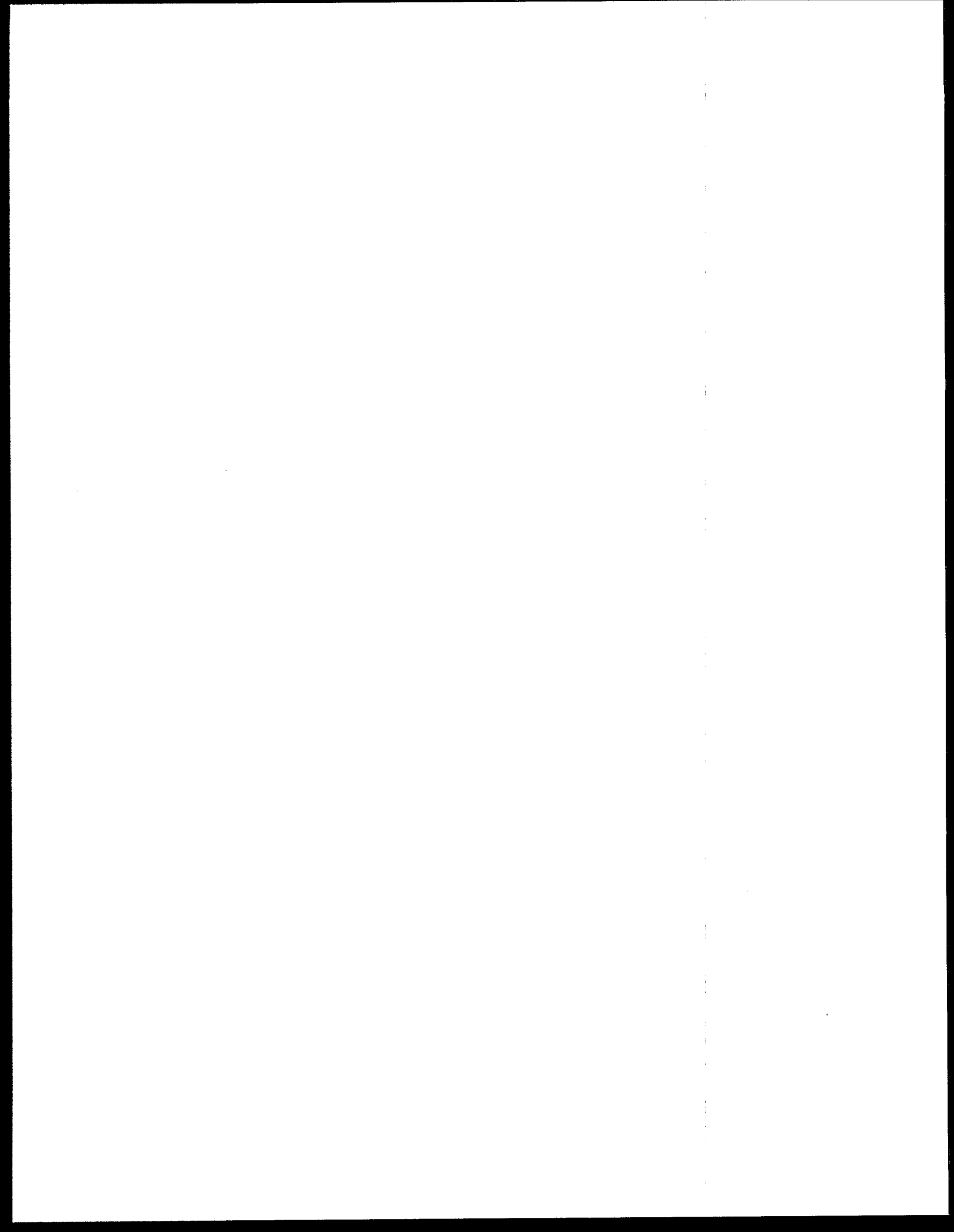
Innovative Screening Techniques for Monitoring Wood Preserving Sites

Two innovative monitoring methods may be considered for use at wood preserving sites. X-ray fluorescence can be utilized on CCA sites and immunoassay techniques can be utilized on PCP sites.

X-Ray Fluorescence

Field-portable X-ray fluorescence (FPXRF) is a site-screening procedure using a small, portable instrument (15-25 lbs) that addresses the need for a rapid turnaround, low-cost method for the in situ analysis of inorganic contaminants. Traditional Contract Laboratory Program (CLP) methods of analysis may take 20-45 days per site to complete and the analysis would cost much more than FPXRF. FPXRF can measure inorganic elements when used with the proper radio-isotope source and the appropriate standards. FPXRF is capable of simultaneous analysis of up to six analytes at a time. This method is useful at various levels of analysis, with data quality dependent upon the extensiveness of the survey, the type of standards used, and the reinforcement of data by other collaboratory methods. FPXRF can be used for periodic monitoring as remediation proceeds.

The following elements have been successfully analyzed by using FPXRF: arsenic, chromium, copper, iron, lead, and zinc. Though detection limits are highly matrix dependent and site specific, the detection limits for these elements using FPXRF have ranged from approximately 100-500 mg/kg (Raab, et al, 1990).

X-ray fluorescence is based on the fact that atoms fluoresce in a unique and characteristic way. By bombarding a sample with energy, the instrument causes an electronic instability. As the instability "relaxes" to a more stable energy level, X-ray fluorescence is emitted. The detector senses and counts this spectrum of radiation which is a "fingerprint" of the specific analyte and, on this basis, identifies the atom. Quantitation is done against a calibration curve that was generated by the analysis of site-specific standards.

Reference

Raab, G.A., R.E. Enwall, W.H. Cole, III, M.L. Faber, and L.A. Eccles, X-Ray Fluorescence Field Method for Screening of Inorganic Contaminants at Hazardous Waste Sites. In: Hazardous Waste Measurements, M. Simmons, Ed., Lewis Publishers, Chelsea, MI (1990).

Immunoassay

Immunoassay techniques have been applied to the measurement of toxic compounds in the environment.

Advantages of immunoassays to other monitoring techniques are their speed, sensitivity, specificity, and cost-effectiveness. Further, there is no need to sample cleanup prior to analysis, which saves solvent costs and minimizes generation of hazardous wastes. Immunoassays can be used for analyzing a wide variety of structures. They can be designed either as rapid, field-portable, semi-quantitative methods or as standard quantitative laboratory procedures. They are well suited for the analysis of large numbers of samples and often obviate the need for lengthy sample preparation. They can also be used to identify which samples need to be further analyzed by classical analytical chemistry methods, and they are especially applicable in situations where the analysis of an analyte by conventional methods is not possible or is prohibitively expensive (Van Emon, et al, 1990).

As with any other method, immunoassays have important disadvantages. Immunoassays monitoring techniques are only applicable for water based samples at this time. Unlike gas chromatography/mass spectrometry (GC/MS), they cannot be used when the environmental sample contains an unknown compound or a complex mixture of compounds. In some cases, immunoassays may not be as accurate and precise as the conventional analytical procedures. Because antibodies are subject to interferences and cross-reactivity with compounds other than the target analyte and must be raised and characterized, more lead time is required of development of immunoassays for monitoring techniques.

Of particular importance to the characterization and remediation of a site contaminated with wood preserving wastes has been the development and successful demonstration of two immunoassays for pentachlorophenol in water. The demonstrations were conducted under the monitoring and measurement technologies portion of the Superfund Innovative Technology Evaluation (SITE) Program. One method demonstrated was a 96-well plate immunoassay, designed primarily for use in fixed or mobile laboratories. The detection limit of the plate assay is about 1 ppb. The second method was a field analysis kit designed to be used on-site to generate qualitative and semi-quantitative data on pentachlorophenol in water. The detection limit of the field kit is about 30 ppb. Both methods are commercially available.

