



## Project Summary

# Laboratory Protocol for Determining Fate of Waste Disposed in Deep Wells

A. Gene Collins and M. E. Crocker

The objective of this research investigation was to develop a laboratory protocol for use in determining degradation, interaction, and fate of organic wastes disposed in deep subsurface reservoirs via disposal wells. Knowledge of the ultimate fate of deep-well disposed wastes is important because provisions of the Resource Conservation and Recovery Act (RCRA) require that by August 1988, the Environmental Protection Agency (EPA) must show that the disposal of specified wastes by deep-well injection is safe to human health and the environment, or the practice must be stopped. The National Institute for Petroleum and Energy Research (NIPER) developed this protocol primarily by transferring some of its expertise and knowledge of laboratory protocol relevant to improved recovery of petroleum; for example, (1) core analysis, (2) brine analysis, (3) oil analysis, (4) dynamic fluid flow systems, which simulate subsurface reservoir conditions, and (5) appropriately trained personnel.

This study was designed to investigate the adsorption properties of a specific reservoir rock which is representative of porous sedimentary geologic formations used as repositories for hazardous organic wastes. Phenol is the principal hazardous waste product that has been injected into the Frío formation; therefore, a decision was made to use phenol and sedimentary rock from the Frío formation for a series of laboratory experiments to dem-

onstrate the protocol. The developed protocol can be used to evaluate mobility, adsorption and degradation of an organic hazardous waste under simulated subsurface reservoir conditions.

This report is submitted in partial fulfillment of Contract Number DW89931947 under the sponsorship of the U.S. Environmental Protection Agency through an interagency agreement between the U.S. Department of Energy and the U.S. Environmental Protection Agency. The report covers the contract period from December 16, 1986 to September 30, 1987, and the work was completed as of September 30, 1987.

*This Project Summary was developed by EPA's Robert S. Kerr Environmental Research Laboratory, Ada, OK, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

## Introduction

The objective of this research was to develop a protocol for use in determining the fate of organic hazardous wastes injected into subsurface geologic reservoirs. To achieve this objective, several areas of work were addressed. The first area was closely related to a state-of-the-art report.<sup>1</sup> This report permitted an assessment of prior research conducted on organic wastes and indicated areas where additional information on degradation, interaction,

and ultimate fate of wastes disposed by deep-well injection is needed. The report indicated that very little laboratory research relevant to the fate of deep-well disposed organic wastes has been conducted.

The second area addressed the experimental conditions which are necessary to develop a laboratory protocol to determine the fate of deep-well disposed organic wastes. The work was performed in stages with refinements and evaluations made after each stage. Items considered included:

1. selection of an appropriate laboratory experimental system,
2. selection of appropriate core samples, and core analysis methods,
3. selection of an appropriate brine system, and brine analysis methods, and
4. selection of the hazardous organic waste materials, and waste analysis methods.

The laboratory protocol described in this report provides data for the purpose of determining the degradation, interaction, and fate of hazardous organic wastes injected into deep subsurface reservoirs. Knowledge generated by implementation of this protocol is needed to predict and/or prove the ultimate fate of deep-well injected wastes. This knowledge is necessary to ensure that deep-well injected wastes do not contaminate ground waters. It is imperative that every possible precaution be taken to protect ground water, because it is estimated that 50 percent of the Nation's drinking water comes from ground water, that 75 percent of our cities obtain all or part of their water supplies from ground water, and that rural areas are 95 percent dependent upon ground water as a source of water.

About 11 percent of all hazardous wastes are injected into deep subsurface geologic rock formations for disposal. This corresponds to about 11.5 billion gallons of hazardous waste that are injected into some 250 Class I wells, which are located in sedimentary basins throughout this country, primarily in the Gulf Coast and Great Lakes regions.

