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4 Chemistry: Fate and Transport

The term "fate and transport" describes how chemicals entering the subsurface from point or nonpoint sources relate to groundwater concentrations elsewhere. The behavior of contaminants in rock formations depends on the physical and chemicals properties of the contaminants and on the rock characteristics. This chapter presents an overview of fate and transport mechanisms and discusses how the unique properties of individual chemicals or mixtures of chemicals influence fate and transport in a fractured rock environment. Understanding the fate and transport of contaminants within various rock types and the hydraulic characteristics of the rock provides a basis for developing a more reliable CSM.

4.1 Fate and Transport Mechanisms

A challenge with managing contaminated fractured rock sites is determining the direction and rate of contaminant transport within the subsurface. Because fractured rock is anisotropic and heterogeneous, fluids travel at variable rates within the rock, including potentially rapid movement of contaminants over long distances through preferential flow paths (secondary porosity). As a result, hydrogeologic and geochemical equations and models developed for homogeneous porous media may fail to characterize or predict contaminant fate and transport for these systems.

The fate and transport of contaminants within fractured rock involves complex processes that depend on interactions among the physical and chemical properties of the contaminants and the rock, as well as the hydrology of the fracture flow. As contaminants flow through the subsurface, they are subjected to a range of physical, chemical, and biological processes that disperse, transform, or degrade the contaminants. Furthermore, different contaminant classes (such as volatile organic compounds or metals) behave differently in the subsurface based on their physical and chemical properties.

The discussion of fate and transport mechanisms is organized as follows:

- movement through fractures
- diffusion into and out from the rock matrix
- retardation (sorption and desorption)
- natural attenuation through biotic and abiotic transformation
- volatilization (unsaturated zone only)

4.1.1 Movement through Fractures: Advection, Capillary Flow, Dispersion, and Diffusion

Four mechanisms control the movement of contaminants through fractures: advection, dispersion, diffusion, and capillary flow.

Advection. Advection is the transfer of a contaminant by the typically horizontal flow of a fluid (either groundwater or the contaminant). Advection is often the primary mode of contaminant transport under single-phase transport (dissolved phase) or multiphase transport (simultaneous water and NAPL, or water and gas migration). By this mechanism, movement of the contaminant occurs because of bulk fluid motion under the influence of gravity or hydraulic pressure and gradients. While advection is a dominant transport mechanism in porous media, the rate and direction of advection in fractured rock can vary significantly over short distances.

In fractured rock, advective transport is controlled by several criteria including: size, roughness or asperity, planarity or waviness, orientation, and connectivity of the fractures within the host rock in relation to the aquifer hydraulic gradient or pressure. For example, interconnected fractures in limestone, enlarged by dissolution, can have high hydraulic conductivity values (10^{-1} to 10^{4} m/day) compared to a fractured shale, where the fracture aperture and interconnectivity may be smaller and result in lower hydraulic conductivity values (10^{-5} to 10^{-3} m/day). Therefore, for rock types characterized by comparatively large fractures that are interconnected or extend for hundreds of feet, advective contaminant transport can potentially occur over a longer distance and in a short period of time. Caves thousands of feet long are capable of transporting contaminants rapidly.

Capillary Flow. While advective flow is the dominant transport mechanism in large aperture fractures, when multiple continuous phases are present (such as water and NAPL), capillary flow or film flow may become important with decreasing

aperture size. Capillary flow of contaminants (the flow of a contaminant into narrow fractures without the assistance of and often in opposition to gravity) is more significant over shorter distances. Capillary flow can dominate flow conditions in small aperture fractures or support thin films along the walls of larger fractures. Within a developed fracture system capillary, or film flow, can travel up to 1,000 times faster than the typical pore water velocity (NRC 2001). Depending on size, orientation, and interconnectedness, capillary or film flow can short circuit matrix flow and substantially increase the transport rate and distance, particularly within the vadose zone. This type of fracture flow can be important in the movement of NAPL.

Diffusion. Diffusion operates independently of bulk flow and results from molecular movement of contaminant solutes within a media from areas of higher chemical concentration to areas of lower chemical concentration. Diffusion within fractures is more significant over shorter distances (such as centimeters to meters).

In porous media with low hydraulic conductivity, contaminant diffusion within fluid-filled interstitial pore spaces can play a major role in contaminant migration in the subsurface. In fluid-filled fractures, as the hydraulic conductivity of fractured rock mass increases with increasing fracture aperture or fracture frequency, the effects of diffusion within the fracture on contaminant transport are overshadowed by physical transport mechanisms (advection, dispersion, and capillary flow).