Reference

Van Emon, J., M.E. Silverstein, W.D. Munslow, R. White, and E.N. Koglin. Demonstration of the Westinghouse Bio-Analytic Systems, Inc. Field Immunoassay Method for the Analysis of Pentachlorophenol in Water (Draft). Environmental Monitoring Systems Laboratory-Las Vegas, U.S. Environmental Protection Agency (1990).
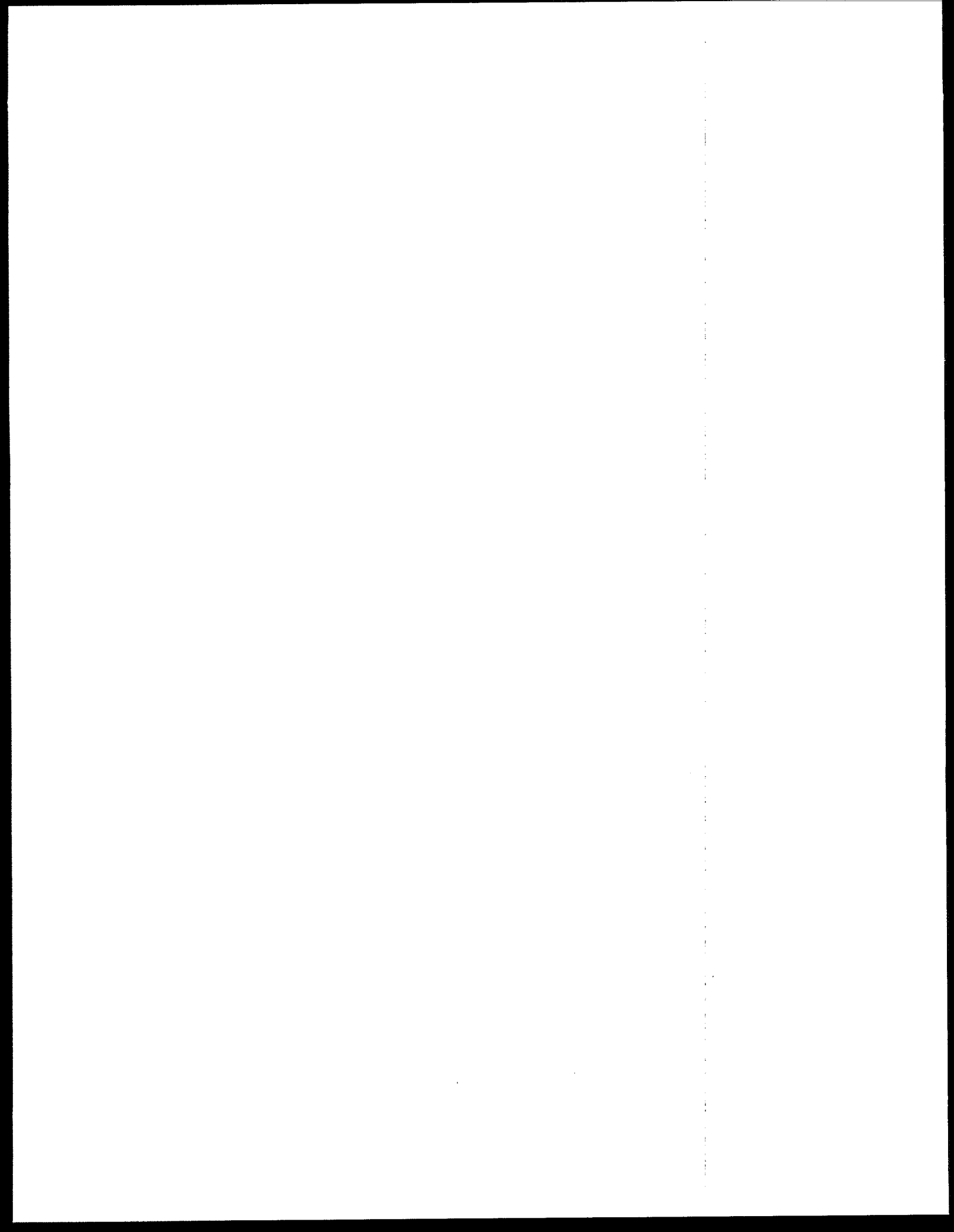
Modeling Wood Preserving Compound Movement

In order to assess the risk to human health and environment from exposure to wood preserving compounds, the movement of waste from its source to a receiving source, such as a surface stream or fish should be modeled.

Pentachlorophenol movement through runoff, erosion, leaching, and ground water transport to a surface stream has been modeled, and the largest source of uncertainty or error in this modeling effort involved the effects of ionization upon uptake, the amount of chemical delivered to the stream from the site, and the effect of daily averaging rather than volume weighted averaging. Further uncertainty was associated with complications arising from PCP behavior within fish (Ambrose, et al, 1988). Figure 4 illustrates the contaminant movement in this modeling effort.

More sophisticated models could be applied to a wood preserving site to give better insight into the behavior of the wastes. MINTEQ--a metal speciation model is capable of predicting the different ionic forms of the metals and other complexes based on the local geochemistry. HSPF--a whole watershed model, which has the capability of simulating both land and water bodies simultaneously and could be applied to multiple and large scale wood preserving sites.

Indicator compounds would need to be selected if modeling creosote movement because of the difficulty of modelling several compounds.

Reference

Ambrose, E., et al. Modeling the Transport and Fate of Wood Preserving Wastes in Surface Waters. Proceedings of the Forum on Wood Preserving Waste, San Francisco, CA (1988).
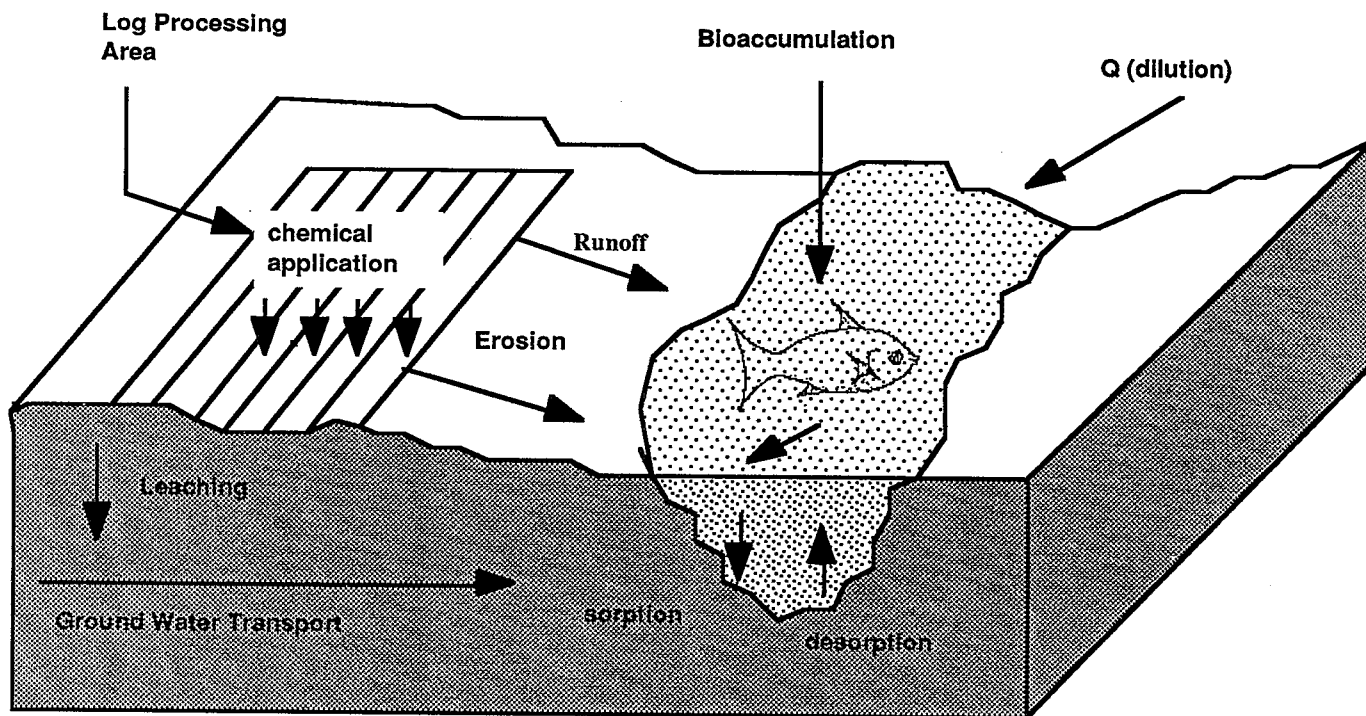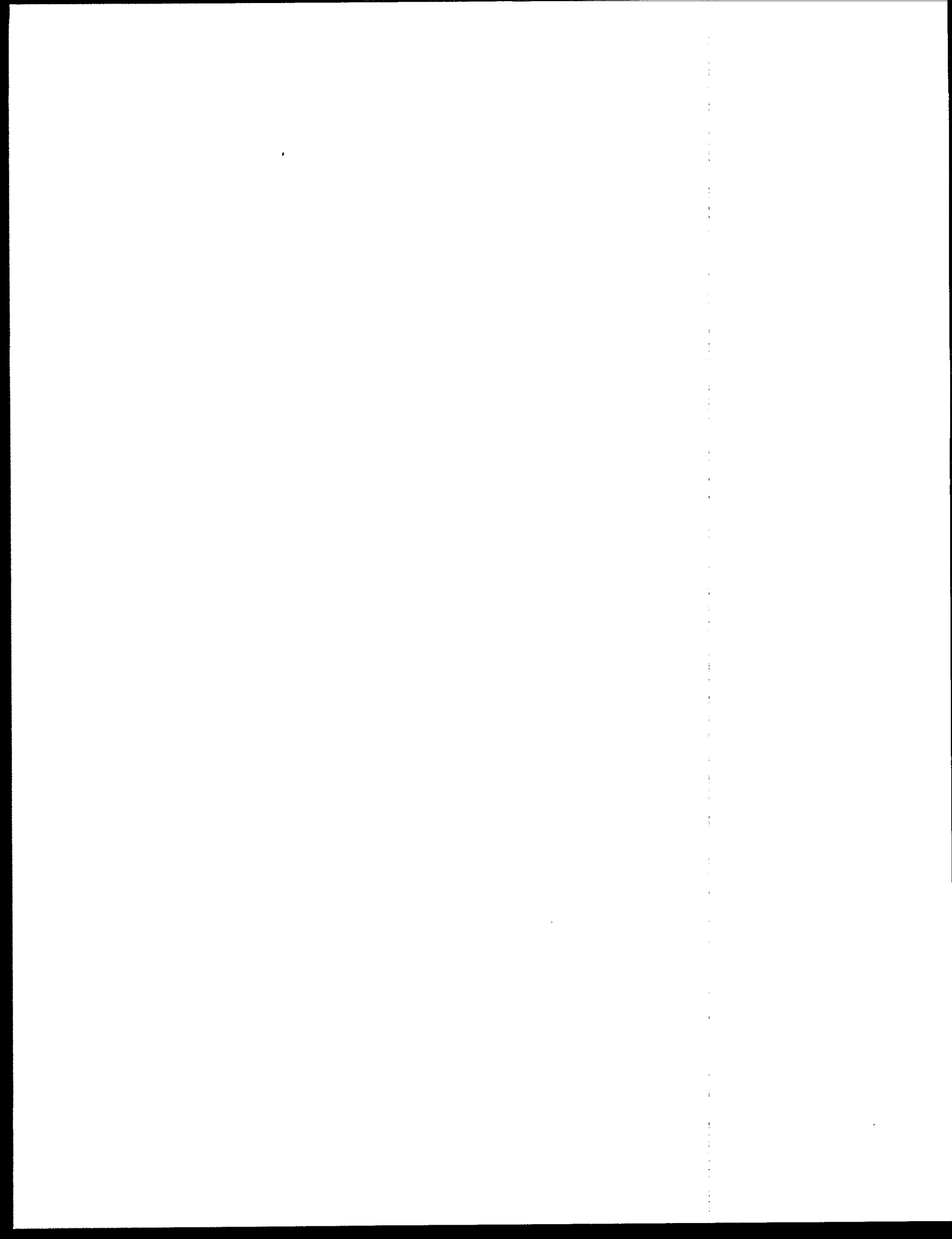