Possible mechanisms whereby injection of hazardous wastes might contaminate ground-water aquifers include: (1) a surface spill followed by migration of the waste into the ground water; (2) unplugged or incompetently plugged wells that penetrate the geologic zone into which the waste is injected providing an escape route whereby the waste can enter an overlying potable ground-water aquifer; (3) vertical

fracturing of the injection and confining strata caused by excessive injection pressures whereby a communication channel allows the injected waste to migrate to a fresh water aquifer; and (4) mechanical failure of the injection system such as corrosion of surface pumps or pipes or subsurface tubing or casing which allows the waste to escape and migrate to a ground-water aquifer.<sup>2</sup>

EPA, in their 1985 report to Congress on hazardous wastes,<sup>3</sup> described four major ways in which subsurface injection practices can cause fluids to migrate into underground sources of drinking water (USDWs). They are: (1) faulty well construction; (2) Improperly plugged or completed wells in the zone of endangering influence; (3) faulty or fractured confining strata; and (4) lateral displacement.

Provisions of the Resource Conservation and Recovery Act (RCRA) require that by August 8, 1988, the Environmental Protection Agency (EPA) must show that the disposal of specified wastes by deep-well injection is safe to human health and the environment or the practice must be stopped. Knowledge of the long-term fate of these wastes in the injection zones is necessary to address the provisions. Further, it is imperative that these provisions be accurately addressed because EPA has a statutory mandate to protect potable ground water.

Demonstration of the fate of wastes injected into subsurface rock formations requires knowledge of the behavior of the waste after injection. The interaction of the waste with other reservoir fluids and reservoir rock constituents such as silicates, carbonates, sulfates and clays must be known. Hazardous wastes often are complex mixtures and when combined with other complex mixtures, the interaction can increase factorially.

Development of appropriate methodology to determine the fate of hazardous organic wastes injected into deep-wells for disposal in subsurface geologic reservoirs represents formidable challenges to the scientist. Current knowledge of deep subsurface geologic reservoirs was established primarily by petroleum-related sciences of geology, engineering, chemistry, physics, hydrology, etc. Subsurface reservoirs into which hazardous wastes are injected consist of sedimentary deposits, which are the same types of sediments from which petroleum is generated and produced.

The present study focused on relevant technology whereby the fate of

hazardous organic wastes could be evaluated in the laboratory. It was determined that both a static system and a dynamic fluid flow-through core system should be used. The static system should be useful to establish longer term degradation information, and the dynamic system should provide knowledge pertinent to migration of the waste in the reservoir rocks. A state-of-the-art report<sup>1</sup> indicated that very little laboratory research has been performed concerning the fate of hazardous organic wastes in deep subsurface reservoirs.

Because phenol is frequently injected into deep subsurface reservoirs for disposal, it was selected to demonstrate the protocol. Phenol was injected into the Frio formation, and a decision was made to use sedimentary rock from the Frio formation in the laboratory experiments.

The indigenous and/or connate brines found in the Frio formation range from less than 16,000 milligrams per liter (mg/l) in some of the geopressed areas to more than 100,000 mg/l in normally pressured areas. The dominant ions are sodium and chloride; however, the usual gamut of alkaline, alkaline earth halide, sulfate and carbonate ions also are present.

Most deep geologic formations used for disposal of hazardous wastes consist of unconsolidated sands and sandstones, as exemplified by the Frio formation. The minerals in these rock formations serve as sites for the adsorption of numerous organic compounds and thus retard or attenuate the migration of the hazardous organic waste from the injection zone. Shale and/or clay or silt dominant formations, which overlie many formations such as the Frio, serve as hydrocarbon traps and also should serve to retard the vertical migration of injected hazardous wastes out of the injection zone. Because adsorption is significant in estimating the migration of injected waste constituents, methodology was developed to determine the equilibrium adsorption properties of organic compounds on formation rocks such as the Frio formation at simulated subsurface conditions of 3,000 psi (20.7 MPa) and temperatures up to 140°F (60°C).

