A Course on . . .

ENVIRONMENTAL REMEDIATION

CYNTHIA L. STOKES
University of Houston
Houston, TX 77204-4792

A new course has been developed at the University of Houston for graduate students and seniors in chemical engineering on the topic of environmental remediation. There are numerous areas throughout the country where soils, surface water, and/or groundwater are contaminated to such a degree that they are unsafe for us to use for business, to reside near, or to consume the water. This has created an increasingly stringent regulatory climate for industry with respect to waste disposal. These conditions were the motivation for development of this course. Today's students must be made aware of waste treatment and environmental reclamation issues in order to function effectively as design, process, and research engineers and managers. A number of our faculty have also begun working on research projects on contaminant transport in soils, dechlorination processes, and bioremediation, evincing the widespread interest in environmental issues within the department.

The purpose of the course is to introduce the students to both the traditional and the developmental methods for removal or destruction of hazardous wastes at contaminated sites and from industrial waste streams. The emphasis of the course is not on hazardous waste management and regulatory issues, but rather on the destruction, removal, and containment methods themselves.

The timeliness of the course was demonstrated by the student enrollment this past spring, the first time the course was offered; with no advertisement, we attracted forty-two graduate students and half of the graduating seniors for the course. The graduates included Master's and doctoral candidates in chemical (twenty-seven), petroleum (one), civil (two), and environmental (ten) engineering, as well as geology (two). Many of the Master's degree candidates were employed full-time in local industry and hence made many interesting and useful contributions regarding problems with waste generation, treatment, and disposal in their companies. The course fulfills a technical elective requirement for undergraduates who have selected the environmental specialty, one of several fields of specialization they can choose.

Cynthia Stokes *is an assistant professor in chemical engineering at the University of Houston. She received her BS from Michigan State University and her PhD from the University of Pennsylvania. She spent eighteen months as a post-doctoral fellow at the National Institutes of Health prior to arriving in Houston. Her major research focus has been in the area of cellular bioengineering.*

© *Copyright ChE Division of ASEE 1992*

The course concentrates on several aspects of the hazardous waste problem while touching on others only superficially. We are mainly concerned with hazardous wastes in soils, groundwater, and waste-water ponds and tanks.

COURSE CONTENT

An outline of the course is shown in Table 1. The course concentrates on several aspects of the hazardous waste problem while touching on others only superficially. We are mainly concerned with hazardous wastes in soils, groundwater, and waste-water ponds and tanks. Air pollution is not covered (a separate course on air pollution control is offered in our department).

A typical scenario considered during the course is, for instance, a hydrocarbon spill in subsurface soil, such as from a leaking underground storage tank. The hydrocarbon may be lighter or heavier than water, and hence it may float on or sink below the water table. It may be carried with or dissolve in the groundwater, adsorb to the soil, break down by thermal, chemical or biological means, or volatilize. Obviously, many physical, chemical, and biological processes influence the fate of the spill and our ability to clean it up. Our discussion of various remediation methods includes consideration of these issues.

We concentrate on hydrocarbon wastes, though some discussion of heavy metals and radioactive waste is included. Hydrocarbons are of particular

interest because of the concentration of the petroleum industry in Texas, and because they are common contaminants throughout the rest of the country as well. Of the various methods of contaminant recovery or destruction, we cover bioremediation in the most depth. Though many bioremediation techniques (other than the long-practiced landfarming) are still generally considered developmental, the potential for contaminant destruction rather than removal, the *in situ* treatment options, and the favor bioremediation is gaining with regulatory agencies motivated this selection.

We begin the semester with a brief overview of the origins and the biological and ecological effects of various types of hazardous wastes, including hydrocarbons (oil industry, agricultural chemicals, wood-treatment chemicals, etc.), heavy metals, and radionuclides. These lectures are designed to help the students understand why certain wastes are considered hazardous and why we must be concerned about their uncontrolled release.

