Water-Quality Principles
QW1022–TEL

Lesson 5, Part 1—Major Ions and Field-Measured Properties: Major Ions

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Major-Ion Evolution Sequence

As groundwater moves along its flow paths in the saturated zone, increases of total dissolved solids and most of the major ions normally occur. As would be expected from this generalization, it has been observed in groundwater investigations in many parts of the world that shallow groundwater in recharge areas is lower in dissolved solids than the water deeper in the same system and lower in dissolved solids than water in shallow zones in the discharge areas.

In a classic paper based on more than 10,000 chemical analyses of well samples from Australia, Chebotarev (1955) concluded that groundwater tends to evolve

chemically toward the composition of seawater. He observed that this evolution is normally accompanied by the following regional changes in dominant anion species:

Travel along flow path $\longrightarrow$

$$HCO_3^- \longrightarrow HCO_3^- + SO_4^{2-} \longrightarrow SO_4^{2-} + HCO_3^- \longrightarrow SO_4^{2-} + Cl^- \longrightarrow Cl^- + SO_4^{2-} \longrightarrow Cl^-$$

Increasing age $\longrightarrow$

These changes occur as the water moves from shallow zones of active flushing through intermediate zones into zones where the flow is very sluggish and the water is old. This sequence, like many others in the geological sciences, must be viewed in terms of the scale and geology of the specific setting, with allowances for interruption and incompletion. Schoeller (1959) refers to the sequence above as the Ignatovich and Souline Sequence, in recognition of the fact that two hydrogeologists in the Soviet Union developed similar generalizations independent of the contributions by Chebotarev.

For large sedimentary basins, the Chebotarev sequence can be described in terms of three main zones, which correlate in a general way with depth (Domenico, 1972):

1. *The upper zone*—characterized by active groundwater flushing through relatively well-leached rocks. Water in this zone has HCO_3^- as the dominant anion and is low in total dissolved solids.
2. *The intermediate zone*—with less active groundwater circulation and higher total dissolved solids. Sulfate is normally the dominant anion in this zone.
3. *The lower zone*—with very sluggish groundwater flow. Highly soluble minerals are commonly present in this zone because very little groundwater flushing has occurred. High Cl^- concentration and high total dissolved solids are characteristic of this zone.

These three zones cannot be correlated specifically with distance of travel or time, other than to say that travel distance and time tend to increase from the upper zone to the lower zone. In some sedimentary basins, groundwater in the upper zone may be years or tens of years old, whereas in other basins ages of hundreds or thousands of years are common. Saline, chloride-rich water in the lower zone is usually very old, but the actual ages may vary from thousands to millions of years.

From a geochemical viewpoint the anion-evolution sequence described above can be explained in terms of two main variables, mineral availability and mineral solubility. The HCO_3^- content in groundwater is normally derived from soil zone CO_2 and from dissolution of calcite and dolomite. The partial pressures of CO_2 generated in the soil zone and the solubility of calcite and dolomite are normally the limiting constraints on the level of total dissolved solids attained. Figure 3.7

indicates that at the CO_2 partial pressures typical of the soil zone (10^{-3}–10^{-1} bar), calcite and dolomite are only moderately soluble, with equilibrium HCO_3^- concentrations in the range 100–600 mg/ℓ. Since calcite or dolomite occur in significant amounts in nearly all sedimentary basins, and because these minerals dissolve rapidly when in contact with CO_2-charged groundwater, HCO_3^- is almost invariably the dominant anion in recharge areas.

Table 3.6 indicates that there are several soluble sedimentary minerals that release SO_4^{2-} or Cl^- upon dissolution. The most common of the sulfate-bearing minerals are gypsum, $CaSO_4 \cdot 2H_2O$, and anhydrite, $CaSO_4$. These minerals dissolve readily when in contact with water. The dissolution reaction for gypsum is

$$CaSO_4 \cdot 2H_2O \longrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O \tag{7.4}$$

Gypsum and anhydrite are considerably more soluble than calcite and dolomite but much less soluble than the chloride minerals such as halite (NaCl) and sylvite (KCl). If calcite (or dolomite) and gypsum dissolve in fresh water at 25°C, the water will become brackish, with total dissolved solids of about 2100 and 2400 mg/ℓ for a P_{CO_2} range of 10^{-3}–10^{-1} bar. The dominant anion will be SO_4^{2-}, so in effect we have moved into the SO_4^{2-}–HCO_3^- composition phase in the Chebotarev evolution sequence. If sufficient calcite and/or dolomite and gypsum are present to enable dissolution to proceed to equilibrium, the water will evolve quickly and directly to this phase and will not evolve beyond this phase unless it comes into contact with other soluble minerals or undergoes evaporation.