A large volume of laboratory results has been compiled on the adsorption of organic compounds onto numerous materials;<sup>1</sup> however, very few results are reported on the equilibrium adsorption properties of subsurface formation rocks. This work was designed to investigate the adsorption properties of a specific

subsurface sedimentary formation rock because it is specific subsurface geologic formations into which hazardous wastes are injected for disposal. The dynamic fluid flow-through porous media equipment developed for this work should be applicable to many studies relevant to the flow and transport of injected wastes.

Many organic constituents are hydrophobic (water disliking) and their movement in ground-water systems is affected by sorption phenomena, where the solute (organic constituent) is transferred from the liquid or solvent phase (ground water) to the solid phase (rock or soil particles). This is a phase partitioning process and is called adsorption and it may be fully or partially reversible (desorption). Many chemical and physical properties of both the solute and solid phases impact adsorption/desorption and the physical chemistry of the phenomena is complex.

Adsorption of a liquid hazardous waste, such as phenol onto the minerals in a subsurface formation rock, could cause the adsorbed waste constituents to be attenuated or retarded and not migrate in hazardous concentrations from the injection zone of a subsurface disposal well. Because adsorption is significant in estimating the migration characteristics of injected waste constituents, this study was designed to investigate quantitatively the equilibrium adsorption properties of specific organic hazardous wastes.

Adsorption can be categorized into three classes: exchange, physical, and chemical. Exchange occurs from the electrostatic attraction of ions or charged functional groups from the solute phase to the solid phase which possesses charged locations. Physical adsorption is transport between the phases motivated by Van der Waals forces or electrostatic interaction between atoms and molecules.<sup>4</sup> Chemical adsorption (chemisorption) is caused by a chemical reaction between the solute phase and the solid phase. Discrete occurrences of these classes are not common and probably a phase partitioning of a solute-solvent-solid system occurs where two or all three of the adsorption classes operate.

## Experimental Considerations

After detailed consideration of various laboratory systems, it was decided to develop both a dynamic flow and a static system. NIPER personnel have experience with both types of systems in

which temperature and pressure simulate those found in deep subsurface environments. The dynamic flow system provides optimum information relevant to interactions between reservoir rock and selected organic hazardous wastes, whereas the static system provides necessary back-up information.

## Development and Demonstration of Protocol

The experimental section in the report consists of design details and operational methods for a dynamic fluid flow-through core system and a static system. Instrumentation and methods used for the identification of organic waste compounds and their degradation products also are described. Essential basic core evaluation techniques for an experiment of this type are described and include: (1) basic core analysis, (2) scanning electron microscopy, and (3) x-ray diffraction. Evaluation of the amounts and types of organic materials and clays present in the core samples is needed to determine their effect upon adsorption, degradation, and transport of hazardous waste constituents. The dynamic flow-through system is capable of simulating a waste-disposal reservoir at various temperatures and pressures. A change in pressure of 3,000 psi (20.7 MPa) would affect the degree of permeability of the core sample tested but should have no effect on adsorption or degradation. The dynamic flow-through units were designed, fabricated, and used at NIPER. Procedures for (1) core preparation, (2) core evaluation and brine evaluation, and (3) analysis of hazardous waste and hazardous waste degradation by-products are described in the report.

## Dynamic Fluid Flow System

A diagram of the fluid flow apparatus is shown in Figure 1. The system resembles a high-pressure liquid chromatograph except that the chromatographic column is replaced by a core sample taken from a subsurface formation.<sup>5</sup>

To simulate reservoir pressure conditions, the core sample is encased in a high-pressure stainless steel cell. The cell is filled with fluid (usually water), which provides the means of simulating an overburden pressure on the core with the hydraulic pump. The core is physically separated from the overburden fluid by a rubber Hassler sleeve.

