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Modern Trends In Tracer Hydrology

Volume I

Editor

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Chapter 2

BEHAVIOR OF ARTIFICIAL TRACERS

Emilian Gaspar

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$$Re = \frac{v_c d}{\mu} \rho_w \quad (65)$$

where v_c is the mean critical speed, d the diameter of pores, ρ_w the specific mass of the fluid, and μ the dynamic viscosity of the fluid.

Essentially, hydrodynamic dispersion is due to the random variations in water flow rates and directions in the individual pores of the porous medium. However, "dispersion" of the water front and of the tracer occurs also when fissures and channels exist in which flow velocity is much higher than the average flow velocity. Channeling is a frequent phenomenon in fissured and karstic rocks.

In assessments on columns, dispersion produces broad and tailing curves with a single maximum.

The variation of tracer concentration in time and space is due not only to the phenomena of diffusion and dispersion but also to physical, chemical, and biological interactions with the traversed medium.

E. Mechanisms of Interaction between Tracers and the Rocks in the Underground Medium

Interactions between tracers and the solid phase of the medium are mainly due to the following processes.

1. Filtration

It is a purely mechanical process that affects only colloids, floating and suspended substances, and sediments. All solid tracers — spores, plants, floating spongy materials, and substances that are less readily soluble — are retained through filtration. The result of filtration is the total loss of the tracer, and in the case of heavy soluble substances their dissolution in time will result in a high dilution of the tracer, below detection limits in general.

2. Physical Adsorption

Adsorption is due to an exchange between two phases at whose separation limit molecules of different species may interact as an outcome of the difference in the polarity of the molecules of the two media. In dynamic systems, in which the mixture of substances in solutions represents the mobile phase which moves along the separation surface in a field of forces of different intensities, molecules in the liquid phase may be attracted to a smaller or larger extent to the solid phase (as motion velocities differ). This fixation through physical processes of the molecules of a tracer on the surface of the granules of the solid medium with which they come into contact is due to the action of weak forces of attraction, such as the van der Waals forces. These interfacial forces depend on the surface which the granules of the solid medium expose at their contact with a tracer.

The energy involved in physical adsorption is of the order of 0.5 kcal per adsorbed molecule. As the bond is weak the adsorbed molecule may be desorbed in its turn, but with a certain delay. This phenomena depends *inter alia* on the capillarity of the adsorbent and the steric compatibility (special configuration of the chemical compound) between the tracer ions or molecules and the interionic or interatomic space of the adsorbent.

Owing to this mechanism, less soluble tracers — more particularly, those boasting a large molecular weight, such as rhodamines — are retained.

Physical adsorption places part of the tracer molecules out of circuit at the very point of injection when the tracer solution has a high concentration. The phenomenon may be of special importance for labelings in sinkholes with small discharges when pourings are effected to "activate" flow after labeling.

3. *Chemisorption or Chemical Adsorption*

This retention process involves strong bonds of the covalent type as chemisorption is an adsorption mechanism typical of electrolytes. The binding energy stands at 20 to 30 kcal/mol.

Chemisorption depends on ionic charge (as an adsorbent may possess a high affinity for cations and a very low, sometimes null, affinity for anions) as well as on ionic size.

The phenomenon of chemisorption is fully manifest in clay media. Clays consist of hydrated aluminosilicates that look like very fine granules made up of lamellae whose faces are negatively charged. The ionic charge of these lamellae facilitates chemisorption.

It is difficult to pinpoint the limit between the two types of adsorption — chemical and physical — as it depends on the kinetics of the reaction, the form of the isotherm, adsorption heat,⁵ etc.

In chemisorption, adsorption may be limited for electrostatic reasons. This effect, however, may be inhibited following the introduction of electrical charges. These charges may be supplied either by the tracer solvent or by the adsorbent medium, in which case an ion-exchange process occurs.

4. *Colloidal Precipitation*

Retention through colloidal precipitation occurs when the tracer appears in the form of a dispersed system. This is the case of dyes in general.