The reason that in most sedimentary terrain groundwater travels a considerable distance before SO_4^{2-} becomes a dominant anion is that gypsum or anhydrite are rarely present in more than trace amounts. In many shallow zones these minerals have never been present or have been previously removed by groundwater flushing. Therefore, although HCO_3^- and SO_4^{2-} stages can be described in terms of simple solubility constraints exerted by only two or three minerals, the process of evolution from stage to stage is controlled by the availability of these minerals along the groundwater flow paths. Given enough time, dissolution and groundwater flushing will eventually cause the readily soluble minerals such as calcite, dolomite, gypsum, and anhydrite to be completely removed from the active-flow zone in the groundwater system. Subsurface systems rarely advance to this stage, because of the rejuvenating effects of geologic processes such as continental uplift, sedimentation, and glaciation.

In deep groundwater flow systems in sedimentary basins and in some shallower systems, groundwater evolves past the stage where SO_4^{2-} is the dominant anion to a Cl^--rich brine. This occurs if the groundwater comes into contact with highly soluble chloride minerals such as halite or sylvite, which in deep sedimentary basins can occur as salt strata originally deposited during the evaporation of closed or restricted marine basins many millions of years ago. The solubilities of other chloride minerals of sedimentary origin are very high. In fact, as indicated in Table 3.6, these solubilities are orders of magnitude higher than the

solubilities of calcite, dolomite, gypsum, and anhydrite. Chloride minerals of sedimentary origin dissolve rapidly in water. The general occurrence of Cl^- as a dominant anion only in deep groundwater or groundwater that has moved long distances therefore can generally be accounted for by the paucity of these minerals along the flow paths. If groundwater that has not traveled far comes into contact with abundant amounts of halite, the water will evolve directly to the Cl^- phase, regardless of the other minerals present in the system. In strata of siltstone, shale, limestone, or dolomite, where Cl^- is present in minerals occurring in only trace amounts, the rate of Cl^- acquisition by the flowing groundwater is to a large extent controlled by the process of diffusion. Cl^- moves from the small pore spaces, dead-end pores, and, in the case of fractured strata, from the matrix of the porous media to the main pores or fractures in which the bulk flow of groundwater takes place. As indicated in Section 3.4, diffusion is an extremely slow process. This, and the occurrence of sulfate- and chloride-bearing minerals in limited amounts, can account for the observation that in many groundwater systems the chemical evolution of groundwater from the HCO_3^- to SO_4^{2-} and Cl^- stages proceeds very gradually rather than by distinct steps over short distances as would be expected on the basis of solubility considerations alone.

The anion evolution sequence and the tendency for total dissolved solids to increase along the paths of groundwater flow are generalizations that, when used in the context of more rigorous geochemical reasoning, can provide considerable information on the flow history of the water. At this point we wish to emphasize, however, that in some groundwater flow systems the water does not evolve past the HCO_3^- stage or past the SO_4^{2-} stage. It is not uncommon in some sedimentary regions for water to undergo reversals in the sequence of dominant anions. Most notable in this regard is the increase in HCO_3^- and decrease in SO_4^{2-} that can occur as a result of biochemical SO_4^{2-} reduction. These processes are described in Section 7.5.

Large variations in the major cations commonly occur in groundwater flow systems. Since cation exchange commonly causes alterations or reversals in the cation sequences, generalization of cation evolution sequences in the manner used by Chebotarev for anions would be of little use because there would be so many exceptions to the rule. For major cation and anion data to provide greatest insight into the nature of groundwater flow systems, interpretations must include consideration of specific hydrochemical processes that can account for the observed concentrations. Examples of this approach are included in Sections 7.3 through 7.5.