Figure 4. Contaminant Migration from Modeled Wood Preserving Site

Treatment Technologies for Recovery,
Source Control, and Ground-Water Contamination

Multiple Technology Utilization

Most uncontrolled wood preserving sites contain contaminated soils and ground water. Remedial processes for both of these problems should be considered together. In most instances, the technologies required for source control treatment (involving liquid, sludges, or soil) would differ from those required for ground water treatment. An exception to this may be in situ biorestoration for organic contamination. In addition, source control measures may require combinations of unit processes (the treatment train approach) to achieve acceptable cleanup levels or to meet cost effectiveness criteria. This is especially true if the site contains both metallic salts and one of the organic classes (an exception may be vitrification). Table 3 shows several options for single technology use or treatment train operations for various types of source control contaminants.

The contaminant behavior of creosote waste lends itself to innovative treatment concepts. Unfortunately, there are limitations on treatment processes for CCA waste because metals can not be destroyed and have different solubilities at varying pHs.

Preliminary Screening Methodology for Determining Feasible Alternatives

Preliminary evaluation of the treatability of wood preserving surface water or extracted ground water constituents can be made by utilizing existing software containing treatability data from traditional treatment processes (USEPA, 1989). Innovative processes such as ion exchange are also being utilized to recover metals from groundwater contaminated with CCA (Hickey and Stevens, 1990).

Soil remediation processes can also be evaluated from the literature or from the performance of bench scale treatability studies. The reader is referred to a more complete guide for evaluating soil treatment technologies (USEPA, 1988). The soil/contaminant matrix must first be understood when evaluating potential treatment technologies. Figure 5 illustrates the distribution of soil constituents. The contaminants may be found in any of the soil constituents.

The soil texture or particle size is useful in determining whether the contaminant would be tightly bound to the soil. Leaching or partitioning tests can also be utilized for this purpose. Stabilization technology can be evaluated by comparing the leachability of the soil before and after treatment.

The following partitioning coefficients between the fluid and solid can be used to determine the migration potential and treatment of potential of a constituent:

Kow - water/oil (general literature)
Kd - water/soil (site specific)
Kh - water/air (general literature)

Partitioning coefficients are beneficial in evaluating extraction technologies or air stripping. A retardation coefficient relates the relative velocity (V) of a constituent to water.

$$R = \frac{V \text{ water}}{V \text{ constituent}}$$

The higher the retardation coefficient, the less likely it is that the constituent will migrate in water. Therefore, retardation coefficients are useful in evaluating pump and treat technologies.

The relative biodegradability of a substance can be evaluated by placing the material (slurry) in a container with or without microbial addition and determining the degradation over time. Air and nutrients may also be introduced. A complete mass balance including the volatilization pathway is vital for performing feasibility evaluation.

British Thermal Units (BTUs) data can be used to measure the incinerability of the material. The heating value of a compound may also be useful in this evaluation and can be found in the literature. Heating value determination is also important when evaluating vitrification because hood systems may be limited by the amount of heat generated.

Recovery: Pump and Treat Systems

Nonaqueous phase liquid (NAPL) compounds such as creosote may be recoverable if the compound is present in concentrations above residual saturation. Normal recovery methods involve flow path management by several methods. NAPL moves in response to pressure gradients and gravity. The movement and recovery is influenced by interfacial tension and by the process of volatilization and dissolution. Over 7,000 gallons of a coal tar liquid containing naphthalene and anthracene were recovered from a site by a well recovery system (Villaume, et al, 1983). Two hundred fifty thousand gallons of creosote were recovered in a drainage line system at a different site (Union Pacific Railroad, 1989).

Recovery operations become less efficient if the NAPL compounds sorb to the soil formation. The extraction flow rate during remediation may be too rapid to allow aqueous saturation levels of the partitioned coefficient to be reached locally. This will result in large volumes of extracted ground water with low levels of contaminant concentration.

