



## Project Summary

# State-of-the-Art Report: Injection of Hazardous Wastes Into Deep Wells

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About 11 percent of all hazardous wastes are disposed of by injection wells into deep subsurface environments. Some 250 of these Class I wells are in the United States, and their record of performance is good.

Provisions of the Resource Conservation and Recovery Act (RCRA) require that by 1988 the Environmental Protection Agency (EPA) must show that the disposal of specified wastes is safe to human health and the environment, or discontinue the practice of deep-well injection of hazardous wastes. These provisions necessitate knowing the long-term fate of these wastes in the injection zones.

A survey of the literature shows that some information is available on nearly all potential chemical and biological transformation processes of hazardous wastes. The literature survey also indicates that additional research is needed in all areas of abiotic and biotic waste interactions before definitive explanations can be given on the long-term fate of hazardous wastes.

Usually, the first experimental test is the fluid-fluid test of the waste's compatibility with the formation fluids. However, research shows that this simple test is not always adequate for determining the interaction of injected wastes with the subsurface environment.

Among the many factors affecting the ultimate fate of injected wastes are the pH-Eh of

the waste and reservoir fluids, brine concentration of the waste fluids, clay type and amount in the reservoir, presence or absence of iron oxides, presence or absence of organic complexing agents, molecular characteristics of organic materials, and the anaerobic or aerobic nature of the environment. Since all of these factors are interrelated, any mixing of different types of hazardous wastes in the reservoir further complicates the situation, making it difficult to predict exactly the action or fate of wastes after their injection. Only limited relevant research has been conducted to date, and the results are insufficient to adequately address this problem.

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## Introduction

The Environmental Protection Agency (EPA) estimates that some 250 Class I wells account for disposal of about 11 percent of all liquid hazardous wastes produced annually in the United States on about 11.5 billion gallons of injected hazardous wastes. Although these wells are located in sedimentary basins throughout this country, most of them are in the Great Lakes region and along the Gulf Coast.

Increased concern of the fate of wastes after disposal has led to changes in chemical processes. Indeed, under the Resource Conservation and Recovery Act (RCRA), the EPA is required to make some decision concerning the safety of underground injection of hazardous wastes by August 8, 1988. Although a study prepared for the Underground Injection Practices Council (UIPC) showed that to date only a few malfunctions have resulted in contamination of water supplies, future practices will have to ensure that no additional contaminations will occur.

The literature survey discussed in this report was initiated to determine what knowledge is available concerning ultimate fate of injected hazardous wastes. The present discussion is limited to the hazardous wastes listed in the Hazardous Wastes and Solids Amendments of 1984. Also, "ultimate fate" of injected wastes are limited to a time determined by available laboratory and field pilot techniques. Since knowledge of the interactions of complex waste mixtures is limited, much of the discussion relates to particular chemicals or chemical groups. Because of the limited research conducted specifically for deep-well formations, literature reports that address the interaction of wastes by any method that has useful applications to deep-well formations also were considered in the survey.

Demonstrating the fate of injected wastes requires knowledge of the behavior of each waste after it enters the subsurface environment. The interaction of a particular waste with other injected wastes, with reservoir fluids, and with reservoir solid materials, such as clays, silicates, and carbonates must be known. Unfortunately, hazardous wastes are complex mixtures of materials, and when combined with other mixed waste streams, the potential number of interactions increase factorially.

Furthermore, since subsurface environments often take many years to reach chemical and biological equilibrium, predicting exactly what will happen *a priori* may be nearly impossible. For example, some toxic metals may adsorb onto clays as they are injected, making the migrating fluids immediately nonhazardous. This adsorption process does not guarantee that some waste injected into the reservoir in the future might lead to desorption of the same metals, thus rendering the fluids hazardous again.

The first section following the introduction of this report discusses what is known about nonorganic hazardous materials. Such major processes as neutralization, hydrolysis, ion exchange, precipitation, complexation, and adsorption are included in the discussion. As might be expected, organic materials not considered in the RCRA list of hazardous wastes may strongly influence these processes and will be discussed as appropriate.

The second following section discusses what is known about organic hazardous materials. Such processes as thermal degradation, adsorption, oxidation, reduction, hydrolysis, and microbial degradation are included in this discussion. Microbial degradation actually is a general term for many biological processes and will be discussed at some length.