We next cover analytical methods that are commonly used to detect and quantify concentrations of contaminants. The methods include gas chromatography (GC) and high performance liquid chromatography (HPLC), and various types of detectors used with them; mass spectrometry and its use with GC and HPLC; and atomic absorption spectrometry. There are numerous reference materials on these techniques.[1-4]

TABLE 1
Course Outline

Introduction
- Hazardous wastes—types and origins
- Biological and ecological effects of hazardous wastes
- Introduction to environmental remediation methods
- Analytical methods

Contaminant Transport Mechanisms
- Physicochemical and geologic factors
- Mathematical analysis

Bioremediation
- Microbiology and growth kinetics
- Methods—*in situ*, surface, bioreactors
- Remedy screening
- Case studies

Chemical, Thermal and Physical Remediation Methods
- *In situ* volatilization
- Low temperature thermal
- High temperature thermal
- Supercritical oxidation
- Extraction
- Adsorption
- Case studies

Regulations

The purpose of the course is to introduce the students to both the traditional and the developmental methods for removal or destruction of hazardous wastes at contaminated sites and from industrial waste streams.

We also illustrate the methods by which one can measure the concentration of organic matter in waters, such as Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), and Total Oxygen Demand (TOD). Chapter 2 of a book on water quality by Tchobanoglous and Schroeder[5] is used, though nearly all such books will include a section on these measurements. We also introduce the existence of the standard numbered analytical methods that the Environmental Protection Agency (EPA) requires for detection of various substances in different media (*e.g.,* drinking water or plant effluent water to be released to a river). A recent paper[6] discusses the need to consolidate and revise these prescribed methods.

Following these introductory lectures, we take a quantitative look at contaminant transport in porous media, such as in a diesel fuel spill in soil. Professor Kishore Mohanty, an expert in transport processes in porous media, was a guest lecturer for this part of the course last spring. He covered mathematical models that can be used to calculate the rate of movement of a fluid, illustrating its dependence on such parameters as groundwater velocity, soil porosity, tortuosity of pore structure, molecular diffusivity, and capillary pressure. He also explained the mechanisms of drainage and imbibition of groundwater and how these processes affect the movement of nonaqueous phase liquids. A recent review[7] is used as a reference, and several other books serve as additional resources for the interested student.[8,9] Since this course concentrates on methods that chemical engineers might utilize to remediate a site, these topics are covered only briefly. However, because one must locate a contaminant before devising an optimal cleanup strategy, this part of the course will likely be expanded in the future.

At this point we begin to examine the various techniques that we can apply to reclaim a contaminated site. We begin with the bioremediation methods, spending four to five weeks on the topic.

The coursework included two take-home exams in which the students had a week to answer two to three problems. Both conceptual and quantitative problems were used.

Because most engineering students have little or no microbiological background, the first couple of lectures cover the basics on bacterial growth kinetics, substrate and oxygen utilization, co-metabolism, and the variety of substances that microbes are known to metabolize. These lectures were given by Professor Richard Willson, who conducts biochemical separations research. He stressed that there is a maximum rate at which microbes can metabolize a substrate and that the rate of metabolism will slow down as substrate concentration decreases. In addition, the concentration of contaminants that can be achieved with biodegradation may not be as low as we require, and many contaminants are not biodegradable or degrade very slowly. The latter includes many chlorinated compounds that, unfortunately, are usually highly toxic and difficult to remove or degrade by other methods as well. Anaerobic microbes appear to dechlorinate hydrocarbons better than aerobic microbes, but the rate is very slow.