A heating mantle around the cell provides simulated reservoir temperatures. Fluids used in the experiment are pumped through the core by a high-pressure, constant-rate pump, and the internal pressure of the system is adjustable using a pressure-control valve.

Dynamic fluid flow experiments were performed by injecting dilute sodium chloride solutions containing 500, 5,000 and 10,000 mg/l concentrations of hazardous wastes into the laboratory apparatus. Effluents were extracted and analyzed to determine adsorption and degradation.

Figure 1 shows that samples eluting from the core may be collected via an automatic fraction collector, or may be diverted to an ultraviolet (UV) spectrophotometer and/or refractometer for on-stream analysis. This arrangement permits the analysis of different simulated core floods, with the method of detection dependent upon the particular type of chemical being analyzed.

The following experimental conditions were used:

|                               |             |
|-------------------------------|-------------|
| Overburden pressure,          |             |
| psi .....                     | 3,400-3,500 |
| Internal pressure, psi ..     | 2,900-3,000 |
| Water pump pressure, psi .... | 2,900       |
| Injection rate, ml/min .....  | 0.3         |
| Temperature, °F .....         | 100/140     |

## Static System

Static systems included Paar bombs and glass vials into which crushed and sized core samples were placed along with stock solutions of hazardous wastes. The systems were sealed, heated to the desired temperature, and after a selected time, samples were taken from the systems and analyzed. The difference in concentration between the initial and reacted solutions represents the amount of reactant hazardous waste which was adsorbed by the core.

## Results and Discussion

The experimental results, although not entirely definitive because of the amount of time required for the experimental design and set-up, are an adequate test of the protocol and are indicative of the results expected from exhaustive testing. The results of this experimental work were compared to previous work involving the evaluation of organic wastes at simulated reservoir temperature and pressure.<sup>6</sup> Correlations between the two separate experiments were found to be

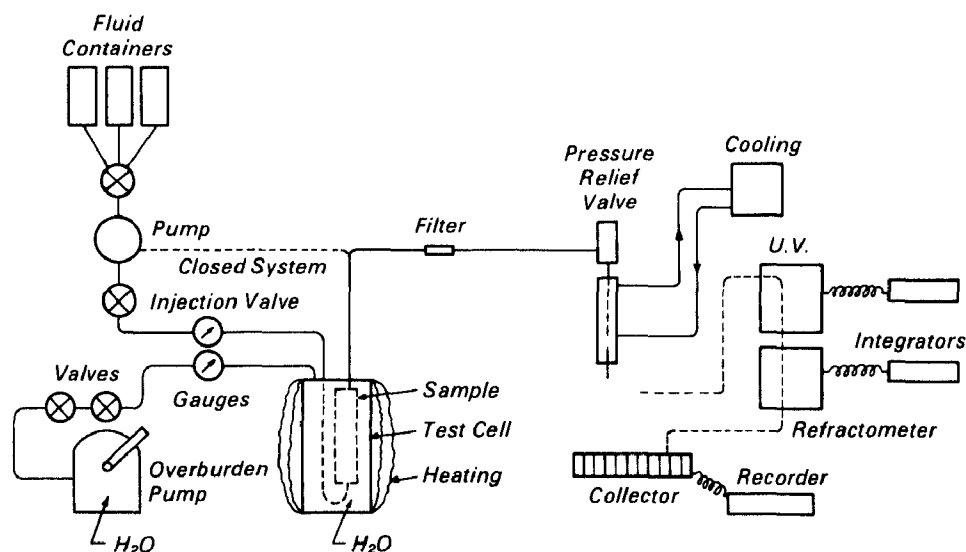


Figure 1. Schematic of fluid flow apparatus.

favorable, further corroborating the viability of the protocol.

The end point of the flow-through method was obtained when the effluent concentration was equal to the initial concentration injected into the core. At this point, the system was assumed to be in equilibrium.