4.1.2 Diffusion and the Rock Matrix

Matrix diffusion is a significant mechanism by which contaminants may enter a rock matrix with appreciable pore space, such as sedimentary rocks. In this process, elevated dissolved concentrations present in the secondary porosity (within fractures) are partitioned toward areas of low concentration in the rock matrix. When a plume is first entering a fractured rock zone, diffusion of contaminant molecules into the matrix retards the advection transport of the plume. The rate of matrix diffusion and the extent of penetration into the rock is controlled by a complex relationship depending on the following:

- contaminant concentration gradient
- contaminant physical and chemical characteristics
- rock matrix biogeochemistry
- rock matrix porosity and tortuosity (a property characterized by many turns)
- degree of saturation
- fracture flow rates, which influence the residence time of the contaminant in the fracture (amount of time for rock matrix diffusion to occur)

Once the contaminant is diffused into the rock matrix, the process of diffusion works in reverse (which is called “back-diffusion”) and releases the contaminant stored within the rock matrix back into the fracture. Back-diffusion is a dynamic phenomenon, causing the passing plume to persist at a point of observation, albeit at a relatively low concentration, longer than it would otherwise, even if the contaminant is removed from the fluid within the fractures, This process increases effective plume longevity and, if not accommodated, can greatly delay remediation times frames. If, however, the flow in the fracture is very high relative to the flow in the porosity, the back-diffusion may be diluted and thus not be an issue.

4.1.3 Retardation: Sorption and Desorption

Retardation is the result of sorption of contaminants to the sides of fracture walls and the rock matrix, which varies with the amount of clay minerals or mineralogy of the rock within fracture surfaces. This process slows the movement of contaminants through fractured rock. Retardation affects the migration of the center of mass of the plume. The rate of contaminant migration varies with dispersion, because retardation is less significant for the more permeable pathways.

Naturally occurring organic matter also affects retardation. Organic carbon (f_{oc}) may line fractures (secondary porosity) or may occur within the rock matrix (primary porosity). Organic matter affects fate and transport and ultimately the remediation of a contaminant, for the following reasons:

- Organic matter retards contaminants so that the rate of dissolved-phase contaminant migration is less than the groundwater velocity.
- Over time, the mass of contaminant in the rock matrix can be greater than in open fractures.
- The time required to remediate the site may be controlled by desorption from organic carbon in the rock matrix and back-diffusion of the dissolved-phase contaminant. Higher f_{oc} in the rock matrix prolongs the time frame for removing the contaminants.

When organic carbon is suspected to be present, organic carbon analysis should be considered. Organic carbon is possibly present at sites underlain by sedimentary, igneous, or metamorphic rock; however, it is more likely to occur in sedimentary rock. Rocks that have undergone crystallization (most igneous and metamorphic rocks) have greatly reduced organic carbon

and demonstrate limited retardation as a function of contaminant sorption. Analysis of organic carbon should be performed for sites where NAPL or dissolved contaminants occur within fractured igneous or metamorphic rock that exhibits primary porosity.

For metals, retardation can occur through sorption onto surfaces such as ferric iron oxy-hydroxides, carbonates, and silicates. For example, trace metals such as cadmium, nickel, lead, and zinc can sorb or complex with natural mineral forms, as well as with secondary precipitate forms such as ferric iron oxy-hydroxides or hydroxysulfates. These secondary precipitates typically form within fractures or underground mine voids because of oxidation or infiltration of precipitation (see Section 4.1.6). The degree of sorption onto these surfaces also depends on pH and redox state.

Retardation of trace metals may be a significant factor in the fate and transport of contaminants at some sites such as mines, industrial sites, or sites where mixed organic contaminants have been released (for example, where DNAPL is also affected by metals). For example, intentional oxidation of a plume of organic contaminants could result in geochemical changes to the rock matrix and lead to the release of trace metals into groundwater. In contrast, the presence of metals comingled with organic contaminants could, due to the competition for surface sorption sites on organic matter, result in the increased mobilization of organic contaminants.

4.1.4 Natural Attenuation through Biotic Transformation

Biotic transformation involves metabolic and enzymatic pathways, which may occur as a component of natural attenuation within fractured rock. For fractured rock, the availability of surface area for microbial attachment and lower organic carbon content (compared to porous media) may limit the rate and capacity for biotic transformation. ITRC provides additional information on aqueous conditions that favor natural attenuation through biotic transformation chlorinated solvents (ITRC 2008).