Standard microbiology textbooks can be used as references, and *Biochemical Engineering Fundamentals*[10] includes mathematical descriptions of substrate utilization and growth rates. Numerous overviews of the use of microbes to degrade environmental contaminants exist; we use a publication by the Office of Technology Assessment[11] and several other recent reviews.[12-14]

Following this introduction, we examine the various methods by which we can utilize biodegradation for waste removal. These include landfarming and its variations (composting, bioleaching), *in situ* bioremediation with and without additional microbes, and several types of bioreactors.[12-15]

Landfarming (the practice of periodically adding fertilizer and moisture, and tilling to expose the contaminated soil to oxygen) has been used in the oil and chemical industries for many years to treat relatively small spills on soil.[15] The idea to use *in situ* bioremediation has gained favor in recent years because of its noninvasive nature and typically low cost. In this method, one only has to inject aqueous solutions of nutrients (typically nitrogen and phosphorous sources), oxygen, and sometimes exogenous microbes into the area to facilitate the *in situ* degradation of the offending contaminants. Contaminated groundwater may be treated simultaneously by pumping it to the surface, treating it through phase separation, carbon adsorption, or other methods, and then typically using it as the water source for the nutrient solution.

We stress that although *in situ* bioremediation has the advantages that excavation is not required, contaminated soils and groundwater can be treated, and manpower and maintenance requirements are low, it also has numerous major limitations. *In situ* bioremediation is typically very slow, so cleaning up a site may take years, low cleanup levels may not be possible, confirmation of cleanup may be difficult (so monitoring may have to be continued for several decades), contaminant migration may occur, low permeability areas may be bypassed and not treated, or the soil may get plugged by the increase in biomass.

An alternative to *in situ* bioremediation that bypasses many of these limitations is the use of bioreactors. We examine several types: the stirred tank reactor can be used for treatment of liquids as well as slurries, whereas trickle bed reactors with a growing biofilm on the packing medium are used with liquid waste streams.[15-18] Bioreactors are typically the most expensive method of bioremediation, but are also the most controlled. Treatment times for the same amount of waste are typically shorter than either surface treatment or *in situ* methods, less space is required, and air emissions can be controlled. As with other types of bioremediation, low cleanup levels may not be possible. If soils are to be treated, a significant water source is required to form a slurry. An electrical source is also required. The bioreactor is much easier to study quantitatively than either *in situ* or surface bioremediation methods, and we derive some bioreactor models that utilize the substrate utilization and growth kinetics in this part of the course.

At this point, when the students have several choices of remediation methods in mind, procedures for remedy screening and design are introduced. The critical idea is that one must design and carry out appropriate laboratory studies to test whether proposed remediation methods are likely to fulfill one's requirements. These studies must provide enough information to narrow the choices of remedy, provide data for pilot-scale studies if necessary, and eventually allow one to obtain the necessary permits and design a full-scale process. The EPA provides various guideline documents for treatability studies; we used one for aerobic biodegradation remedy screening.[19]

Several case studies are used to illustrate the implementation of bioremediation methods, the decision

processes that lead to their utilization, and the possible pitfalls involved. A well-documented site that is on the National Priorities List (Superfund) is an abandoned wood-treatment facility in Montana.[17,18] Both soils and an aquifer are contaminated from uncontrolled releases of creosote and pentachlorophenol during its twenty-three years of operation. *In situ* bioremediation, landfarming in contained land treatment units, and bioreactors for the most contaminated groundwater are all being used. Another wood-treatment facility in Minnesota that has contaminated water with pentachlorophenol is being remediated with a fixed-film bioreactor.[16] Numerous other reports of bioremediation application can be found in the waste treatment, water quality, and environmental literature.

Professionals in local industry are also invited to speak to the class about their involvement in bioremediation activities. We had two such guests last spring. The first, Joseph Jennings (President of Waste Microbes, Inc.), presented his company's involvement in treating wastewater ponds and tanks. The company has developed a consortium of microbes that they add along with nutrients and sparging air at the bottom of a body of water. His presentation helped us focus on the common and important issues of whether aqueous contaminants may be stripped into the atmosphere rather than degraded, and whether the addition of exogenous microbes is necessary or helpful.

The second speaker, Sara McMillen (a microbiologist at Exxon Production Research), gave a presentation on bioremediation in general which included her work on composting and Exxon's experimentation with bioremediation in Prince William Sound following the Exxon *Valdez* oil spill (also described in reference 11).