## Discussion

### PROCESSES INVOLVING NONORGANIC HAZARDOUS WASTES

The most likely reactions or transformations for nonorganic hazardous wastes include precipitation, adsorption/desorption, ion exchange, hydrolysis, complexation, oxidation/reduction, acid/base reaction, and mineral dissolution. Only a small percent of total wastes injected actually contain toxic metals ( $\leq 1.0$  percent). Included are arsenic, barium, cadmium, chromium, lead, mercury, nickel, and selenium. Most of the nonorganic wastes injected are classified as nonhazardous and contain various alkali metal salts, such as lithium, sodium, and potassium. The presence and concentration of these nonhazardous metals are important considerations, however, when evaluating the fate of hazardous wastes. The particular

hazardous materials addressed as hazardous in this section include free metal and associated salts of arsenic, cadmium, chromium (VI), lead, mercury, nickel, selenium, thorium, inorganic salts of cyanide, and any solution with a pH lower than 2.0 derived from mineral acids.

Subsurface reservoir fluids have equilibrated with reservoir minerals and clays during geologic time. All of the minerals, rocks, hydrocarbons, and gases are interrelated and contribute to the final stable solute/solvent matrix that exists in the reservoir. On the other hand, waste solutions considered for deep-well injection were generated in a different environment and have attained a thermodynamic equilibrium under different circumstances. Consequently, upon injection into the formation, adjustments must occur before a new solute/solution equilibrium is reached. Some injected wastes result in immediate precipitation of solids from solution and potentially may plug the formation from further injection. Other wastes may result in less immediate problems, but still may reduce the life of the injection well significantly. Thus, injection well operators usually conduct laboratory tests on injected hazardous wastes and native reservoir fluids to determine their compatibility.

Some research studies in the literature show that the type of precipitate produced from incompatible fluids is important in determining the resulting degree of permeability reduction. For example, ferric hydroxide appreciably blocks the flow of fluid through a porous matrix, but barium sulfate and calcium sulfate do not. Ferric hydroxide is gelatinous in nature while barium sulfate and calcium sulfate are finely crystalline. The type of precipitate seems to determine the effectiveness of blocking in the porous matrix. One method of preventing injection wells from becoming plugged due to incompatible waters has been the injection of a buffer zone of nonreactive water. The effectiveness of this method has been demonstrated.

Other problems with incompatible fluids may result from extreme pH values. High pH solutions tend to dissolve silica and release fines that migrate and plug the pores, resulting in permeability damage to the formation. Additional formation damage may occur as the dissolved silica reprecipitates

another section of the reservoir.<sup>1</sup> Alternatively, low pH solutions may lead to silica gels or the dissolution of some clays and carbonate (either matrix or cements). All of these problems are not as evident in carbonate formations. However, later deposition of materials with changes in pH may also be a problem in carbonate formations.

Studies of compatible and incompatible fluids with reservoir fluids also show that simply mixing the fluids together in a flask is inadequate to treat the many complexities that often occur. Examples of apparently incompatible fluids causing little trouble in contrast to apparently compatible fluids plugging the injection wells were noted and further illustrate the inadequacy of this simple test.

Precipitation is only one of many interactions possible. Although reactions between hazardous wastes and silica, dolomite, etc., are relatively straightforward and reactions between waste and reservoir fluids can often be easily characterized, the interactions between waste materials and formation clays have been difficult to characterize. Obvious interactions such as clay swelling and clay particle migration are possible with any injected fluid. In secondary and/or tertiary petroleum recovery operations, petroleum engineers usually avoid injecting alkaline solutions, and sometimes all aqueous solutions when water-sensitive clays are present. Damage to the clays can result in drastically reduced permeabilities, and often specialized products that stabilize clays are used in treating fluids to prevent damage to reservoirs.

Adsorption of organic and nonorganic materials varies, depending upon the amount and type of clay present in the formation, because different clays have different amounts of surface area and different charge densities. Since clays possess an overall negative charge, cations such as moderately soluble metal wastes are attracted to these clays. The more soluble ions previously attached to the clays may resolubilize when other less soluble ions replace them on the clay surface. This process is termed ion exchange. Some of the metals associated with the clay, may bond so tightly that they may be considered immobile, or permanently adsorbed.

Heavy metals are particularly susceptible to this behavior.

Champlin conducted flow experiments through cores and measured the ion and particle concentrations throughout.<sup>2</sup> He found that when the salinity of the effluent was low, both the ions and particles were strongly retained by the sand in the core. When the salinity of the water was high, both the ions and suspended particles passed through the core and were not retained by the sand. Most importantly, isotopic labeling led him to further postulate that when the ions and particles passed through the core, the ions were still attached to the migrating particles. Thus, a mechanism was proposed where salinity affected the attractive forces between the suspended particles and the sand grains. The physical and chemical forces of the metal ions were sufficiently strong to remain attached to the clay particles.