Table 3. *Technology Options for Source Control*

| Contamination	Single Unit Operation	Treatment Train
Metallic salts	Stabilization Vitrification	Soil Washing ⟶ Stabilization
Creosote or PCP	Incineration Vitrification In situ biorestoration Land treatment	Soil Washing ⟶ Biotreatment
Metallic salts and Creosote or Metallic salts and PCP	Vitrification	Incineration ⟶ Stabilization Soil Washing ⟶ Biotreatment ⟶ Stabilization Land Treatment ⟶ Stabilization
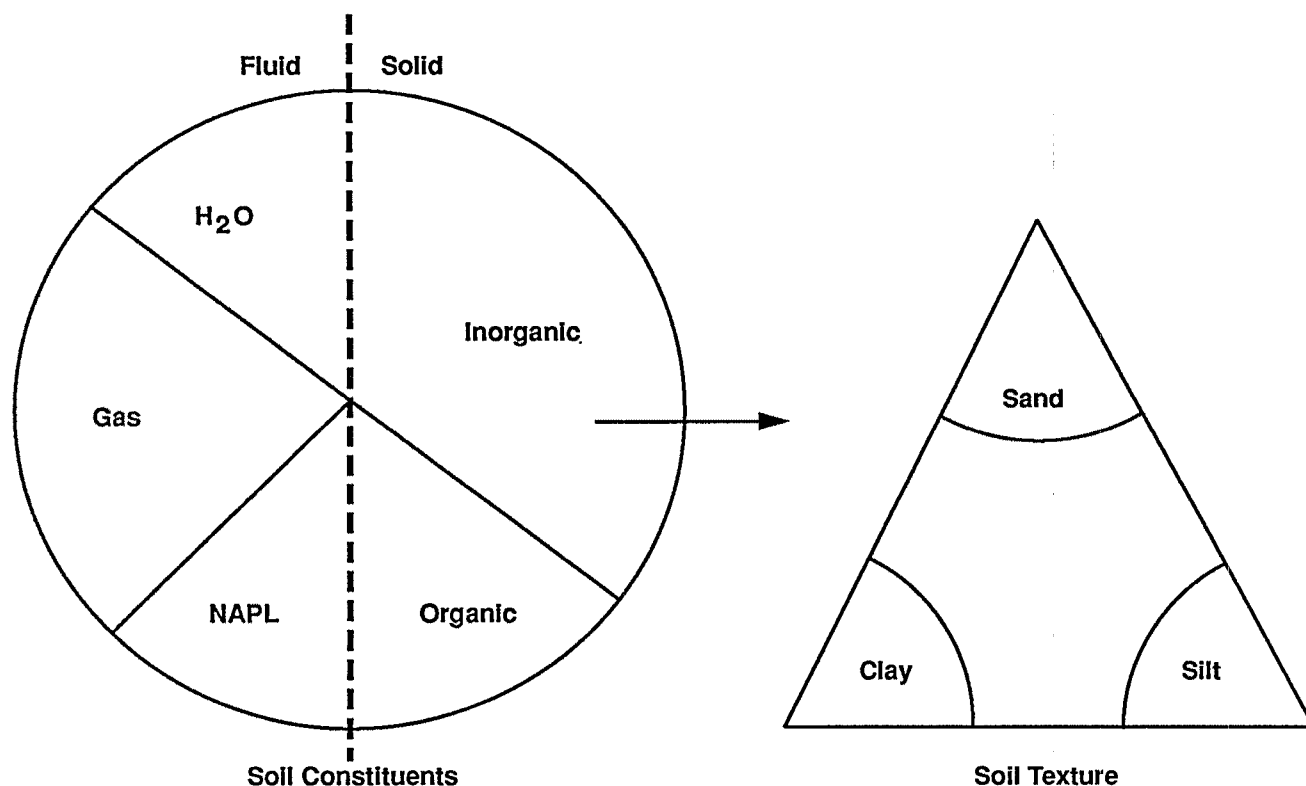
Figure 5. Distribution of soil constituents, contaminant may be found in any or all constituents

The required data for evaluating the recoverability of the material and predicting the time for restoration can be found in the literature (USEPA, 1990).

Bioremediation

On-site biological treatment is generally accomplished using one of three types of systems: (1) in situ, (2) prepared bed, or (3) bioreactor. An in situ system consists of treating contaminated soils in place, often with the use of naturally occurring microorganisms to treat the contaminants. In some instances, supplemental populations of adapted organisms may serve to enhance treatment. In a prepared bed system, the waste may be either physically moved from its original site to a newly prepared area, which has been designed to enhance biological treatment and/or to prevent transport of contaminants from the site; or removed from the site to a storage area while the original location is prepared for use, then returned to the bed, where the treatment is accomplished. Bioreactor systems typically are based on reactor designs from chemical or environmental engineering processes and may be either unsaturated (e.g., composting) or saturated (e.g., slurry).

Before implementing a biological remediation technology for a soil contaminated with wood preserving waste, an evaluation of the potential of the contaminated system to accomplish

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detoxification and degradation of hazardous constituents present in the waste should be conducted. Preliminary treatability studies can be used to evaluate detoxification and degradation processes as they affect the fate and behavior of hazardous constituents in a contaminated waste or soil. Treatability studies can provide specific information that can be used to determine migration (leaching) potential; correlate chemical disappearance with changes in bioassay response; compare treatment of different wastes under similar experimental conditions; and evaluate approaches for enhancing treatment. Persistent hazardous constituents that occur as co-substrates, (e.g., high molecular weight PAHs in wood preserving waste), in a matrix where other hydrocarbons are serving as readily available growth substrates may be degraded through the process of co-oxidation (Foster, 1962a,b), (Keck, et al.,1989).

Factors that may be evaluated in laboratory and field studies to enhance biological treatment, including degradation and detoxification, include: (1) soil incorporation or mixing to reduce the initial (toxic) concentration; (2) application of waste more frequently and at lower concentrations to acclimate soils to toxic complex wastes and to avoid application of toxic concentrations; (3) addition of mineral nutrients; (4) addition of microbial carbon and energy sources to stimulate co-oxidation; and (5) use of different soil types as the treatment medium.

There have been few published studies concerning wood preserving wastes in which bioassays have been combined with chemical assays to evaluate the extent of both detoxification and degradation of hazardous substances in soil systems and to characterize the toxicity of potential leachates. Chemical analyses may be used to define the types and concentrations of hazardous compounds in a waste or soil, but the results must be extrapolated to estimate the toxicological effects on biological systems (Donnelly, et al., 1986).

Apparent degradation, expressed as changes in concentrations of PAH constituents for creosote sludge and pentachlorophenol (PCP)-creosote mixed sludge in a sandy loam soil are presented in Tables 4, 5, and 6 (Aprill, et al., 1990). Generally, results indicated greater apparent degradation for low molecular weight PAHs, which are non-carcinogenic, and less apparent degradation for high molecular weight PAHs, which are carcinogens or co-carcinogenic. The group of non-carcinogenic PAHs, including naphthalene, fluorene, phenanthrene, and anthracene, were compared with the group of carcinogenic and co-carcinogenic PAHs, including fluoranthene, pyrene, benzo(a)anthracene, and chrysene with regard to apparent degradation. Results are summarized in Table 4. Greater

apparent degradation was indicated for the non-carcinogenic group, ranging from 54-90% of mass added for the four wastes evaluated. The carcinogenic group of PAHs exhibited apparent degradation ranging from 24-53% of mass added for the four wastes. The greater apparent degradation of the non-carcinogenic PAH was not unexpected, since these compounds serve as carbon and energy sources for soil microorganisms, whereas the carcinogenic PAHs generally cannot serve as ubiquitous carbon and energy sources for soil microorganisms but are believed to be degraded through co-oxidation processes (Park 1987a,b), (Keck, et al., 1989).

Significant degradation of PCP and creosote compounds was observed in a pilot-scale treatment train process consisting of soil washing, aqueous treatment system and slurry bioreactor (Ellis and Stinson, 1990).

The integration of information concerning apparent degradation of hazardous constituents of complex wastes with bioassay information represents an approach for evaluation of the effectiveness of biological treatment of wood preserving wastes. When combined with information from site and soil characterization studies, the data generated in treatability studies may be used in predictive mathematical models to evaluate the effectiveness of biological treatment for a specific site scenario and to develop appropriate containment and monitoring strategies.

Incineration

Organic wood preserving waste (creosote and PCP) are amenable to incineration because of the organic structure and heating value of the compounds. Inorganic wood preserving mixtures are not as amenable to incineration because some metals may be emitted during the combustion process. Therefore mixtures of organic and inorganic waste may require an additional treatment train.

Tables 7, 8, 9, and 10 contain incineration performance data for organic wood preserving compounds or similar waste types. These data indicate that incineration was effective in destroying or removing the compounds tested.

Table 11 shows that some dioxins and furans were emitted from the incineration stack. It is believed that these pollutants were not completely destroyed because temperatures below 1800° F were prevalent in this particular incinerator.

One processing problem that may occur with soil contaminated with wood preserving waste is the initial materials handling operation. Incompatible equipment design may cause problems such as dusting or feed stock processing jams.