The bulk effluent was compared to the original solution injected into the core. This result was on a  $\mu\text{g}/\text{ml}$  basis. The differences between these amounts were considered adsorption and were calibrated using a range of standards for each concentration tested. The total amount of adsorption for each concentration was determined in micrograms. The adsorbed concentration ( $\mu\text{g}/\text{g}$ ) was plotted versus time to obtain equilibrium amounts adsorbed at a

specific saturation. The total adsorption (micrograms) was divided by the total mass of the core. This yielded adsorption on a  $\mu\text{g}/\text{g}$  basis. Results of the adsorption/desorption series for phenol at 100° and 140° F are presented in Table 1.

The equilibrium amounts adsorbed were then plotted on log-log paper versus the concentration in equilibrium with the rock surface to obtain the Freundlich isotherms. The plot was fitted using a linear regression. The experimental measurements made in this work were based on the changes of the solute concentration as a result of adsorption. The measurements represent a displacement of the solvent from an active site with simultaneous adsorption of the solute; hence, an exchange

mechanism takes place at the site of adsorption.

The rate constants showed a consistently slow rate of adsorption, but were numerically close and (1) an increase in temperature caused a decrease in the adsorption rates for the compounds, and (2) an increase in concentration produced an increase in the adsorption rate. Chemical reaction was not involved in the adsorption process for the organic compounds studies.

The pH of the solutions changed after reaction with the Frio rock. Analysis of the reacted solutions indicate that sodium concentrations decreased while calcium and magnesium increased. This was attributed to both acid-base and ion exchange reactions.

Table 1. Analytic Results for Flow-through Method Using Phenol

| Compound | Initial concentration mg/l | Temperature, °F | Micrograms adsorbed/gram of rock | Micrograms desorbed/gram of rock |
|----------|----------------------------|-----------------|----------------------------------|----------------------------------|
| Phenol   | 500                        | 100             | 9                                | 0                                |
|          | 5,000                      | 100             | 76                               | 0                                |
|          | 10,000                     | 100             | 312                              | 0                                |
| Phenol   | 500                        | 140             | 5                                | 0                                |
|          | 5,000                      | 140             | 55                               | 0                                |
|          | 10,000                     | 140             | 276                              | 0                                |

Subsequent to completion of the adsorption experiments with the dynamic flow system, sodium chloride solution was injected to try to desorb the adsorbed hazardous waste. No desorption occurred.

The effluents generated during the adsorption experiments were analyzed, and no hazardous waste degradation products were found. The reacted aqueous phase from the long-term 83-day static tests contained no hazardous waste degradation products.

## Recommendations for Future Use of Protocol

The protocol was designed for application in evaluating mobility, adsorption, and degradation of hazardous organic chemicals in a simulated deep subsurface environment. The following section outlines the developed laboratory procedures.

## Core Analysis

The core consists of an appropriate sample of the subsurface reservoir rock, the sample can be obtained by using a core sampling device while drilling a deep well<sup>7</sup> or it can be a sample obtained from an outcrop of the appropriate rock formation.<sup>6</sup> The core is analyzed for organic and inorganic constituents and minerals of interest by application of procedures in the report.

Next, an appropriate sample of the core is prepared and analyzed for brine porosity and permeability as described in the report. The usual core size is 1.5 in. (3.81 cm) in diameter by 4 to 6 in. (10.16 cm to 15.24 cm) long. The dispersion experiments are performed as described in the report to assure that the assembled system is an integral unit and does not contain channels, bypass or other inconsistencies.

## Organic Hazardous Waste and Brine Analysis

The organic hazardous wastes usually are mixed with an aqueous brine solution prior to their injection into a deep subsurface reservoir. The amount of organic hazardous waste that can be thus mixed is dependent upon its solubility in the aqueous brine, and relevant information should be determined. Appropriate organic hazardous waste and brine mixtures are prepared and analyzed using the desired procedures as described in the report.

