Mechanisms for Detoxifying Soil

Les Mécanismes pour Faire le Sol Nontoxique

K.H. KASTMAN P.E., M. ASCE, Soil Testing Services, Inc., Northbrook, Illinois, USA
K.R. HUIBREGTSE P.E., AIChE, Enviro Consulting Services, Sussex, Wisconsin, USA

SYNOPSIS Soil detoxification may be needed when soil is contributing to continued water contamination. Detoxification involves both physical displacement of loosely held contaminants and desorption or reaction of chemically bound material. Desorption from soil may be indirectly related to adsorption and critical variables affecting adsorption will also impact detoxification. Contaminant type, soil organic content, initial water content and gradation appear to be most important. In situ and above grade methods can be used to detoxify soil. Detoxification mechanisms evaluated both displacement and actual chemical reaction. However, the chemical reaction method is presently limited to simple one-step reaction systems. Soil scrubbing using high pressure jet sprays and counter-current extraction was evaluated on organic and inorganic soil types. Phenol, arsenic and PCB's were removed with decreasing effectiveness. Higher soil organic content further reduced removal efficiencies. In situ flushing using dilute neutralizing agents was successful for several inorganic compounds in granular soil.

INTRODUCTION

Engineers are reluctantly, but constantly being faced with contamination problems brought about by past indiscriminant burial of industrial and municipal wastes. Site remedial actions have centered around ground water. However, even after significant effort has been expended to remove and treat ground water, the total problem may not be solved due to continued leaching from contaminated soils. Chemical detoxification of these contaminated soils must then be considered.

Research into soil/chemical interactions has largely centered upon the attenuation of a leachate within the soil structure. Attenuation by a soil environment and subsequent detoxification from the soil are not necessarily directly related. Most past research has centered around limited or specific aspects of a soil/chemical environment and has produced some seemingly conflicting data, possibly because the impact of the soil environment as a whole has not been completely understood.

The intent of this paper is to review the concepts of soil detoxification, evaluate important soil environment parameters and to provide an overview of soil detoxification options.

CONCEPTS OF DETOXIFICATION

Detoxification is the process whereby a contaminant which has affected a subsurface environment is either removed or rendered immobile or innocuous. Detoxification can either be provided by physical displacement of the contaminant or leaching for subsequent treatment or by a chemical reaction with the contaminant. Detoxification can be performed either in situ or upon soil which has been removed for treatment above grade.

Detoxification procedures require an understanding of how the contaminant may be held within the soil environment. Two basic mechanisms are involved. One is chemical adsorption of the contaminant to the soil particles and the second involves the portion of contaminant which is retained or entrained within the pore space surrounding the soil particles. The relative apportionment of the contaminant in either condition depends on site specific variables. Both mechanisms are important and total detoxification should include procedures for chemical reaction with the adsorbed contaminants as well as methods for flushing contaminants from the pore space within the soil structure.

SOIL ENVIRONMENTS

The basic concepts of soil, water and air relationships within a soil environment must be considered to allow a more complete understanding of detoxification. As contaminants seep into the environment, they can potentially fill all available void space within a soil structure. Once into the pore space, a portion of the contaminant can be adsorbed onto and into the soil. The volume which can readily be filled by free flowing contaminant is a function of soil gradation, whereas the adsorption is more a function of soil surface area and organic content. Since soil environments vary widely in all three of these parameters, the degree and type of contaminant retention will vary significantly. The rate of detoxification will also vary significantly depending upon these soil parameters.

Water is held within the soil in several different ways. Conceptual relationships between soil, water and air for four soil types studied are shown in Figure 1. Tightly bound water is fluid held strongly within the soil itself. Loosely bound water can be involved in detoxification mechanisms and includes mobile, gravity-held and entrainable states. Conceptually, contaminants could exist within a specific soil system in a manner similar to any of the three loosely bound waters, depending upon the initial soil moisture content and nature of the contaminant. Contaminant remmoval or detoxification, however, requires significantly different energy levels and methods depending upon how the contaminant and natural soil water are being held.