Table 4. *Apparent Degradation of PAH Constituents* in Creosote Sludge in Unacclimated Kidman Sandy Loam Soil.*

PAH constituents	Initial waste concentration (mg kg⁻¹ waste†)		Initial waste/soil concentration (mg kg⁻¹ soil†)		Waste/soil concentration at day 354 (mg kg⁻¹ soil †)		Decrease during incubation (%)
Naphthalene	28,000 ±	1,200≠	273.0 ±	11.5≠	n.d.§		100
Fluorene	23,000 ±	5,900	177.0 ±	11.5	72.1 ±	18.9†	59
Phenanthrene	76,000 ±	15,000	833.0 ±	23.0	500.0 ±	98.5	40
Anthracene	15,000 ±	6,800	243.0 ±	110.0	131.0 ±	52.0	46
Fluoranthene	72,000 ±	17,000	567.0 ±	11.5	397.0 ±	90.7	30
Pyrene	64,000 ±	12,000	573.0 ±	5.8	353.0 ±	76.4	38
Benzo(a)anthracene	7,400 ±	1,600	52.5 ±	0.7	36.0 ±	8.0	31
Chrysene	8,300 ±		50.5 ±	1.0	35.1 ±	8.0	30

*   Results are presented for eight PAH compounds, which represent 96% of the mass of the 14 PAHs analyzed in the waste sample
†   Results are presented on a dry weight of waste or soil basis
≠   Results are expressed as mean concentration of three replicate analyses ± one standard deviation
§   n.d. = not detected (from Aprill, 1990)

Table 5. *Apparent Degradation of PAH Constituents* in PCP-Creosote Mixed Sludge in Unacclimated Kidman Sandy Loam Soil.*

PAH constituents	Initial waste concentration (mg kg⁻¹ waste†)		Initial waste/soil concentration (mg kg⁻¹ soil†)		Waste/soil concentration at day 354 (mg kg⁻¹ soil †)		Decrease during incubation (%)
Naphthalene	42,000 ±	28,000≠	n.d.§		n.d.--		
Fluorene	22,000**		49.2 ±	1.7≠	1.6 ±	1.8†	97
Phenanthrene	52,000 ±	6,200	120.0 ±	0.0	4.2 ±	0.8	97
Anthracene	11,000 ±	6,800	69.4 ±	7.2	17.5 ±	5.4	75
Fluoranthene	46,000 ±	6,200	73.3 ±	63.5	55.3 ±	14.7	25
Pyrene	56,000 ±	13,000	143.0 ±	5.8	353.0 ±	76.4	74
Benzo(a)anthracene	16,000 ±	2,400	14.0 ±	1.6	10.9 ±	1.5	22
Chrysene	6,900 ±	2,200	20.7 ±	1.8	14.2 ±	1.7	31

*   Results are presented for eight PAH compounds, which represent 96% of the mass of the 14 PAHs   analyzed in the waste sample
†   Results are presented on a dry weight of waste or soil basis
≠   Results are expressed as mean concentration of three replicate analyses ± one standard deviation
§   n.d. = not detected
**   One sample was analyzed (from Aprill, 1990)

Table 6. *Apparent Degradation of Four Non-carcinogenic and Four Carcinogenic PAH Compounds in Four Complex Wastes in Unacclimated Kidman Sandy Loam Soil During 354 Days Incubation*

PAH Group	Creosote sludge		PCP--creosote mixed sludge	
Non-carcinogenic				
Initial concentration (mg kg⁻¹)	1,527 ±	150	239 ±	9
Final concentration (mg kg⁻¹)	703 ±	154	23 ±	8
Mass removed (%)	54		90	
Carcinogenic				
Initial concentration (mg kg⁻¹)	1,243 ±	19	251 ±	64
Final concentration (mg kg⁻¹)	821 ±	183	118 ±	47
Mass removed (%)	34		53	

(from Aprill, 1990)

Table 7. Incineration Trial Burn Data on PCP

Test Facility:	Los Alamos National Laboratory, (DOD) Controlled Air Incinerator by Environmental Control Products, Model 500-T (Nominal 500 Lbs./Hr.), with Minor Modification to Factory Unit.
Waste Description:	Korean War-Vintage Army Ammunition Boxes Treated with Pentachorophenol (PCP), Crushed
Waste Analysis:	Chlorine Content -0.07 Percent by Weight; PCP Content - 0.103 to 0.106 Percent by Weight; Pine Wood with 7960 (Actual) and 9066 (dry) BTU/Lb
Results:	DRE for PCP was Greater than 99.99% - No TCDD in Stack Emissions (Det. Limit 1 PPB). No TCDF in Stack Emissions(Det. Limit 5 PPB), Ash - Not Sampled and Analyzed
Waste Feed Rates:	60-100 Lbs/Hr.
Incineration Conditions:	1800 · F for a Gas Residence Time of 1.5 Seconds
	(from USEPA, 1984)

Table 8. Data on Incinerating Wood Preserving Wastes

Test Facility:	EPA Combustion Research Facility Rotary Kiln, Summer, 1987
Waste Description:	K001 - Pentachlorophenol (PCP) Type. Allied Chemical's American Wood Division of Timber Company, Richton Mississippi. Bottom Sediment/Sludge from Wastewater Treatment Containing PCP (including Penta - and Tetrachlorophenols, Volatile Organic Solvents, e.g., Benzene, Toluene, and Polynuclear Aromatic (PNA) Parts of Creosote)

Analysis:		
	Soil	40%
	Water	30%
	Wood Chips	10%
	Active Organics	20%
		100%
	Ash Content	12-51%
	Heating Valve	3800-8300 BTU/LB.
	PCP	970-3800 PPM

Results:	Non-Detectable for all Priority RCRA Volatile and Semi-Volatile Compounds in Ash and in Scrubber Water (Including Dioxins/Furans)
	(from USEPA, 1988a)

Table 9. Data on Incinerating Wood Preserving Wastes

Test Facility:	John Zink Company Rotary Kiln
Waste Description:	K001-C (Creosote Type) Allied Chemical's Birmingham, Alabama Plant, Bottom, Sediment Sludge from Treatment of Wastewaters from Processes using Creosote, This Material Obtained from the Pearl River Wood Preserving Corporation, Picayune, Mississssippi

Analysis:		
	Soil	30.0%
	Water	20.0%
	Wood Chips	10.0%
	Naphthalene	4.0%
	Phenanthrene	3.5%
	Fluoranthene	2.5%
	Other Active Organics	30.0%
		100.0%
	Ash Content	12-51%
	Heating Value	10,000-11,000 BTU/LB.
	Volatile Matter	57-81%

Results:	Non-Detectable for all Priority RCRA Volatile and Semi-Volatile Compounds in Ash and in Scrubber Water (Including Dioxins/Furans), Stack Testing Results Not Available
	(from USEPA, 1990a)

TABLE 10. *Summary Results of Test Burn on Simulated Creosote Pit Waste*

Test Conditions: Waste Feed Rate - 121.0 lb/hr in the Shirco Portable Pilot Test Unit

Waste Analysis (% wt) -	Creosote	22.20%
	Pentachlorophenol	0.85%
	Water	7.71%
	Inert Dry Soil	69.24%

Operating Conditions -	Residence Time	15.00 min.
	Layer Thickness	1.00 in.
	Primary Chamber Temps	1612/1725 °F
	Secondary Chamber Temp	2189°F

P O H C ANALYZED	Gas Phase Analysis *D R E (%)*[a]	Residual Ash Analysis *(ppm)*
Pentachlorophenol	>99.9999	ND
Phenol	>99.9995	ND
2,4-Dimethylphenol.	>99.9999	ND
Indeno (1,2,3-CD) Pyrene	>99.9820	0.030
Benzo (B) & (K) Fluoranthene	>99.9999	0.120
Benzo (A) Pyrene	>99.9985	0.137
Benzo (A) Anthracene/Chrysene	>99.9999	ND
Naphthalene	99.9998	0.248
Acenapthene	99.9999	ND
Acenapthylene	99.9999	ND
Fluorene	99.9999	ND
Anthracene/Phenanthrene	99.9999	0.403
Flouranthene	99.9998	0.362
Pyrene	99.99995	0.164
	Total ppm	1.464

[a] *DRE calculated at detection limit*

Measured Particulate Grain Loading: (Corrected to 7% O_2)	0.010 gr/dscf

(from Berdine, 1987)

Table 11. *Incineration Data by EPA's Tier 4 National Dioxin Study 1986-87*

Test Facility:	Industrial Controlled Air Incinerator with Waste Heat Boiler
Waste Description:	Paint Filters and Dry Paint, Paint Sludge, and Wood /Plastic Scrap Material from Manufacture of PCP-Treated Wood/ PVC Plastic Coated Storm Windows, Wood Framing Treated with 0.1 Lb/Ft³ PCP
Results:	For an Average Feed rate of 2390 Lb/Hr to the Incinerator:

Total PCDD Emissions:	1370 Micrograms/Hour (Stack)
2,3,7,8 TCCD	8.62 Micrograms/Hour (Stack)
Total PCDF Emissions:	4600 Micrograms/Hour (Stack)
Ash Analyses:	

Total PCDD:	1 TO 302.6 PPB
2,3,7,8 TCCD	ND to 0.2
Total PCDF:	0.07 To 17.7 PPB

Incinerator Temperatures:	Primary Chamber:	1100 TO 1800 °F (Avg. 1392 °F)
	Secondary Chamber:	940 to 1820 °F (Avg. 1480 °F)

(from USEPA, 1987)

Soil Washing/Soil Flushing/Extraction

Soil washing and extraction technologies are used to separate contaminants from the host matrix. These systems commonly utilize an extractant, a separation stage, and produce a more concentrated waste and also less contaminated residuals.