Naturally occurring organic matter, or another contaminant release such as petroleum hydrocarbons, may provide a carbon substrate in fractured rock for some forms of biotic transformation, such as reductive dechlorination of chlorinated solvents. For metals, biotic transformation may alter the geochemical state of the aqueous environment and that of the metal contaminant to a more stable (nonmobile) form. With the presence of organic carbon, sulfate-reducing bacteria (SRB) (ITRC 2003) can reduce sulfate to sulfide and form metal sulfide precipitates to attenuate the metals from solution.

Biotic transformation may also be referred to as biotransformation, biodegradation, and biocatalyst (Suthersan 2005). This biotic process may occur due to indigenous microorganisms or cultured microorganisms added to the subsurface to degrade contaminants. Four common types of transformations that can occur in fractured rock are described in the following sections.

Reduction and oxidation (redox) reactions ▼*Read more*

Microorganisms can gain energy for growth by coupling reduction-oxidation reactions by electron transport systems. DNAPL and dissolved chlorinated aliphatic hydrocarbons, such as PCE, can serve as electron acceptors in these biocatalyzed reactions.

$$CCl_4 + 2H_2 \rightarrow CH_2Cl_2 + 2H^+ + 2Cl$$

For example, under anaerobic conditions, alternative electron acceptors, including nitrate, nitrite, Mn (IV), iron (III), sulfate, and CO_2, can be used by specific groups of microorganisms. Using these alternative acceptors in electron transfer bioprocesses is termed anaerobic respiration. In anaerobic environments, hydrogen can also serve as an electron donor for the reduction of contaminants. Halorespiration refers to biological reduction of organic solvents to produce energy for growth. In this process, hydrogen is oxidized while the chlorinated solvent is reduced.

Cometabolism ▼*Read more*

Cometabolism is a fortuitous reaction in which a compound is degraded by a substance that organisms produce for other purposes. The cometabolic process does not benefit the organism producing the substance (such as an enzyme or cofactor). For example, bacteria produce metallocoenzymes, such as cytochrome P450 and iron (II) porphorins, that are capable of dechlorinating carbon tetrachloride. Bacteria produce another class of compounds, oxygenases (including mono- and dioxygenase enzymes), which are among the most important inducible enzymes for cometabolism of chlorinated compounds. Cometabolic transformation kinetics are complex and not well understood. The models developed to describe these kinetics are likewise complex, and often make quite different assumptions about system behavior, growth kinetics, substrate utilization kinetics, and cometabolite oxidation kinetics.

Assimilation ▼*Read more*

Assimilation refers to the incorporation of substances into biomass. In some cases, groundwater contaminants can be

converted into biomass by microorganisms. To produce biomass, microorganisms require sources of carbon, hydrogen, oxygen, and nitrogen, as well as trace nutrients. For example, microorganisms can use ammonia (NH_4), nitrate, or nitrite as sources of nitrogen for growth. Although assimilation processes may involve redox reactions, these processes are different from dissimilatory redox reactions because the latter produce energy for the growth of microorganisms. In contrast, assimilatory reactions (anabolic reactions) often require energy. For example, the assimilation of ammonia via the glutamine synthesis reaction utilizes adenosine triphosphate (ATP) (energy), yielding adenosine diphosphate (ADP) and inorganic phosphate (Pi):

$$\text{Glutamate} + NH_3 + \text{ATP} \rightarrow \text{Glutamine} + \text{ADP} + \text{Pi}$$

Sequential transformations ▼*Read more*

Transformation of contaminants in groundwater is often sequential with various intermediates (or degradation products) appearing before the contaminant is completely mineralized. For example, the generally accepted sequence for denitrification is:

$$NO_3 \rightarrow NO_2 \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

The presence of intermediates from sequential transformations is often used as an indicator of contaminant degradation by natural attenuation. For example, in the case of groundwater contaminated with carbon tetrachloride, the presence of chloroform and methylene chloride may indicate that contaminant degradation has occurred. The reaction rates for the various steps in a sequential transformation may be considerably different. Thus, an intermediate in the sequence that is formed quickly, but consumed slowly, can accumulate during sequential degradation.

