

GROUND AND SOIL WATER CHARACTERISTICS

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Summary

Water bedded under the earth's surface in the crust is called ground water. Geological structures holding groundwater are located in different physico-chemical conditions—this determines the different aggregative states of water: liquid, solid, and gaseous.

Liquid water is located in the upper part of the earth's crust under relatively low temperature and pressure. Water deeper than 20-70 km is in gaseous state under high pressure. Water in the solid state is located in the zone of permafrost.

Liquid water in rocks is in different forms: in the crystal lattice of minerals, physically bound with rocks, and free. The maximum volume of physically bound water is found in clay—up to 40%.

Free water moves under gravity and possesses extraordinary ability to dissolve rock. All ground waters are solutions of different chemical composition—their characteristics depend in part on their location in the crust.

The chemical composition of soil and subsoil waters forms as a result of stage-by-stage transformation of the chemical composition of water that fell as precipitation. Other transformations are controlled by many factors: climate, relief, lithology, intensity of water exchange, the biological production of the landscape, and the geochemical situation. The complex combination of these factors creates the mixed character of soil and subsurface waters.

Chemical composition of artesian water is created under the influence of interactions between water and rocks. The scale of the interaction is determined by the duration of the contact between water and rocks as well as by the composition of the rocks. The duration depends on the intensity of water exchange in the hydrogeological structure.

In recent decades the increase in groundwater use and human economic activity has led to noticeable deterioration in groundwater quality. As it is extremely difficult to remove existing groundwater contamination, the best strategy is to eliminate sources of contamination.

1. Introduction

The extraordinary mobility, high chemical activity, diversity of forms, and ability to change phase determine the unique role of water in all geochemical processes in the atmosphere, hydrosphere and lithosphere. All natural waters are linked to each other. It does not matter in which state they are. Changes of state take place steadily. Transfer of chemical elements happens with the help of water. Groundwater plays a key role in this eternal movement of water and soluble substances, circulating in global and many other smaller cycles.

Groundwater is usually understood as water found in the crust, in different aggregative states—liquid, gaseous and solid. It lies in soil, in sedimentary beds and in cracks in massive-crystal rocks. The lower border of liquid water may be as much as 70 km beneath the surface. In other words the zone of water distribution includes virtually all the crust. The total volume of the Earth's groundwater is estimated to be 23.4 million km³, i.e. approximately 65% of all terrestrial water.

Soil and ground water are always aqueous solutions of various chemicals. The source of the water is precipitation. The chemical composition of soil and ground water is closely related to geographical conditions. A high flushing regime, low water mineralization and high sediment loads are associated with land with low annual temperature and rapid biomass accumulation. In arid zones the concentration of organic acids is very low, and water mineralization is high, as products of weathering and soil formation are not removed from the soil profile due to the low precipitation. The chemical composition of deep ground water is determined by the geological characteristics of the environment and is controlled by processes of interaction between water and rocks. All this gives rise to an extraordinary diversity of chemical composition in soil, subsurface and ground waters. In recent decades groundwater use has increased, as have changes in its physical and chemical characteristics, under the influence of anthropogenic activity. Anthropogenic pollution of ground water now occurs all over the world. The best strategy for maintaining good water quality is preventive measures, such as elimination of pollution sources.

2. Water structure and its physical characteristics.

Ground water in rocks is found in different states: water in the crystal lattice of minerals, water physically bound with rocks, free water, ice and vapor.

Water in the crystal lattice of minerals is chemically bound with its atoms and ions and may be removed from the lattice only by heating.

Physically bound water is located in rocks as a hydrated covering surrounding mineral particles and can be subdivided into hard-bound and low-bound. Hard-bound or hygroscopic water is found in clay material and is firmly held there by molecular and electric cohesion. It only moves when it goes into the gaseous state, and it can be removed by heating (up to 100 – 120 °C).

The maximum volume of hard-bound water in rocks is called maximum hygroscopic rock moisture capacity, and this does not exceed 1% for massive-crystal rocks, or 18-20% for clays. Plants cannot use this kind of water.

Low-bound or film water forms films on hard-bound water when the rock moisture exceeds rock hygroscopicity. The bond strength between rocks and this kind of water is significantly lower than the hygroscopic one. On the other hand, the power that keeps the water in rocks is 70 000 times greater than the power of gravitational acceleration, as water moves in rocks from a thicker to a thinner film. Maximum film water concentrations are: in clays – 25-40%, in loamy soils – 15-23%, in clay sands – 9-13%, in sands – up to 6%.

Physically bound water may be removed from rocks by heating (up to 110 °C). The characteristics of this kind of water differ strongly from those of free water. Its permittivity is significantly lower, and the freezing point is significantly lower than 0 °C, dropping to -100 °C when converting to hygroscopic water. The dissolving power of this water is also low. The maximum volume of physically bound water is called 'maximum molecular rock moisture capacity'.

Free water moves under gravity and is located in rock cracks and pores. It is formed in rocks when the humidity within the rock is higher than the maximum molecular rock moisture capacity.

Water in the solid state—ice crystals—is formed under temperatures below zero in the layer of winter freezing. In the zone of permafrost, ice consolidates separate rock particles.

Water in the gaseous state is located in pores free of liquid water. It moves from layers with higher pressure and temperature to layers with lower pressure and temperature.

The diversity of water forms and states creates various interactions of water with the lithosphere, atmosphere and biosphere. During the process of such interactions the physical and chemical characteristics of the water undergo changes.