Onsite soil washing systems are likely to cause volume reduction of hazardous material by separating coarse material from fine material. Soil washing systems have been evaluated for metal contaminated soils (Esposito, et. al, 1989), although their effectiveness for CCA waste has not been evaluated. They have also been evaluated and are commercially available for their use as a pretreatment step in biological treatment of creosote waste.

The effectiveness of in-situ soil flushing systems for organic wood preserving and similar compounds is currently being evaluated at several uncontrolled waste sites.

Extraction systems can separate creosote or PCP waste from contaminated soils. In a batch pilot scale test at the United Creosote site, over 95% of the total PAH was removed from untreated soil (Table 12). PCP removals were 85%. Removal efficiencies for dioxins and dibenzo furans were not as substan-

tial; however, the initial concentrations of these compounds were low.

In a bench scale study designed to extract chromium from a contaminated soils from a mining operation, 64% of the total chrome and 93% of chrome (VI) were extracted utilizing acid. The original concentration of total chrome was 1467 mg/kg and 700 mg/kg of chrome (VI) (Taylor, et al., 1990)

Limitations on the process would be the efficiency and costs of the extraction process to produce a clean material as well as disposal or reuse of the extracted material.

Dechlorination

Chemical dechlorination processes have been developed and pilot-tested for chlorinated organic compounds. The general chemical equations for this process are:

$$ROH + KOH \longrightarrow ROK + H_2O$$

$$ArCl_n + ROK \longrightarrow ArCl_{n-1} \; OR + KCl$$
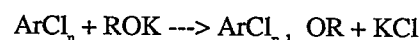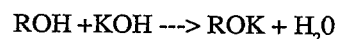
(R = organic)
(Ar = aryl)

Table 12. Summary of Results for Solvent Extraction

Compound	Untreated Soil (mg/kg) Sample/Duplicate	Treated Soil (mg/kg) Sample/Duplicate	Water (mg/L)	Removal (%)
PAHs (mg/kg)				
Acenapthene	360/200	3.4J/3.3J	ND(0.12)	
Acenaphthylene	15J/8.6J	3.0J/2.9J	ND	
Anthracene	330/210	8.9/9.1	ND	
Benzo(A)Anthracene	100/56	7.9/7.6J	ND	
Benzo(A)Pyrene	48/24J	12/11	ND	
Benzo(B)Flouranthene	51/24J	9.7/13	ND	
Benzo(G,H,I)Perylene	20J/11J	12/12	ND	
Benzo(K)Flouranthene	50/28J	17/11	ND	
Chrysene	110/59	9.1/9	ND	
Dibenzo(A,H)Anthracene	ND/370	4.3J/4.4J	ND	
Flouranthene	360/270	11/11	ND	
Flourene	380/220	3.8J/3.8J	ND	
Indeno(1,2,3-CD)Pyrene	19J/10J	11/11	ND	
Naphthalene	140/69	1.5J/1.5J	ND	
Phenanthrene	590/450	13/13	ND	
Pyrene	360/220	11/10	ND	
Total PAH Conc.(mg/kg)	2,879/2,124	123/110	0	95.7
Pentachlorophenol (mg/kg)	380/210	58/52	0.470J	84.7
Dioxins (mg/kg)				
Total TCDD	ND(0.4)/NA	ND/NA	NA	-
Total PeCCD	ND(2)/NA	ND/NA	NA	-
Total HxCCD	16/NA	4.8/NA	NA	68.8
Total HpCDD	360/NA	180/NA	NA	50.0
Total OCDD	1300/NA	690/NA	NA	46.9
Dibenzofurans (mg/kg)				
Total TCDF	ND(0.2)/NA	0.015/NA	NA	-
Total PeCDF	1/NA	2.6/NA	NA	-
Total HxCDF	30/NA	18/NA	NA	40.0
Total HpCDF	160/NA	75/NA	NA	53.1
Total OCDF	160/NA	87/NA	NA	45.6

ND = Not Detected (Detection Limit in Parentheses)

J   = Estimated Value - The Result is Less than the Detection Limit but Greater than
        Zero (Detection Limit in Parentheses)

NA = Not Analyzed (not part of sampling plan)

(from Litherland, 1990)

A pentachlorophenol/oil waste from the Montana Pole site was treated by a dechlorination process. Table 13 show that reductions in the chlorine content of specific classes of compounds occurred. Table 13 shows 2,3,7,8 reduction in another study. Table 14 shows 2, 3, 7, 8 reduction in another study involving dechlorination processes.

In another laboratory test utilizing KPEG for treating a wood preserving slurry, 97% of the PCP and 59% of the total PAHs were removed (Table 15). Dioxin removal was higher although some initial values were low.

Several technical considerations must be addressed when evaluating this technology such as air emissions and toxicity of residual by-products.

TABLE 13. Results of Laboratory Tests on PCP/Oil Waste from Montana Pole Site

CDD/CDF in Treated and Untreated Waste	Untreated Waste Oil	Following KPEG Treatment at 70 °C for 15 Minutes	Following KPEG Treatment at 100°C for 15 Minutes	Average MDC (ppb)
		Concentration in Parts-Per-Billion (ppb)[a]		
TCDD (2378)	28.2	ND	ND	0.65
TCDD (total)	422.0	ND	ND	0.37
PeCDD (total)	822.0	ND	ND	0.71
HxCDD (total)	2982.0	ND	ND	2.13
HpCDD (total	20671.0	11.2	2.25	--
OCDD	83923.0	6.5	4.40	--
TCDF (2378)	23.1	12.1	ND	0.28
TCDF (total)	147.0	33.3	ND	0.35
PeCDF (total)	504.0	ND	ND	0.30
HxCDF (total)	3918.0	4.9	ND	0.76
HpCDF (total)	5404.0	5.8	ND	1.06
OCDF	6230.0	ND	ND	2.62

[a]"ND" indicates "none detected" in excess of the minimum detectable concentration (MDC) indicated.

(from Tiernan, et al., 1989)

TABLE 14. Results of Laboratory Tests of KPEG Reagent on Kent, Washington Wastes

Time (Hours) Following KPEG Treatment[a]	Concentration of 2,3,7,8-TCDD (ppb) in Treated Waste Sample
0[b]	120[b]
5.5	5.5
6.5	2.5
12.0	ND (0.3)

[a]A 250-g aliquot of the waste was treated with 25g KOH, followed by 75g KPEG and 25g dimethyl sulfoxide at a temperature of 115°C.

[b]Refers to the original waste, prior to treatment.

(from Tiernan, et al., 1989)

Table 15. Dechlorination Summary Results Concentration (mg/kg)

Parameter	Untreated Soil	Treated Soil	Reduction (%)
Total PAH's	1746	721	58.7
Pentachlorophenol	1100	31	97.2
Dioxins			
TCDD	0.004	<0.0003	92+
PCDD	0.011	<0.0004	96+
HxCDD	0.692	<0.0003	99+
HpCDD	5.280b	<0.0004	99.99+
OCDD	16.400b	<0.0008	99.99+

(from Litherland, 1990)

Immobilization

Immobilization technologies have been widely considered for the treatment of metals contaminated soils and sludges. They do not destroy the metal but decrease the leaching rate to an acceptable level by chemical reaction and surface area reduction. The effectiveness of these processes will be defined by the waste type, the binder utilized, and the leaching test that applied as the criterion.