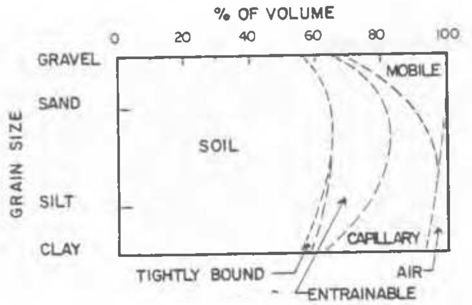

Fig. 1 Conceptual Water, Soil & Air Relationships

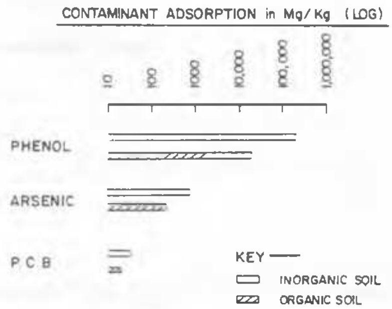

Fig. 2 Contaminant Adsorption on Two Soils

Soil Adsorption

The adsorbed contaminants are typically the most difficult to remove or detoxify. The amount and strength of the adsorption is a function of many interrelated variables including: 1) contaminant type; 2) soil organic content; 3) soil gradation; 4) clay content and type; 5) soil water content; 6) in-place density; 7) soil pH; and 8) contact time. Of these parameters, the contaminant type, soil organic content, and soil gradations appear to be the most important.

Contaminant Type - The nature of the contaminant and its miscibility or solubility in water is critical. Much research has indicated that inorganic, highly soluble, small molecule contaminants, such as chloride, can be highly mobile within a soil/water environment. Conversely, large molecular weight and insoluble organic contaminants, such as PCB's, will only travel short distances within a soil structure. Contaminants which are not soluble or miscible in water will tend to form a second layer upon contacting the ground water. This layer can be found at the surface of the water system or at a lower depth within the water system, depending upon the specific gravity of the contaminant. The first step in evaluating possible detoxification systems is to determine the contaminant's specific gravity and solubility and then estimate its potential location and flow path within the subsurface environment.

Organic Content - The impact of soil organic content on adsorption capacity is important, as demonstrated by results of on-going soil/chemical contamination research by the authors. Three contaminants, phenol, arsenic and PCB's were added to two different soils, one organic and one sandy. The inorganic soil was a naturally occurring sandy material which contained 77% sand, 17% silt, and 5% clay. The organic soil was a manufactured peaty topsoil with an organic content of 18%, a generally silty sand texture, and contained 3% clay. The contaminants were added as an 87% phenol solution, a 0.96% arsenic solution and a 7.5% PCB solution. Figure 2 indicates the results. In each case the organic soil absorbed more contaminant than the inorganic soil. Also, significantly more of the highly soluble phenol was absorbed than the moderately soluble arsenic than the nearly insoluble PCB's.

Soil Gradation - The adsorptive capacity is also highly dependent upon the soil gradation. Adsorption is generally a function of soil particle surface area which increases by the inverse of at least the square of the average particle diameter. Griffin (1978) has studied the adsorptive capacity of clay particles, and the potential attenuation of landfill leachate contamination has been directly correlated to the ion exchange of the particular clay and its mineral components.

A significant amount of a contaminant can be adsorbed not only onto the particle's outside surface, such as for clays, but also into the particle's internal surface, available in larger size silt, sand and gravel. In a series of tests, the two soils previously noted were divided into distinct fractions by grain size, and each of these fractions was dosed with the contaminant solutions. The amount adsorbed into each size fraction was compared on a unit weight basis. In general, a large amount of adsorption occurred on the clay particles, then there was a decrease of adsorption onto the silt particles, but then an increase on the coarse silt and sand fractions. The adsorption on the coarser particles appeared to be due to adsorption into the initially dry interior pore space of the larger sized particles.

The adsorption to internal soil pores is significant when considering detoxification methods. While adsorption into the particles is related to a surface tension phenomena, which draws the contaminant within the pore space, there is generally no available detoxifying mechanism, which tends to draw the contaminant outward from the inside of the particle. This indicates that total detoxification of a soil which retains contaminant internally may be difficult.

Initial Water Content - The initial water content of the soil system which has been contaminated is also important to the amount of adsorption which can occur. Initial water reduces the amount of pore space for liquid contaminants to be retained by the soil system. The test results confirmed this fact. The phenol and arsenic tests of fractionated soils were performed upon initially dry samples. Additional tests performed upon initially moist or saturated soil samples showed adsorption concentrations which were much lower.

DETOXIFICATION BY CONTAMINANT TRANSFER

One method of detoxification is to physically remove the contaminant from the soil environment. This can be performed on excavated soils by a washing or scrubbing process, or by in situ flushing of the contaminant.

Soil Scrubbing

One research project conducted by the authors' organizations included evaluation of a mobile system to excavate contaminated soils and physically wash the contaminant from the soil surface. Water or water with additives were considered as washing solutions. Organic solvents, such as hexane, acetone or freon were initially investigated, but ruled out due to their potential explosiveness, air quality considerations, and high cost. The water washing systems evaluated included: 1) water submergence; 2) high pressure jet spray; 3) froth flotation mixing system; and 4) hydrocyclone separation.