Electrochemical Evolution Sequence

Recognition of the anion evolution sequence as a characteristic feature of many groundwater systems resulted from the compilation and interpretation of chemical data from regional flow systems. It is a generalization initially founded on observation and later supported by geochemical theory. We will now look briefly at another evolution sequence, referred to as the electrochemical evolution

sequence. This sequence is founded on geochemical theory, but as yet has not been rigorously appraised on the basis of field measurements.

The electrochemical evolution sequence refers to the tendency for the redox potential of groundwater to decrease as the water moves along its flow paths. This tendency was first recognized by Germanov et al. (1958). As water from rain and snow enters the subsurface flow system, it initially has a high redox potential as a result of its exposure to atmospheric oxygen. The initial redox conditions reflect high concentrations of dissolved oxygen, with p*E* values close to 13, or, expressed as *Eh*, close to 750 mV at pH 7. In the organic-rich layers of the soil zone, the oxidation of organic matter commonly removes most of the dissolved oxygen. This process, represented by Eq. (7.3), causes the redox potential to decline. The question can be asked: How far does the redox potential decline as the water passes through the soil zone to the water table? It is reasonable to expect that the consumption of oxygen in the soil zone will vary depending on numerous factors, such as the soil structure, porosity and permeability, nature and depth distribution of organic matter, frequency of infiltration events, depth to water table, and temperature. Although dissolved oxygen is an important factor in the characterization of the hydrochemical nature of groundwater, very few studies of dissolved oxygen in groundwater have been reported in the literature. From the data that are available, however, the following generalizations can be drawn:

1. In recharge areas with sandy or gravelly soils, shallow groundwater commonly contains detectable dissolved oxygen (i.e., greater than about 0.1 mg/ℓ).
2. In recharge areas in silty or clayey soils, shallow groundwater commonly does not contain detectable dissolved oxygen.
3. In areas with little or no soil overlying permeable fractured rock, dissolved oxygen at detectable levels commonly persists far into the flow system. In some cases the entire flow system is oxygenated.

The common occurrence of appreciable dissolved oxygen in shallow groundwater in sandy deposits is probably a result of low contents of organic matter in the soil and rapid rates of infiltration through the soil.

Even after dissolved oxygen is consumed to levels below detection by normal means, the redox potential can still be very high, as indicated in Section 3.9. The consumption of free molecular oxygen by bacterially catalyzed reactions that oxidize organic matter may continue until dissolved O_2 levels are considerably below the normal limits of detection. Eventually the point is reached where the aerobic bacteria involved in these reactions can no longer thrive. In the aerobic zone there are other reactions, such as those represented in Table 3.10 for the oxidation of ferrous iron, ammonia, manganese, and sulfide, that consume oxygen. Even though these oxidation processes may consume only a small portion of the total oxygen relative to the oxidation by organic matter, they can have a major effect on the chemical evolution of the water.

We will now consider what may happen as water moves deeper into the groundwater flow system. Stumm and Morgan (1970) state that in closed aqueous systems containing organic material and the other nutrients necessary for growth of bacteria, the oxidation of organic matter accompanied by consumption of O_2 is followed by reduction of NO_3^-. Reduction of MnO_2, if present, should occur at about the same p*E* or *Eh* as NO_3^- reduction, followed by the reduction of the ferric iron minerals, such as the various compounds represented by $Fe(OH)_3$. When sufficiently negative redox levels have been reached, the reduction of SO_4^{2-} to H_2S and HS^- and the reduction of organic matter to the dissolved gaseous species CO_2 and CH_4 may occur almost simultaneously. This electrochemical sequence of reduction processes is summarized in Table 3.11, with the initial processes of oxygen consumption represented in Table 3.10. Stumm and Morgan present the electrochemical evolution sequence as a phenomenon based on thermodynamic theory. They indicate that this sequence is consistent with observations of the chemical nature of nutrient-enriched lakes and batch digestors in sewage treatment facilities. With the possible exception of MnO_2 and $Fe(OH)_3$ reduction, the reactions described in the electrochemical evolution sequence are biologically catalyzed. The sequence of redox reactions is paralleled by an ecological succession of microorganisms, with various bacterial species adapted to the different stages of the redox sequence.