Following bioremediation, we move on to other remediation methods. They are grouped in terms of the physical or chemical means of contaminant separation or destruction utilized. We start with *in situ* volatilization or soil venting, the removal of organic compounds from subsurface soils (and possibly groundwater) by mechanically drawing or venting air through the soil matrix.[15] We stress the physical parameters that determine the success of this method, which include the volatility of the compounds, their adsorption into the soil, and the ease of drawing or venting air through the soil.

We next cover low temperature thermal treatment because it also utilizes volatilization, though in a controlled, heated chamber.[15,20] In this case, excavation of the contaminated soils is required. In both methods the off-gases are typically burned or adsorbed on activated carbon or water in scrubbers, depending on the concentration and type of contaminant. An advantage of low temperature thermal is that it allows the recovery of the hydrocarbon if desired.

High temperature thermal operations are considered next. We discuss methods, design parameters, and operating conditions of incineration, vitrification, and pyrolysis. A major advantage of high temperature methods is the greater than 99% destruction of organic contaminants that is usually attainable.[15,20] Major scientific limitations include the need for substantial air emissions equipment if elevated levels of halogenated organic compounds or volatile metals are present, and the production of residual ash that might need additional treatment or special disposal. A nonscientific limitation is the societal objection to incinerators near residential areas. High temperature methods are typically very expensive because of the high energy usage, and the permitting process can be extremely lengthy and costly.

Some problems on both exams were designed to illustrate the idea . . . that one has many types of remediation methods to choose from and one must weigh the advantages and limitations of each on scientific, social, and economic scales . . .

Supercritical water oxidation is also included. Last spring this was discussed by Professor Vemuri Balakotaiah, who specializes in analysis of various chemical reactors and reaction mechanisms. He demonstrated how oxidation in supercritical water can provide very high destruction efficiencies—in many cases greater than 99.99%, even with very dilute waste streams.[21,22] He also compared the operation and destruction efficiencies of supercritical water oxidation processes with several typical incinerator designs to illustrate their similarities and differences.

The last major technology that we study is separations, specifically adsorption and extraction. An unpublished review by D. W. Tedder at the Georgia Institute of Technology, entitled "Separations in Hazardous Waste Management," is used as an overview of the topic. Activated carbon adsorption is discussed in some detail because of its extensive and long-time use for air emissions control and polishing wastewater.[23,24] We also discuss several chemical extraction methods that are used to separate contaminated

sludges and soils into their respective phase fractions: organics, water, and particulate solids. These include the supercritical fluid extraction processes based on carbon dioxide or propane and the Basic Extraction Sludge Treatment (B.E.S.T.) process of the Resources Conservation Company (Bellevue, WA) based on the temperature-dependent separation of water and aliphatic amines.[15]

In situ soil leaching and the potential use of surfactants are also briefly discussed. While separations processes for soil and sludge decontamination may be considered developmental, they have the advantages of obtaining a reusable oil phase, can be used with high moisture content soils and oil concentrations up to forty percent, and are usually less expensive than incineration or commercial landfilling. The potentially limiting problems include not being able to handle soil clay content above about twenty-to-thirty percent and high volatiles content, and difficulty in handling soils that have been contaminated for extended periods of time because of weathering and adsorption. Again, case studies are included where possible.

Following our study of these major areas, we briefly introduce a number of other methods so that the students are aware of the many options that have been used or are in development. We include solidification and stabilization, which involve the addition of materials that combine physically and/or chemically to decrease the mobility of the original waste constituents. Next are *in situ* and *ex situ* isolation and containment, which involve isolating the contaminated soil from the surrounding environment with physical barriers such as clay caps, synthetic liners, slurry cut-off walls, and grout curtains. Finally, we describe the idea of beneficial reuse, such as incorporating soils containing petroleum hydrocarbons in hot asphalt mix, or using contaminated soil as road base material or construction material for structures such as containment berms.