Certainly, clays provide a surface capable of attracting certain nonorganic hazardous wastes. The adsorption of these wastes onto the clays in the injection zone is desirable, since the mobile fluids would be rendered less hazardous, and the clays may be protected from additional swelling and migration. Of course, the adsorption of materials is not desirable when such processes result in the plugging of the well. Predicting how much waste will be adsorbed, how long the waste will remain immobile, and under what circumstances the waste will be desorbed is difficult.

#### *Processes Involving Organic Hazardous Wastes*

Unlike that of most nonorganic hazardous materials, the organic hazardous wastes can be made non-hazardous by molecular transformations of the compounds. Such processes as ion exchange, oxidation, reduction, hydrolysis, cyclization, and biological transformation are all possible means of rendering the wastes nonhazardous. Alternatively, these same processes can lead to increased toxicity for certain wastes. Because the number of potential products is almost infinite, assessing the "ultimate fate" of these wastes is even more difficult than for the nonorganic hazardous wastes.

A brief discussion of the various processes of degradation available to organic wastes will be presented in this

section. The details of the discussions are shorter than the corresponding discussions for nonorganic materials for two reasons: (1) less definitive work has been done, and (2) the number of possible interactions is much greater than for that of nonorganic materials, making definitive fate predictions more difficult to determine.

As with nonorganic hazardous wastes, adsorption is a major mechanism of fluid-solid interactions that affect the mobility of organic wastes. Adsorption has been found to be dependent upon the particular clays present, that is, montmorillonite and vermiculite have very high adsorption capacities, while kaolinite has a very low adsorption capacity. Illite and chlorite are intermediate in their ability to adsorb. These properties have been attributed to the available surface area for the respective clays.

Many factors influence the degree of adsorption of various chemicals, including chemical shape and configuration, acidity, water solubility, charge distribution, polarity, molecular size, and polarizability. Most organic compounds that adsorb on clay materials have contribution from all of these properties. Thus, predicting the degree of adsorption according to relative acidity, may lead to incorrect predictions if resonance stabilization is not considered. Molecular shape may increase or decrease the adsorption energies of any particular compound, even though the other chemical properties may be very similar. All of these listed properties have been demonstrated to be important, and are found to be interdependent.

Another important factor that influences adsorption is temperature. Since adsorption processes are generally exothermic and desorption processes are generally endothermic, an increase in temperature would normally reduce adsorption processes. However, a number of exceptions have been found. The pesticide EPTC is an example.

Mortland<sup>3</sup> discusses some of the mechanisms by which organic chemicals are adsorbed. These include the replacement of metals with cationic molecules, replacement of metals by neutral molecules that are protonated to become cationic, ion exchange with polyvalent metals attached to the clay, coordination with metal cations, and by hydrogen bonding. Many of these

mechanisms have been studied and demonstrated using such techniques as adsorption, isotherms, calorimetry, X-ray diffraction, UV-visible spectroscopy, electron spin resonance spectroscopy, and infrared spectroscopy.

Another process by which certain hazardous organic wastes can be transformed into other compounds is by oxidation reactions. Such compounds as phenols, aromatic amines, olefins, dienes, alkyl sulfides, and eneamines are particularly susceptible. The exact species of different oxygen radicals present in aqueous and soil environments that initiate the oxidation process may include such oxy-radicals as  $\text{HO}\cdot$ ,  $\text{RO}\cdot$ , and  $\text{O}_2$ , depending upon the environmental conditions. The evaluation of the potential importance of this process at typical injection well conditions to hazardous waste injection has not been done. However, if certain hazardous wastes containing chromium (VI) are co-injected either simultaneously or sequentially with organic wastes, the oxidation process most certainly would be important. Chromium (VI) can be an excellent oxidizing agent.

Hydrolysis is another process of waste transformation, and is the process by which some functional group attached to a molecule is replaced by an -OH functional group originating from a water molecule. Hydrolysis can be catalyzed by either an acid or a base, as defined in chemistry for Lewis acids and bases. Mabey and Mill<sup>4</sup> provide a good review of hydrolysis processes of organic materials in the environment. Factors such as pH, temperature, and the presence of other ions are known to affect the rate of hydrolysis. Depending upon whether the pH is high or low, different mechanisms may apply. At low pH, the hydronium ion ( $\text{H}_3\text{O}^+$ ) predominates in hydrolysis, while at high pH, the hydroxide ion ( $\text{OH}^-$ ) predominates. While the effect of temperature is known, the magnitude for the influence temperature has on different compounds is not always known. The presence of certain alkaline earth and heavy metal ions may catalyze hydrolysis for a variety of esters.