The stability of a colloidal solution, which depends on the equilibrium of coulomb and cohesive forces, may be easily broken through a mere change in pH value.

This phenomenon takes place especially in the presence of clay-humic compounds in the soil, most of which are to be found in a fine, colloidal state. The hygroscopic nature of these complexes favors the formation of gels through swelling.

To a large extent, the phenomenon of colloidal precipitation is responsible for substantial losses of fluorescent dye tracers in the case of labelings of karsts when the given waters contain colloids.

The retention of tracers (and of other categories besides dyes) is, in fact, a more intricate process.^{6,7} Besides their hygroscopic character, humic compounds have weakly acidic properties. Thus, they can adsorb large amounts of exchangeable cations, which boosts their exchange capacity. According to estimations,⁵ humic acids have a cationic exchange capacity of 3.00 to 4.00 meq/g.

5. *Ion Exchange*

It is a phenomenon of equilibrium between the ions already fixed on the natural ion exchanger and those of the tracer in the contact solution. Ion exchange is a process that contributes most substantially to retaining or delaying the tracer wave. Through ion exchange, tracers in the form of cations are preferentially retained. For this effect to produce a change disequilibrium must exist between the solid and liquid phases, and there must be a high specific surface for the solid phase. The exchange process is a highly rapid ionic reaction. It is characterized by the exchange capacity of the solid, the equilibrium constant, and the quantity exchanged.

Exchange processes take place preferentially at the contact between tracer solution and oxides (Si, Fe, and Al) zeolites, and clay minerals, with the latter holding the largest share. The cations of the tracer substance will be exchanged with the natural cations of the clay minerals in the composition of most terrains. Clay minerals have a large specific surface (hundreds of m²/g) which leads to a high surface energy. The intensity of the exchange depends on the proportion and type of clay mineral present in the terrain, and exchange properties are determined by the structure of the clay and the distribution of minerals in clay.

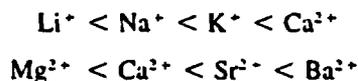
Clay minerals are made up of lamellar clays and fibrous clays, a structure which is responsible for the cationic exchange capacity in each case. For instance, the cationic exchange capacity of two-layer clays (kaolinite, halloysite) is 0.02 meq/g, that of the so-called expanding three-layer clays (smectites) is approximately 0.8 meq/g, and that of nonexpanding three-layer clays (illite) is 0.16 meq/g.

The group of zeolites contains a large number of hydrated aluminosilicates whose general formula is $\text{MeO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2 \cdot m\text{H}_2\text{O}$, where Me stands for one of the following metals: sodium, potassium, calcium, strontium, barium, or, less often, magnesium or manganese. Zeolites boast a crystal structure in the form of three-dimensional lattices with channels which may retain substantial amounts of water. Zeolites are usually found in hydrothermally modified magmatic rocks and in the depositions of thermal springs. They play an important role in retaining the artificial tracers employed in investigations of thermal waters.⁴

Although there are many media which have a rather low exchange capacity, to the extent that they are not saturated, they too will retain the tracers passing through them. The extent to which an ion displaces another ion depends on ionic charge and ionic radius. Thus, anions will be weakly retained in clays through ion exchange, while ions with small ionic radii (radius of the hydrated ion) will be more powerfully retained than the ions with large ionic radii.

The fact is noteworthy that the pH value of the medium in which the tracer travels plays an important role in ion exchange, as exchange capacity grows as pH value rises and concentrations decrease. When the concentration changes, the phenomenon becomes reversible. If the tracer solution is acidic, the H ion will be retained more than any other cation, and contrariwise, when a basic solution is used the tracer will be retained with predilection.

In the case of exchange of alkali metals ions on clays, the order of affinity growth is as follows:



When alkali cations are filtered on zeolites, exchange selectivity (from the liquid to the solid phase) is



As ion exchange is a process of equilibrium, in the case of utilization of radioactive tracers, retention may be lowered by adding inactive ionic material (carrier) which should be involved in exchange (e.g., NaI for Na^{131}I).