The design suggested for the mobile system included combinations of the above four washing systems, as each had its advantages and disadvantages. For example, the jet spray rapidly broke down the slightly cohesive soil particles and stripped contaminants from the surface. However, it was not effective on clay lumps, which required a much longer spraying time and consequently a much higher volume of washing fluid. When a water bath submergence step was included after the jet spray, the clay lumps softened and could then be broken up by a second jet spray operation.

The effectiveness of the submergence and water knife rinse process for treatment of phenol, arsenic and PCB's which had been absorbed onto the total soil sample is illustrated in Table 1.

TABLE I

Water Knife Test and Submerged Washing Results

Soil	Process	Phenol*	Arsenic*	PCB*
Inorganic				
	Initial (1 minute rinse)	3558.0	337.7	14.0
	15 minute submerged wash and rinse	74.8	237.2	11.0
	60 minute submerged wash and rinse	42.8	193.1	11.0
Organic				
	Initial	402,800	6794	-
	15 minute submerged wash and rinse	158,400	3552	-
	60 minute submerged wash and rinse	56,560	3097	-

*Values in mg/kg on soil samples

The froth flotation unit was utilized as a mixing contact chamber for soil particles less than 2.0 mm. However, alone it was not capable of mixing larger soil or breaking down cohesive or semi-cohesive lumps.

A counter-current extraction system was tested to establish the feasibility for removing contaminant from fine soils. The four stage counter-current operation utilized a last stage clean water rinse and allowed solvent reuse in a typical counter-current mode. The soil/water separation was accomplished by hydrocyclones. This equipment was most suitable for trailer mounting and high throughput although a significant fraction of the very fine soil did remain entrained in the overflow.

Laboratory testing of the counter-current extraction approach using phenol contaminated soil illustrated the effectiveness of the treatment. Removals of phenol from the soil into the cleanest water were quite high and resultant phenol concentrations, especially for the inorganic soil, were low. Less effective treatment was obtained for the organic soil because of the affinity between organic compounds.

In Situ Flushing

Soil systems can sometimes be detoxified by natural ground water flow, precipitation, or can be cleansed by a forced fluid injection. Unless the fluids are removed, this method of detoxification is just mass dilution, which renders the contaminants innocuous, due to their new lower concentration. When fluids are removed, it is usually through the use of well points or purge well systems. All ground fluids should be removed and treated to provide total system detoxification.

Research relating to the evaluation of the potential long term effects of natural precipitation leaching through highly contaminated sandy soils is currently underway. The soils have received various amounts of dibromochlorophenol (DBCP), Endrin, Arsenic and chlorides. The study includes the performance of isotherm tests on five representative soil types in order to establish the maximum adsorption attainable at various concentration levels. Also, column tests are being performed to simulate occasional precipitation and soil drying as well as continuous slow ground water flow. The tests are in progress and a sufficient data base has not yet been collected in order to formulate conclusions regarding the leachate potential or possible remedial action steps.

Other projects have indicated the occurrence of a "piston" effect when adding flushing water into a soil system. For silty and most fine sand soils, the introduction of a hydraulic head generally tends to result in this piston or plug flow, and contaminant/water mixing generally occurs only at the interface of the two fluids. The flow is essentially laminar. In coarse sand and gravel soils, the flow may be more turbulent and better mixing may occur. In clay and fine silt soils, the flow is so slow that fluid mixing will not occur; however, chemical diffusion may occur.

DETOXIFICATION BY CHEMICAL REACTION

Some contaminants within a soil environment may be detoxified by chemical reaction. The reactions may involve formation of innocuous by-products such as water and anions or may immobilize the contaminant by precipitation or polymerization. However, in order for in situ detoxification to be effective, the reaction must be straight forward, one step, and occur under ambient or easily controlled conditions. If this is not possible, above grade detoxification involving more complex reactions should be considered.

In Situ Detoxification

The author's firms have researched in situ soil detoxification methods which ultimately resulted in the design and construction of a mobile soil detoxification treatment trailer. The trailer, currently in the U.S. EPA spill response arsenal, was developed for the isolation of the contaminant by the formation of a grout envelope, and subsequent detoxification by injection of chemicals into the contaminated soil. The design was based upon research conducted on four soils and four chemical reactions. The soils included relatively inert gravel (traprock), silica sand, silica silt and kaolin clay. The reactions included evaluation of oxidation/reduction, neutralization, precipitation and polymerization. The laboratory research involved the addition of a contaminant onto a soil surface, and the subsequent addition of a detoxifying reactant. The polymerization reactions were ineffective mainly due to the inability to control the in situ reaction and the potentially toxic by-products. However, the detoxification results using the other reactions were more successful.