Immobilization technologies include solidification/stabilization and vitrification. The term solidification suggests the conversion of a liquid or a semi-solid into a solid. Many waste materials are amenable to solidification. The term stabilization refers to a chemical reaction that decreases leachability. Not all waste can be successfully stabilized. For metal waste treatment, both terms can be used, but this is not true for many organic wastes. Solidification/Stabilization is a residuals management technique that can be used as part of a treatment train when organics and metals are both present.

Vitrification is a high-temperature thermal process that converts sludges or soils into an obsidian-like material and pyrolyzes organic compounds.

Metal waste solidification/stabilization has been demonstrated to be generally effective for reducing the leachability of several metals as evaluated by the TCLP test in the EPA's S.I.T.E. program and B.D.A.T. program. Stabilizing CCA waste is more difficult because the minimum solubilities of each metal is at a different pH value. Table 16 shows solidification/stabilization treatment data for a synthetic Superfund soil. Copper was successfully immobilized but variable results were obtained for arsenic whereas chromium data was inconclusive. Variable results for stabilization treatment of arsenic and chromium from wood preserving waste are also shown in Tables 17 and 18. Although these results are generally unsatisfactory, chrome reduction and arsenic reactions with sulfide or iron may increase the effectiveness of the stabilization process.

There have been several successful bench scale demonstrations of the vitrification process for reducing the leachabil-

ity of waste containing several metals. Arsenic may be incorporated into the melt instead of being volatilized (Timmons, 1990).

Regardless of which immobilization process is evaluated, several leach tests beyond the regulatory tests are encouraged. Both of these processes can be implemented in situ.

Solidification/stabilization has not been conclusively proven to be effective for organic waste. Many organic compounds such as oil and grease can interfere with cementacious reactions (USEPA, 1989a). Regulatory acceptance levels have been based on destruction processes such as incineration. These levels are based on a strong extraction test using methylene chloride or hexane. In general, pozzolonic material will not form a strong bond with organic compounds and will not meet cleanup criterion.

Recent research with organophilic (organic modified) clays has shown promise for reducing organic leaching because of strong bonding or reaction between the binder and waste (Soundararajan, et. al, 1990, and Sell, et.al, 1990). Polynuclear compounds and PCP have been treated with orgnaophilic clays. Table 19 shows that destruction levels were met for three of the four compounds evaluated. In another study with actual PCP waste, reduction in the total waste analysis and TCLP were noted after stabilization with three vendors, although dilution was not considered (Table 20). Evidence of dechlorination of polychlorinated compounds has been observed in other studies but has not been evaluated in detail.

The evaluation of organophilic clays needs to go beyond regulatory testing techniques to include Fourier Transform Infrared spectrophotometry (FTIR) and mass balances. Engineering controls to minimize ground water contact are also suggested.

Vitrification destroys organic materials by pyrolysis. The technology may be limited by the moisture content because of increased energy requirements and total organic concentration because of capture hood thermal limitations.

Alternatively, recovery mechanisms such as smelting may eventually be applicable for CCA waste.

Table 16. *Solidification/Stabilization Treatment Data for Synthetic Soils (TCLP Test)*

Metal	Raw (mg/l)	Treated
As	6.4, 9.6	ND, ND
Cd	33.1, 35.3	ND, ND
Cr	ND, .06	.07, .07
Cu	80.7, 10.0	.09, .17
Pb	19.9, 70.4	ND, .37
Ni	17.5, 26.8	ND, ND
Zn	359, 396	.69, .74

ND - Non Detectable

(from USEPA, 1988b)

Table 17. Solidification/Stabilization Treatment Data for CCA Waste

Element	E.P. Tox (mg/1) Raw	Treated	Binder
Chromium	90	16.0	cement/silicate
	90	0.5	potassium silicate
	90	150.0	proprietary
	90	13.4	portland cement
	90	4.1	portland cement
Arsenic	1.8	2.3	cement/silicate
	1.8	0.01	potassium silicate
	1.8	3.0	proprietary
	1.8	13.8	portland cement
	1.8	4.3	portland cement

(from Conners, 1990)

Table 18. Solidification/Stabilization Treatment Data for CCA Waste

Compound	E.P. Tox (mg/1) Raw	Vendor 1	Treated Vendor 2	Vendor 3
Arsenic	1.8	2.3	1.4	2.5
Chromium	98.4	116.0	12.4	106.0
Copper	13.6	0.2	4.7	0.1

·(from Weston, 1988)

Table 19. Solidification/Stabilization Treatment Data for Organic Waste

Compound	Mean Conc. in Raw Waste (µg/kg)	Mean Conc. in Stabilized Waste (µg/kg)
Bis-2-chloro-isopropyl ether	8,582	ND[a]
Napthalene	18,060	1,445[b]
Phenanthrene	20,184	ND[a]
Benzo(a)anthracene	30,460	ND[a]

[a]Not Detected

[b]Value corrected for dilution
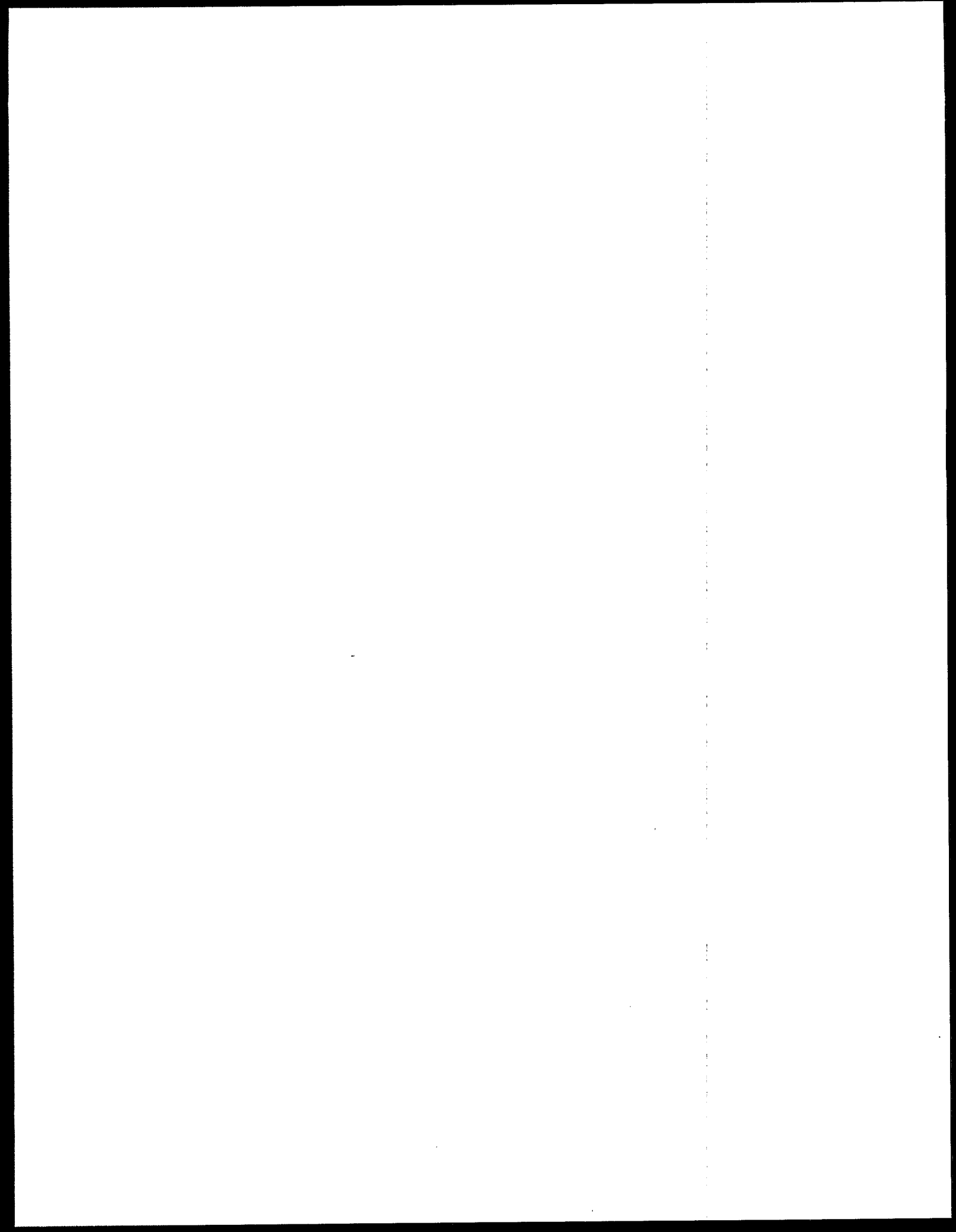
(from Soundaarajan, et al, 1990)