Regulatory issues are not covered in depth because of time constraints, though the major national legislation is introduced early in the course. It includes the Resource Conservation and Recovery Act (RCRA), the Comprehensive Environmental Response Compensation and Liability Act (CERCLA), the Superfund Amendment and Reauthorization Act of 1986 (SARA), the Clean Water Act (CWA), the Toxic Substances Control Act (TSCA), and Underground Storage Tank (UST) regulations. In addition, the process of obtaining a Record of Decision by the EPA for a remediation plan is described.

We also bring in an outside expert to discuss the regulatory climate in Texas. Last spring Marilyn Long (Senior Geologist at the Texas Water Commission, Texas' partial equivalent of the EPA), gave a lecture on dealing with hazardous wastes in Texas. She described the various regulatory agencies in Texas and their jurisdictions. She discussed the legal ramifications of statutes, rules, and guidelines, and how a company must work with the regulations and regulators. She also discussed her involvement in several bioremediation and low temperature thermal treatment projects.

COURSEWORK

The coursework included two take-home exams in which the students had a week to answer two to three problems. Both conceptual and quantitative problems were used. For example, one problem on the first exam gave a sketchy description of a "superfund" site, including volumes of contaminated surface water, groundwater, soils, and sludge at the bottom of a pond, types of contaminants (hydrocarbons and some heavy metals), and a history of the site. An "approved" clean-up scenario was described, which consisted of incineration of the contaminated soils and sludges, use of ash as backfill, natural attenuation of the aquifer (to be monitored), and discharge of the water to a nearby river after polishing. The problem then stated that the responsible party is requesting permission to evaluate the use of bioremediation for the site as an alternative to the selected remedy. The student, as the company's expert on bioremediation, was to outline the types of bioremediation that may be appropriate for each of the contaminated media, outline a laboratory remedy screening study to test the feasibility of his suggestions in the first part, and then describe how he would actually implement an overall reclamation plan utilizing bioremediation for the site. Some aspects of the site description were purposely left vague so that the student could make assumptions or specifications about anything that was not explicitly stated. His solution then had to be consistent with the assumptions made.

Some problems on both exams were designed to illustrate the idea, emphasized throughout the course, that one has many types of remediation methods to choose from and one must weigh the advantages and limitations of each on scientific, social, and economic scales in order to devise an optimal solution.

The students also complete a term paper or project of their choosing. The topics are allowed to range from site characterizations, critical reviews of ongoing site cleanups, critiques of particular remediation

methods, and mathematical models of a method (*e.g.*, reaction kinetics in an incinerator) or contaminant transport. A major requirement for the paper is a critical evaluation of the selected topic. Last spring, specific titles included "Dioxin formation in pulp bleach plants," "Naturally occurring radioactive material accumulated as a result of hydrocarbon production—waste minimization technology," "The MOTCO superfund site: an evaluation," and "Distributed control in wastewater treatment systems." Several students selected topics that were relevant to their present jobs so they could learn something that might help them immediately, whereas others chose such popular topics as the use of bioremediation for the Exxon *Valdez* oil spill in Alaska.

RESOURCE MATERIALS

Because of the broad nature of the material that is covered, we do not use a specific textbook. Rather, a number of papers from the literature, as well as chapters from several books, are used (a number of which are cited herein). Literature papers are especially useful for case studies.

A particularly useful resource is a manual prepared by Environmental Solutions, Inc., under contract by the Western States Petroleum Association, entitled *Onsite Treatment: Hydrocarbon Contaminated Soil.*[15] It is used extensively for summaries of the various soil-treatment methods. While the manual does not deal with design of the processes, it includes excellent qualitative summaries of various methods, their applicability, advantages and limitations, permitting requirements, whether a method is developmental or proven, costs, capacity and manpower estimates, and references for actual usage of the method. It also provides guidelines for selecting the best method for site-specific conditions, which is very useful. Most of the remediation methods the manual discusses were mentioned above and are touched on at least briefly during our course.