4.1.5 Natural Attenuation through Abiotic Transformation

Abiotic transformation of contaminants in fractured rock may be an important natural attenuation mechanism for reducing the magnitude and extent of pollution effects. Depending on the contaminant, abiotic transformation (without direct biological transformation) can involve chemical, redox, and electron transfer reactions. An example of a chemical reaction is hydrolysis (such as for 1,1,1-TCA to 1,1-DCE).

Redox reactions are catalyzed or promoted by reactive surfaces such as those associated with certain metals, metal sulfides, and clay particles. An example of an abiotic redox reaction is β-elimination, such as for rapid mineralization of TCE through acetylene. The reactive surfaces may be of basic geologic origin, or derived from abiotic geologic and weathering processes, or from biogeochemical processes. For example, many ferrous sulfides originated as products of iron and sulfate reduction over time. Thus, knowledge of the fracture and matrix mineralogy, morphology, weathering, and microbiology is necessary to assess the potential for redox-based abiotic transformation.

At some sites, rocks with high metal sulfide mineral content, such as pyrite (FeS_2), chalcopyrite ($CuFeS_2$), sphalerite (ZnS), galena (PbS), and cinnabar (HgS), can become oxidized, release metals into solution, and generate acidity (low pH and elevated aluminum, iron, and manganese). For mines, this acidified water is often called *mining-influenced water*. In the presence of carbonate or other rock forms that can contribute alkalinity, neutralization or pH increases can occur, resulting in secondary precipitate forms. Secondary precipitates can also form in fractures as seasonal groundwater elevations decrease, leaving a mineral crust in the drying voids. Stability of these secondary precipitates (for example, their potential for redissolution into the aqueous phase) is subject to pH and the geochemistry of the surrounding water and rock matrix when submerged. The lower the pH and water ionic strength, the greater the tendency for precipitates to redissolve. For dried precipitates within fractures, seasonal changes in groundwater elevations (increase) can result in subsequent dissolution of the secondary precipitates, which again mobilizes the metals and potential acidity into the groundwater system. USGS and other sources in the research literature describe the geochemical transformations associated with hard-rock and coal mines, or similar geologies in other nonmine environments.

When heavy metals are present in the subsurface, natural contaminant chemistry interactions with rock matrix often release undesirable metal concentrations into groundwater. When leached from the rock and minerals, toxic heavy metals can exceed drinking water criterion. Arsenic, cadmium, selenium, and a variety of other heavy metals are documented to have been released at attenuation sites. Metal and ore deposits are often found in trace to significant quantities in many igneous, metamorphic, and intrusive rocks. Sandstones are also known to contain significant concentrations of arsenic and other heavy metals when their depositional basins were derived from granitic and Canadian shield deposits. Significant release of metals is possible if the site-specific contaminants or treatment processes release metals through lowering pH or through other electron donor processes that use metals (for instance, iron and manganese). Aesthetic drinking water problems can occur downgradient of these sites due to increased iron, total dissolved solids, taste, and odor problems.

4.1.6 Volatilization

Depending on their properties, contaminants present in fractured rock may volatilize into the unsaturated fractures or into overburden soils where they can be detected through passive/active soil gas surveys. A soil gas survey can be a valuable tool to detect and characterize the extent and migration pathways for contaminants migrating through fractured rock.

Once contaminants volatilize, transport in fractured bedrock is governed by the fluid flow conditions. Factors such as the depth to groundwater, the nature of fractures, and the characteristics of overburden soils can affect the migration of soil vapors. The nature of fractures within the bedrock and the heterogeneity or anisotropy of overburden soils are important controls on the transport of contaminated vapors, the effects to receptors, and detection in shallow soil gas surveys.

4.2 Contaminant Properties Affecting Fate and Transport

The fate and transport mechanisms that affect the behavior of contaminants in fractured rock depend on the properties of the contaminants. Several examples of how specific contaminant properties affect fate and transport in fractured rock are provided in this section. Table 4-1 includes a list of common contaminants encountered at contaminated fractured rock sites. For each contaminant, physical and chemical properties are identified and the implications for fate and transport in fractured rock are highlighted. Properties that have specific implications for the fate and transport of the contaminants are color-coded in the table. This information can be useful in developing the initial CSM.

Table 4-1. List of common contaminants and characteristics

Click Here to view Table 4-1 in Adobe Acrobat format.

▼*Read more*

Liquid density. Contaminants with a density greater than that of water (such as DNAPL) typically migrate downward into groundwater (sink below the water table) and can also infiltrate bedrock fractures beneath the water table. A detailed discussion of the fate and transport of high-density contaminants is presented in Integrated DNAPL Site Characterization (ITRC 2015b).