Each in situ chemical reaction followed a similar pattern when fluids flowed rapidly through the soils. For the silt and coarser soils, when the reactant was added to the soil surface, it forced some of the entrained contaminant outward. A chemical reaction, in some cases quite violent, resulted at the interface between the reactant and contaminant. The reactant, as it continued to flow through the soil system, continued to react with the adsorbed contaminant until nearly all of the contaminant had either been flushed from the system or had chemically reacted. Thus, for these "flow through" tests, there was a two stage detoxification occurring, that of flushing or displacement and that of a chemical reaction. The net result in each case was quite good; up to 99% efficiency. Table 2 summarizes the results for these flow through tests.

TABLE 2

Soil Detoxification by Flow-Through Chemical Reaction

Soil	Reaction Type	Average* Contam. Entrained	Average* Contam. Reacted	Average* Total Detoxification
Gravel	Redox.	21.6	20.0	100
Gravel	Neut.	20.5	4.8	100
Gravel	Ppt.	30.4	20.0	99.7
Sand	Redox.	98.0	37.3	100
Sand	Neut.	88.8	22.3	100
Sand	Ppt.	97.9	41.8	99.9
Silt	Redox.	99.9	57.3	100
Silt	Neut.	100.0	57.7	100
Silt	Ppt.	99.7	72.1	99.1

*Values in % of Initial Concentration

Tests on clay soils also showed good levels of soil detoxification. The contaminant was allowed to stand on a clay surface for 48 hours, resulting in penetration of several centimeters. The reactant was added to the surface and allowed to stand for up to 48 hours. Surprisingly, the detoxification efficiencies ranged from 60 to 90 percent for these tests. Apparently, the reactant followed the same path through the clay structure as the contaminant with the resulting high detoxification efficiencies.

Above-Grade Chemical Reactions

Another method of soil detoxification is to remove the contaminated soil to above grade mixing tanks or containers and then to add detoxifying chemicals. Above grade chemical reaction or treatment is a common method for detoxifying contaminated ground waters and has been used in some cases for soil detoxification. However, this technique requires extensive dewatering of soils after reaction and rinsing which can be a difficult process. Similarly, large volumes of mixing water and chemicals may be needed. Therefore, the procedure may not be cost effective for large volumes of contaminated soil.

CONCLUSIONS

The review of available literature and evaluation of current research have resulted in several conclusions regarding mechanisms of soil detoxification:

1. Certain methods and procedures are available to detoxify contaminated soils. Both in situ and above grade detoxification methods can be considered.

2. Detoxification relies upon both removal of contaminants entrained within the soil pore space as well as chemical reaction of contaminants held onto the soil surface. Detoxification should not be considered simply a reversal of adsorption.

3. The retention of a contaminant within the soil is related to the parameters and conditions of the soil environment. The most important parameters which affect retention include the type and nature of the contaminant, the soil organic content, soil gradation and initial moisture content. The in situ density and contaminant contact time are important for generally granular systems, whereas the clay mineralogy is important for cohesive soils.

4. Research has resulted in development of some methods and equipment suitable for soil detoxification. A soil washing system has been found to be effective for detoxifying certain contaminants from excavated soils. The washing system included a high pressure jet spray, submergence, a countercurrent extraction and hydrocyclone separators. In situ detoxification by chemical addition has been shown to be effective for oxidation/reduction, precipitation and neutralization reactions on four different soils.

5. With the existing state-of-the-art, few alternatives to soil detoxification or handling methods are available. Current detoxification methods and procedures are relatively slow and would be quite expensive for actual large scale use. More research and field performance testing needs to be performed to develop cost effective soil detoxification systems.

REFERENCES

Griffin, R. and Shimp, N. (1978). Attenuation of Leachate in Municipal Landfill Leachate by Clay Minerals. EPA Pub. 600/2-78-157, Cincinnati, Ohio.

Huibregtse, K. and Kastman, K. (1980). Construction and Preliminary Testing of a System to Protect Groundwaters from Hazardous Spills. Proc. 1980 National Conference on Control of Hazardous Material Spills, 77-81, Louisville, KY.

Huibregtse, K., Scholz, R., Kastman, K. and Brugger, J. (1980). Development of a Mobile System for Extracting Spilled Hazardous Materials from Soil. Proc. 1980 National Conference on Control of Hazardous Material Spills, 134-140, Louisville, KY.

Kastman, K. and Zimmerman, E. (1977). Cyanide Waste Disposal Site Neutralization. Proc. Geotechnical Proctice for Disposal of Solid Waste Materials (1), 831-849, ASCE, New York.

Kolakowski, J. (1979). Migration Potential of Contaminants in the Soil of Rocky Mountain Arsenal. Pub. U.S. Army Aberdeen Proving Ground, Edgewood, N.J.