Many potential processes are available for biodegradation. These processes include mineralization, detoxification, cometabolism, activation,

and defusing. Mineralization is the conversion of organic wastes to inorganic wastes. Detoxification is the conversion of toxic compounds to nontoxic compounds. Cometabolism is the conversion of one organic compound to another without the microorganism using this process as a nutrient. Activation is the conversion of a nontoxic compound to a toxic compound. Defusing is the process of converting a compound potentially capable of becoming hazardous to another nonhazardous compound by circumventing the hazardous intermediate. Although defusing has been confirmed in the laboratory, it has not been identified in the environment.

The first question with respect to biodegradation most certainly is: Do any microbes exist in the injection zone, or can microbes capable of converting organic wastes to nonhazardous wastes exist at those conditions? A number of researchers have attempted to answer this question.

DiTommaso and Elkan<sup>5</sup> analyzed a saline aquifer at the depths of 850-1000 ft. Much of the waste injected into this zone contained organic compounds such as acetic acid, formic acid, and methanol. About 3000 organisms/ml were isolated from the unpolluted aquifer. Most of the organisms identified were aerobes typically found in aquatic environments. The most common genera include *Agrobacterium*, *Pseudomonas*, *Proteus*, *Bacillus*, *Aerobacter*, *Corynebacter*, *Arthobacter*, and *Micrococcus*. Conversely, samples taken after waste injection were found to contain primarily anaerobic methanogenic bacteria.

Horvath<sup>6</sup> provides a good review of some of the studies conducted on biodegradation of wastes in subsurface environments, and summarizes some of the processes involved in the degradation of such compounds as acetate, formate, methanol, formaldehyde, and aromatic acids. Horvath also developed a laboratory model to evaluate these processes. These studies indicated an interesting observation concerning methanogenic and sulfate-reducing bacteria. Apparently, even though the required nutrients were available, methanogenic bacteria did not proliferate, whereas the sulfate-reducing bacteria did in the zone studied. This behavior may have occurred because of the pH that predominated for the test and

supported work done by others who indicated that the two types of bacteria are mutually exclusive. Obviously, the degradation of injected wastes will depend upon which type of bacteria prevails. Methane-producing and sulfate-reducing bacteria do not degrade the same compounds.

In summary, microbial degradation often is a very important mechanism by which certain hazardous wastes may be transformed to nonhazardous wastes. Bacteria have been identified in the subsurface environment. Within certain reasonable limits, bacteria are capable of surviving relatively hostile environments. Studies have also shown that transformation processes via biological pathways can be very complicated and difficult to establish. Therefore, this method should not be depended upon for waste detoxification in the subsurface environment, unless pilot studies have established the existence of these processes.

## Conclusions

Many conclusions were presented by the papers reviewed in this report; some of the more significant ones are as follows:

- The basic compatibility test conducted by mixing waste fluids and reservoir fluids does not always give meaningful results. The test must be conducted under reservoir conditions. Precipitates, if formed in the compatibility test, may or may not plug the well depending upon the type of precipitate formed.
- For nonorganic wastes, solution pH is critical for determining the ultimate fate. The identity of soluble species, solubility products, adsorption characteristics, and chemical interactions are some of the variables affected by pH.
- The brine concentration, even though not listed as hazardous, is important in affecting clay stability and adsorption characteristics.
- The presence of organic complexing agents may or may not affect the mobility of heavy metals in the reservoir.
- Adsorption of nonorganic wastes is dependent upon a number of factors, such as Eh, pH, clay type, and the presence or absence of iron oxides and hydroxides.
- Mathematical models do successfully predict certain reactor processes. However, some interactions have not been modeled

- The major mechanism of degradation for certain halogenated hydrocarbons is hydrolysis.
- Microbial degradation of organic hazardous wastes has been shown to be useful in decontamination after deep-well injection. Wastes can support growth of certain bacteria during the injection process. However, results are not always predictable, and studies suggest that each case should be evaluated individually to determine the feasibility of the process.
- Some case studies corroborate the interrelationships of degradation processes discussed in this report.

## References

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The complete report, entitled "State-of-the-Art Report: Injection of Hazardous Wastes into Deep Wells," (Order No. PB 87-170 551; Cost: \$13.95, subject to change) will be available only from:

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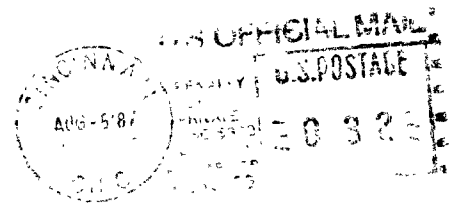
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