Vapor density. Vapor density drives the vertical migration of contaminants. For example, chlorinated solvents generally have a higher vapor density relative to air and migrate at the lower portion of the unsaturated zone that may correspond with fractured rock.

Vapor pressure/Henry's constant. Contaminants with higher vapor pressures/Henry's constants are likelier to partition into the vapor phase. These chemicals are candidates for use of soil gas surveys.

Boiling point. The boiling point for a contaminant can be a significant when selecting remedial strategies. Contaminants such as chlorinated solvents may form a heteroazeotrope with groundwater. A heteroazeotrope is an azeotrope in which the vapor phase coexists with two liquid phases. When two liquids form a heteroazeotrope, their partial pressures are additive, and are effectively boiled out at temperatures below the boiling point of water. This property is relevant, for instance, when evaluating thermal remedial technologies in amenable rock types such as poorly cemented sandstones.

Solubility. Highly soluble contaminants tend to readily partition into groundwater and have the potential to both migrate long distances from the point of release and to enter matrix porosity through matrix diffusion. Contaminants that diffuse into matrix porosity provide a long-term reservoir for dissolved contaminants through gradual back-diffusion. This property can significantly affect remedial actions and should be carefully considered when developing the CSM.

Henry's constant. At a constant temperature, the amount of a gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid

Sorption. Contaminants, such as ammonia, that strongly sorb to soil or rock may be restricted in their vertical migration and may not be encountered in significant concentrations within fractured rock. However, many contaminants with moderate sorption (such as chlorinated solvents) are commonly encountered within bedrock fractures, but also tend to sorb to both soils and the rock matrix. High levels of natural organic matter further retard the vertical and lateral movement of contaminants and are evaluated as they are in unconsolidated media. Typical parameters for the measuring sorption potential include the partitioning coefficient (Kd), the carbon and water partitioning coefficient (Koc), and the octanol water partitioning coefficient, Log Kow.

Reactivity (biogeochemical transformation). Some dissolved contaminants are amenable to biogeochemical transformation because of contact with the rock matrix. For example, many chlorinated solvents (PCE, TCE, DCE) undergo biogeochemical transformation or degradation if the rock matrix is iron-rich.

4.2.1 Contaminant Mixtures (LNAPL and DNAPL)

Highly viscous LNAPLs tend to be restricted in their vertical migration and may not always infiltrate into bedrock fractures. These viscous mixtures of contaminants are seldom encountered within fractured rock settings as separate phase liquid. These mixtures can, however, partition to dissolved or gas phases and contribute to dissolved phase contamination within bedrock fractures. ITRC is updating its guidance on LNAPL characteristics and fate and transport of LNAPL compounds in fractured rock; this update is expected to be published in late 2017 (ITRC 2017).

DNAPL behavior in fractured rock is complex because of the varying degrees of matrix and secondary porosity found in fractured rock. DNAPL flow through fractures may result in dissolution, dissolved-phase advection, sorption and desorption, biochemical transformation, and diffusion into the rock matrix. After migrating vertically through the fracture network, the DNAPL becomes relatively immobile or trapped in small or dead-end fractures because there is no longer a hydraulic gradient or pressure to overcome the pore entry pressures in the rock or displace the water from the fractures. The DNAPL (or ganglia) then begins to dissolve into the water in the fractures and diffuse into the rock matrix. The dissolved-phase constituents migrate with the water flowing through the fractures, forming a plume downgradient of the initial release. As this plume migrates, molecular diffusion occurs within the fractures from the plume to the matrix porosity, where porosity is present.

If a reverse concentration gradient comes into effect, the dissolved-phase contaminants that have diffused into the matrix porosity may then back-diffuse from the same rock matrix into the groundwater traveling within the fractures. This back-diffusion process may sustain elevated concentrations of contaminants in the zones that formerly contained the DNAPL, as well as the previous dissolved-phase plume. The presence of DNAPL constituents presents a potentially persistent reservoir of contaminant mass that can continue to release dissolved contaminants into the groundwater over time. As a result, DNAPLs may persist in the subsurface for several decades or longer, depending on their specific properties. For a more detailed discussion on the fate and transport of DNAPL in fractured rock, see Chapter 3 and Chapter 4 in *Integrated DNAPL Site Characterization and Tools Selection* (ITRC 2015a).