From a hydrogeologic viewpoint, the important question is whether or not the electrochemical evolution sequence occurs in the groundwater environment and, if so, where and why? The sequence, or at least parts of the sequence, are known to occur in the groundwater zone. It is known, for example, that in many areas dissolved oxygen is absent from water that recharges the groundwater zone. This is indicated by the absence of detectable dissolved oxygen in shallow wells. Presumably, the oxygen has been consumed by the processes described above. In some groundwater systems, NO_3^- occurs at shallow depth and diminishes in concentration as the water moves deeper into the flow system. Edmunds (1973) and Gillham and Cherry (1978) attributed this type of NO_3^- trend to the process of denitrification, which requires denitrifying bacteria and a moderate redox potential. It is known that in some regions groundwater has a very low redox potential. This is indicated by low SO_4^{2-} concentrations and H_2S odor from the water, characteristics that are attributed to the process of sulfate reduction in the presence of sulfate-reducing bacteria. Methane (CH_4) is a common constituent of deep groundwater in sedimentary basins and is observed at many locations, even in shallow groundwater. Its origin is attributed to bacterial fermentation of organic matter within the groundwater system. It is known that in some groundwater flow systems, the redox potential measured by the platinum-electrode method decreases along the apparent paths of regional flow. To illustrate this type of trend, redox potential data from two regional flow systems are presented in Figure 7.2.

In the Chebotarev evolution sequence, the gradual changes in anion composition and total dissolved solids were attributed to two limiting factors: mineral availability and rate of molecular diffusion. In the electrochemical evolution

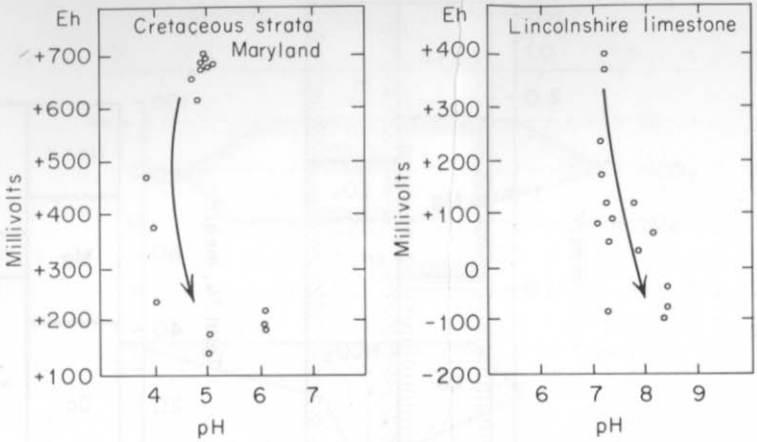

Figure 7.2 Trends in measured platinum-calomel electrode potential along regional flow paths in two aquifer systems. (a) Cretaceous strata, Maryland; (b) Lincolnshire limestone, Great Britain (adapted from R. E. Jackson, written communication, 1977, based on data from Back and Barnes, 1969, Edmunds, 1973).

sequence, other factors must control the amount and rate of decline of the redox potential along the flow paths. Because H_2S (or HS^-) and CH_4 are not present in significant amounts in many groundwater zones and because considerable SO_4^{2-} is present in these zones, it appears that it is common for groundwater not to evolve to conditions of low redox potential even during long periods of residence time. The redox reactions that would lead progressively to low redox potential probably do not proceed in many areas because of the inability of the necessary redox bacteria to thrive. The hostility of groundwater environments to bacteria is probably caused by the lack of some of the essential nutrients for bacterial growth. It may be that even in hydrogeologic regimes in which organic carbon is abundant, the carbon may not be in a form that can be utilized by the bacteria. As the emphasis in hydrochemical investigations is broadened to include organic and biochemical topics, a much greater understanding of the redox environment of subsurface systems will be developed.