## Determination of Adsorption-Fluid Flow Method

Mount the core in the fluid flow test cell apparatus as shown in Figure 1, and introduce the test fluids through the core as described in the report. Analyze effluent samples periodically to determine when the concentration of the organic hazardous wastes is equal to the concentration of the injected fluid; this is the end point or the equilibrium point.

Use the total mass of the core and calculate the adsorption in  $\mu\text{g/g}$ . Plot the equilibrium amounts adsorbed versus the concentration in equilibrium with the rock surface to obtain the Freundlich isotherms. A rate constant can be calculated by using the equation in the report and the coefficients of molecular diffusion can be calculated to determine if diffusion is the controlling mechanism.

Using equations in the report, the constants,  $F$  and  $n$ , can be calculated to determine the probable nature of adsorption. The isosteric heats of adsorption can be calculated to determine the probable mechanism of adsorption.

Desorption experiments may be performed by injecting or pumping brine solutions containing no organic hazardous waste compound through the core and analyzing the effluents produced for the compounds that were previously adsorbed.

## Determination of Adsorption-Static Method

The static method can be used, not only for determining the degree of adsorption, but also for evaluation of core dimension and adsorption potential for the flow-through method. Using the static method, the crushed core material is introduced into vials and the hazardous waste is brought into contact with the core material. Each individual test series consists of a blank plus the samples to be tested. The test series consists of a 2-, 4-, 6-, and 24-hour set. The units are placed in a shaker bath at the appropriate temperature. At the selected time, samples are collected and the adsorption is evaluated using a gas chromatograph. The results are compared to standards made from the appropriate hazardous waste. Final evaluations include the analysis of a blank to validate the integrity of the static test procedure. Determination of the level of desorption for the hazardous waste is difficult using the static test due to the unconsolidated nature of the core sample.

Degradation of the sample due to the flow-through method and static method is observed during the normal sample evaluation of the hazardous wastes. If changes are noted in the spectra for the hazardous wastes, appropriate chemicals should be utilized for comparative purposes or the sample should be evaluated using GC/MS for a more quantitative identification.

## Conclusions

The following conclusions are supported by the research described in the report:

1. A protocol was developed whereby organic hazardous wastes can be evaluated for mobility, adsorption, and degradation potentials under simulated subsurface reservoir temperatures and pressures.
2. Long-term (months, not years) evaluations of the organic hazardous waste phenol did not indicate the formation of degradation products.
3. The results obtained with the developed protocol correlated with some previous work performed at NIPER, thus providing a means of corroboration.

## References

1. Strycker, A., and A. G. Collins. *State-of-the-Art Report, Injection of Hazardous Wastes Into Deep Wells*, Environmental Protection Agency Report 600/8-87/013, NTIS PB87-170551, February 1987.
2. Collins, A. G. *Geochemistry of Oilfield Waters*. Elsevier Scientific Publishing Co., New York, N.Y., 1975, p. 434.
3. Environmental Protection Agency *Report to Congress on Injection of Hazardous Waste*. Environmental Protection Agency Report 570/9-85-003, August 1985.
4. Miller, C. T. *Modeling of Sorption and Desorption Phenomena for Hydrophobic Organic Contaminants in Saturated Soil Environments*, The Univ. of Michigan PhD dissertation, 1984, p. 403.
5. Donaldson, E. C., R. F. Kendall, E. A. Pavelka and M. E. Crocker. *Equipment and Procedures for Fluid Flow and Wettability Tests of Geologic Materials*. Dept. of Energy Report No. DOE/BETC/IC-79/5, May 1980.
6. Donaldson, E. C., Michael E. Crocker, and F. S. Manning. *Adsorption of Organic Compounds on Cottage Grove Sandstone*. ERDA Report No. BERC/RI-75/4 July 1975.

---

7. Monicard, R. P. Properties of  
Reservoir Rocks: Core Analysis. Gulf  
Publishing Co., Houston, TX, 1980.