SUMMARY

The environmental remediation field is changing rapidly as new methods are developed to handle the numerous hazardous substances that pollute the soils and groundwater in many areas of the country. Chemical engineers are ideally suited to work in this field because of our expertise in transport phenomena, thermodynamics, reaction kinetics, and unit operations—all of which are required to quantify the movement of contaminants in the subsurface and devise optimal methods of remediation.

This course is designed to introduce both graduates and seniors to the field. We expect the course will evolve to include more emphasis on hydrogeology and contaminant transport calculations and increased use of models and design equations to evaluate the applicability and efficiency of methods in different contexts.

Inviting outside speakers from local industry will continue. The speakers were well received and the students welcomed the chance to hear from people experienced with specific remediation technologies.

REFERENCES

1. Hassan, S.S.M., *Analysis Using Atomic Absorption Spectrometry,* Ellis Horwood Limited, Chichester (1984)
2. Howe, I., D.H. Williams, and R.D. Bowen, *Mass Spectrometry Principles and Applications,* 2nd ed., McGraw-Hill, New York (1981)
3. Jennings, W., *Analytical Gas Chromatography,* Academic Press, Orlando, FL (1987)
4. Miller, J.M., *Chromatography: Concepts and Contrasts,* John Wiley and Sons, New York (1988)
5. Tchobanoglous, G., and E.D. Schroeder, *Water Quality: Characteristics-Modeling-Modification,* Addison-Wesley, Reading, MA (1985)
6. Hites, R.A., and W.L. Budde, *Env. Sci. Tech.,* **25**, 998 (1991)
7. Mercer, J.W., and R.M. Cohen, *J. Contam. Hydrol.,* **6**, 107 (1990)
8. Dullien, F.A.L., *Porous Media, Fluid Transport and Pore Structure,* Academic Press (1979)
9. Lake, L.W., *Enhanced Oil Recovery,* Prentice-Hall, New York (1989)
10. Bailey, J.E., and D.F. Ollis, *Biochemical Engineering Fundamentals,* McGraw-Hill, New York (1986)
11. U.S. Congress, Office of Technology Assessment, *Bioremediation for Marine Oil Spills—Background Paper* OTA-BP-O-70 (Washington, DC: U.S. Government Printing Office) (1991)
12. Nichols, A.B., *Water Env. Tech.,* p. 52, February (1992)
13. Saylor, G.S., *J. Haz. Mat.,* **28**, 13 (1991)
14. Shorthouse, B.T., *Remediation,* **1**, 31 (1990)
15. *Onsite Treatment: Hydrocarbon Contaminated Soils,* Environmental Solutions, Inc., Irvine, CA (1991)
16. Frick, T.D., R.L. Crawford, M. Martinson, T. Chresand, and G. Bateson, *Environmental Biotechnology,* G.S. Omenn, Ed., Plenum Press, New York, pp. 173-192 (1988)
17. Piotrowski, M.R., *Hydrocarbon Contam. Soils,* **1**, 433 (1991)
18. Piotrowski, M.R., and J.W. Carraway, "Full-Scale Bioremediation of Soil and Groundwater at a Superfund Site: A Progress Report," presented to HazMat South '91, Atlanta, GA (1991)
19. U.S. Environmental Protection Agency, Guide for Conducting Treatability Studies Under CERCLA: Aerobic Biodegradation Remedy Screening, Interim Guidance, EPA/540/2-91/013A (1991)
20. Freeman, H., *Innovative Thermal Hazardous Organic Waste Treatment Processes,* Noyes Publication, Park Ridge, NJ (1985)
21. Helling, R.K., and J.W. Tester, *Environ. Sci. Tech.,* **22**, 1319 (1988)
22. Thomason, T.B., and M. Modell, *Haz. Waste,* **1**, 453 (1984)
23. Perrich, J.R., *Activated Carbon Adsorption for Wastewater Treatment,* CRC Press, Boca Raton, FL (1981)
24. Voice, T.C., in *Standard Handbook of Hazardous Waste Treatment and Disposal,* H.M. Freeman, Ed., p. 6.3, McGraw-Hill, New York (1989) ❐