6. Chemical Reactions

Three types of reactions of the tracer solution may be distinguished⁵:

1. Reactions in the liquid phase
2. Reactions in the solid phase (the solute phase catalyzes the reaction)
3. Reactions with the solid phase (precipitation, solubilization, and changes in the solid structure)

Chemical reactions are generally influenced by the concentration of each chemical species and by temperature.

Concerning solubility of substances in the aqueous phase, it is noteworthy that a slight change in the medium may cause the precipitation of the tracer: contact with a precipitating liquid and an electrolyte, changes in pH value, etc.

Retention through chemical precipitation occurs also when a weakly soluble salt attains a concentration that is higher than its solubility. This type of retention, however, is less frequent as the ion concentrations of a tracer are generally weak.

Owing to certain chemical reactions, especially oxidation-reduction or complexing reactions, a chemical alteration of the tracer occurs. Most oxidation reactions are reactions of autooxidation in which the oxidizing agent is molecular oxygen.

Water (in particular surface waters and karstic waters with vadose flow) contains sufficient amounts of oxygen to set the oxidation process in motion. Afterwards, chain decomposition occurs which is virtually independent from the oxygen concentration.

Pollution of waters plays an essential role in the chemical decomposition of a tracer. Thus, tracers of slightly oxidized metals are enough to catalyze an oxidation-reduction reaction. Light, too, may activate the occurrence of such reactions.

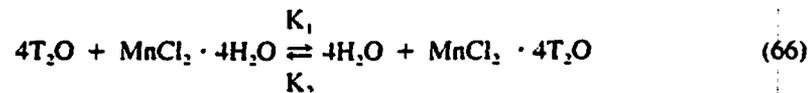
7. Isotope Exchange

This is a phenomenon which has special importance for the interpretation of assessments made with the help of environmental isotopes. Isotope exchange affects determinations with artificial tracers to a far smaller extent. In the case of radioactive isotopes used as tracers, they may change places with the same element in another compound in the investigated medium.

This effect is negligible in general (with the exception of elements with a low atomic number). Tritium features the most marked isotope effect as ${}^3\text{H}^1\text{H} = 3$. Thus, in the case of the evaporation of tritiated water, the vapor phase is poorer in tritium than the liquid phase: in this case, $\text{HTO}:\text{HOH} = 20:18$. The most sensible effect occurs in water electrolysis, and the enrichment method is used to produce heavy water or concentrate natural tritium.

As a matter of fact, tritium has been considered an ideal water tracer for a long time. Subsequently,¹⁰⁻¹³ it was noted that, though it is an intrinsic tracer, tritium is nonconservative in the case of determinations of water velocity in clay media. Surrounding the clay particles in aquifer layers is a layer of strongly attached water molecules which is not affected by pumping and is not involved in mass transit. An exchange which leads to tritium retention occurs between the hydrogen contained in these molecules and the tritium used as tracer. Subsequently, tritium is released and further participates in water transit, but the duration of tracer transit is longer than that of water transit.

This isotope exchange occurs when hydrates of the $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ type exist in the underground. The general exchange reaction is



where K_1 and K_2 are exchange constants.

For the respective phenomenon to be of significant importance for the experiment conducted a longer contact time is needed, which occurs in the case of low velocities, below 10^{-4} cm/sec. These velocities are frequent in clay media.

F. The Influence of the Chemical Nature of the Labeled Medium on Tracers

The interactions between the rocks in the underground and tracers are the latter's general reactions with the solid phase. Other chemical reactions between tracers and the elements of the solid phase are rare. An altogether different situation develops when a tracer comes into contact with the liquid phase. Whereas, naturally, waters can have a pH value, a temperature, and a salt content that are greatly varied, owing to pollution the chemical composition of water may modify to such an extent that phenomena occur conducive to