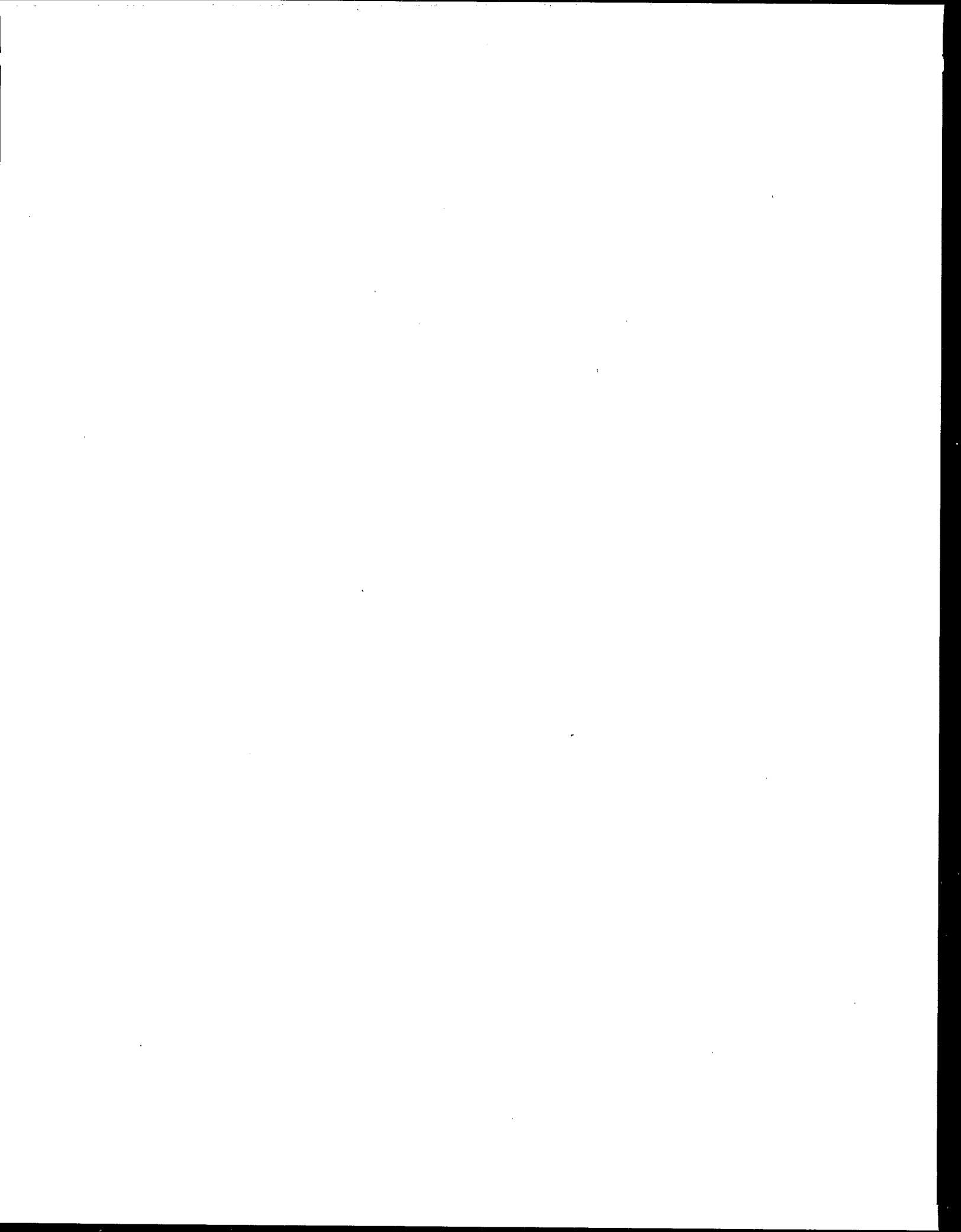*Table 20. Solidification/Stabilization Treatability Study Results for PCP Waste*

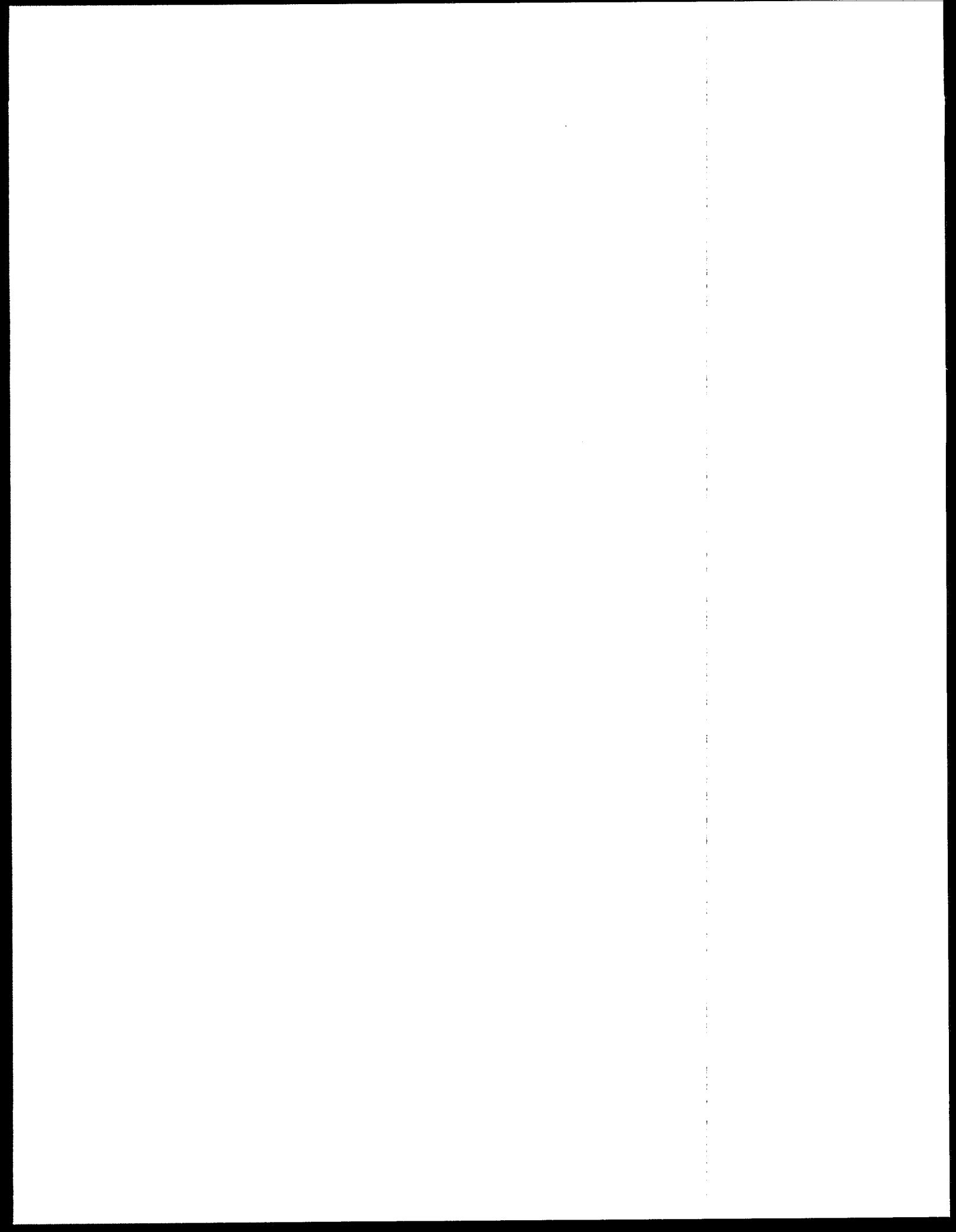| Test Method	Untreated	Treated Vendor 1	Vendor 2	Vendor 3
Total Waste Analysis (mg/kg)	521	150	34	51
TCLP (ug/l)	13,000	190	2700	230

(from EBASCO, 1990)

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