As a result of the development of human activity, the characteristics of water consumers have changed over time, and these changes pose hazard to the populations of many countries, particularly those that suffer from deficit of suitable water. The study of soil and ground water chemical composition formation is therefore a priority line of investigation dedicated to medical, biological and environmental problems.

The unique structure of the water molecule, caused by the presence of the hydrogen bond, determines its anomalous physical and chemical characteristics. For instance, according to the calculations of D. Herd, the melting point of water, by analogy with the hydrides of other elements, should be minus 120 °C, and boiling point - minus 112 °C. Water melting is accompanied by compression, not expansion. The maximum density temperature is plus 4 °C. The specific heat of evaporation and surface tension are the highest among all other liquids. Most substances are perfectly soluble in water. This characteristic can be explained by the high permittivity of water that equals 80 at a temperature of 22 °C.

The key point about the hydrogen bond is that the hydrogen ion, having a small radius, is capable of electrostatically attracting other ions similar to electrons. In each water molecule four hydrogen bonds are formed: 2 at the expense of 2 hydrogen protons and 2 – 2 pairs of unshared electrons. Because of the presence of 2 plus and 2 minus poles, a water molecule is an electric dipole with dipole moment (1844 debye). Each water molecule is surrounded (as a tetrahedron) by 4 other molecules. Owing to the hydrogen bonds, these molecules have a high degree of orderliness. This fact gives the structure of water similarities to the structure of solid substances. However, the orderliness of a solid substances' molecules is the same throughout the solid, but it is only the orderliness of the closest atoms in water that is similar to that of solid substances. O.Ya. Samoylov considered the orderliness of water to be an ice-like frame that is slightly fuzzy because of thermal motion. The frame's cavities are filled with monomolecular water molecules. In ice, all water molecules are bound to each other but in water there are always some (10 to 50%, according to different publications) monomeric molecules.

When ice melts the water molecules change from being in a hexagonal arrangement to a closer tetrahedral modification, the volume of which is 20% less. Similarly expansion of the liquid state, as determined by the increase in thermal motion of water molecules, causes a 10% increase in volume. The overall result of contraction of water molecular volume at the moment of ice melting is 10%. Contraction of volume together with temperature increase prevails up to 4 °C. As a result of increase in thermal molecular motion, the number of monomeric molecules and the water volume are increasing. Complete destruction of hydrogen bonds and transfer of the molecules to a monomeric state occur at 250 to 370 °C, according to different sources.

The structure of physically bound water adsorbed onto the surface of rocks is close to the monomeric condition. There are no hydrogen bonds there. This leads to a change in permittivity value to 2.2, and, consequently, to acute decrease in the dissolving power of the water and lowering of the freezing point. This is why adsorbed and film water have few solutes as compared to other forms of water.

The structure of water changes under the process of dilution. If ion size exceeds the size of cavities in ice-like water frames it “tears” the hydrogen bonds. If the ion charge is not high, broken hydrogen bonds will not be effectively substituted by the interaction between the ion and water, and water molecules will have higher mobility than they have in pure water. The elements K, Rb, Cs, Br and I are among the ions that disorder the structure of water. The influence of ions on water structure is proportionally related to polarizing power; to put it more precisely its charge density equals the ratio of ion

charge to radius. The ions of K, Rb, Cs, Br and I have a high charge density. Ions with this characteristic strengthen the ice-like water structure and lower water mobility.

In order to go out of the nearest ion entourage, a water molecule has to go through a so-called potential barrier the value of which increases under the restorative influence of ions with high charge density. Conversely, the value of the potential barrier decreases under the destructive effect of ions with low charge density.

The value of the potential barrier E is for pure water and equals $E + \delta E$ in the case of ion presence, where δE is the value characterizing changes in potential barrier under the influence of ions.

If $\delta E > 0$, ions are effectively bound to the nearest solution molecules. This phenomenon is called positive ion hydration. If $\delta E < 0$, water molecules located near ions become more active than in pure water. This phenomenon is called negative ion hydration.

Ions with low charge density, i.e. with negative hydration, are not sufficiently protected by water molecules and are easily sorbed in natural conditions. The low potassium concentrations in natural waters—despite the abundance of this element in the lithosphere and the high water solubility of its compounds—exemplifies this phenomenon. Its low charge density and large radius lead to destruction of water structure and fast ion capture by natural sorbents.

Ions with positive hydration have the same influence on water structure as increased pressure. According to the Le Chatelier principle, increased pressure leads to the transition of ions with negative hydration to solution.

Thus, in near-surface conditions, carbonaceous and sulfate minerals are easily dissolved in water and at the same time ions with positive hydration go into solution (Ca^{2+} , Mg^{2+} , SO_4^{2-} , HCO_3^{2-}).

At a certain depth these minerals become solution-resistant, and new formations of tufa, anhydrite, etc. are usual there. Furthermore ions with negative hydration (Pb^{2+} , Rb^{2+}) migrate in waters of artesian basins and hardly migrate in subsurface water.

When ions with positive hydration prevail, water polarity and dissolving power are higher.

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Biographical Sketch

Andrey G. Kocharyan graduated from the Geological Faculty, Institute of Chemistry and Oil, Baku, in 1960. He received his Ph. D. in geochemical techniques of deposits' search in 1968 at Baku State University, Geological faculty. Since 1979 he has held a position of Head of the Laboratory of Water Quality, Institute of Water Problems, Russian Academy of Sciences, Moscow. Dr. Kocharyan is the author of more than 150 scientific publications. His research interests are in the fields of water quality and water resources protection. He is currently concerned with water quality formation in catchment areas.

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