CHEMISTRY AS A TOOL IN GROUNDWATER INVESTIGATIONS

by

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Abstract

This paper highlights the principles of using various important chemical parameters of water to determine the origin of groundwater, to understand the flow mechanism, the suitability of the water for various purposes and to determine the groundwater aquifer characteristics. This hydrochemical study gives many clues to solve mysterious and doubtful flow mechanisms and to understand the geological structures in the groundwater system with a very low cost compared to other processes such as drilling additional investigation holes. Finally a few case histories are shown to explain the valuable place of hydrochemistry in groundwater studies.

1.0 Introduction

Basically water is a chemical compound of Hydrogen and Oxygen having the molecular formula H₂O at least in the gaseous state. In case of liquid water and ice; the same formula is used but there is a noticeable difference in their chemical (atomic) structure. Existence of three isotopes of Hydrogen and three of Oxygen makes 18 varieties of water molecules possible. Water has unique physical and chemical properties because of its structure of H₂O molecule. The two bonds between the oxygen and the hydrogen form an angle of 105°. Therefore, both hydrogens are on the same side of the molecule and that side of the molecule has a net positive charge relative to the other side. When the molecules approach each other closely, a considerable degree of coherence is brought by the attraction forces between the positive and the negative sides of adjacent molecules. The presence of dissolved ions in water changes some of its physical properties notably its ability to conduct electricity.

The chemical composition of water is derived from many different sources of solutes including gases and aerosols from the atmosphere, weathering and erosion of rocks and soils, solution of precipitation reactions occurring below the land surface, and cultural effects resulting from activities of man. The chemical composition of the crustal rocks of the earth and composition of the ocean and the atmosphere are also significant in evaluating sources of solutes in natural fresh water. The rate of movement of water is rapid in rivers but much slower in groundwater or soil water environments. Even though the mineral composition of the solids in the groundwater system commonly is heterogenous, and poorly known, the activities of solute species can be determined completely and because of this slow movement of water, there is a considerable time span available for completion of slow reactions.

The application of Chemistry in groundwater studies can be grouped into:

(a) Major ions chemistry,
(b) Trace elements chemistry,
(c) Isotope chemistry,
(d) Detrital chemistry,
(e) Pollution chemistry.

Of the above, usually the first three fields provide so many valuable clues in understanding the flow mechanisms and properties of aquifer. The Detrital Chemistry enables one to determine the degree of possibility of natural detrital effects such as corrosion and incrustation, whereas Pollution chemistry would explain the methods of pollution and their impacts on the use of water. Generally, all the above informations throw light in finding out the suitability of groundwater for different purposes such as drinking, recreational, agricultural and industrial.

2.0 Major ions Chemistry

The important major ions considered are Ca²⁺, Mg²⁺, Na⁺, K⁺, Cl⁻, SO₄²⁻, CO₃⁻ and HCO₃⁻. Unless the water contains unusually higher concentrations of other ions such as NO₃⁻ (where there is organic pollution of water), there should be an ionic balance between these cations Ca²⁺, Mg²⁺, Na⁺, and K⁺ and the anions Cl⁻, SO₄²⁻, CO₃⁻ and HCO₃⁻ when these are expressed in milli equivalents per litre.

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When the precipitated rain reaches the surface of the earth, the water has very low concentrations of all the constituents except for Na+, Cl−, and possible SO₄²⁻, depending on the proximity to oceans and urbanised areas. This water passes through soil zone where CO₂ is generated by plant matter and reaches the groundwater table. The following processes are the more important of many processes which may occur underground. These processes may occur simultaneously.

**Process I: Solution Precipitation**

According to the law of mass action all minerals are soluble to a greater or lesser extent and solution will occur until saturation is reached and equilibrium is obtained. Equilibrium may take sometimes many thousands of years. For example the effective concentrations of Ca++, and SO₄²⁻ would obey the principle of:

\[ [\text{Ca}] [\text{SO}_4] = K \]

where K is the solubility product of Gypsum. This process results in a general increase in total Dissolved Solids (TDS) down the flow line.

**Process II: Reaction**

Chemical reactions occur due to the presence of CO₂ producing a weak acidic solution.

\[ \text{H}_2\text{O} + \text{CO}_2 + \text{CaCO}_3 \rightarrow \text{Ca}^{++} + 2\text{HCO}_3^- \]

or rock cement

This process results in an increase of Ca²⁺ and thus hardness down the flowline while the alkalinity also increases until all the CO₂ is used up.

**Process III: Cation Exchange**

A natural softening may occur whereby Ca²⁺ in the water exchanges with Na⁺ in the clay minerals.

\[ \text{Ca}^{++} \xrightarrow{} \text{Na}^+ \]

This process results in a decrease in hardness and an increase in Na⁺. But when saline water comes into contact with a Ca++ rich rock, reverse ion exchange may also occur.

**Process IV: Sulphate Reduction**

Under anaerobic conditions, sulphate reducing bacteria reduces the sulphate ion producing H₂S.

\[ \text{SO}_4^{2-} + 2\text{CH}_3\text{O} \rightarrow \text{H}_2\text{S} + \text{H}_2\text{O} + \text{CO}_2 \]

This process results in a reduction in SO₄²⁻. The increase in CO₂ allows further reaction mentioned in process (2) whereby the alkalinity increases.

**Process V: Mixing**

Mixing can occur with either saline water at depth or water from an adjacent aquifer.

Type A + Type B = Type AB

This results in a sharp change of chemistry of the water and in particular the T.D.S. (Total Dissolved Solids) Value.

Generally in an isotropic aquifer the flow lines can be drawn across the lines of equal concentrations of each of the major ions, hardness and T.D.S. Value, unless any changes occur as a result of any of the above processes.

### 2.1 Presentation of Data

When the major ion chemistry as studied, it is convenient to present the data in form of graphical representation. Out of the available methods, the more popular ones are Schoeller Diagram, Trilinear Diagram (Piper 1953) and Durov Diagram, each method having its own merit in comparing the waters. In the Schoeller Diagram, the concentrations are plotted with values expressed in milligram per litre and the relative milliequivalents per litre can be directly observed on the diagram itself. Waters of similar composition plot as near parallel lines. This diagram however has the disadvantage that the use of logarithmic scales might complicate the interpretation for waters that differ greatly in concentrations and that plotting more than a limited number in a diagram complicates to visualise the representation of each water separately.

In the trilinear diagram (Piper 1954) the ion concentration are plotted with values expressed as percentage of total milliequivalents per litre all the ions. Plots of waters of some group concentrate at the same relative position in the diagram and the circles plotted in the central field have areas proportional to the total dissolved solids. Also this would indicate the different types of water and the resulting types when they mix in different proportions under different environments.

Durov diagram is an improved version of the piper's trilinear diagram. The grouping can be more easily identified and the chemical change in the groundwater during its movement through an aquifer can also be studied easily. The only drawback in adopting this diagram is that the waters of various TDS values would fall into one group if they have the constituents in the same proportion. However, this could be avoided by studying the waters with the same order of TDS values.
2.2 Suitability of Groundwater

Using the results of the chemical analysis the suitability of groundwater for the purpose of drinking can be determined by referring to the suitable drinking water standards such as those published by U.S. Public Health Service and by W.H.O. Moreover, the bacterial quality of the water for drinking purpose has to be also checked. Similarly there are standard limits available for various industrial purposes to find out the suitability of any water for using in each industry. Standard limits on the chemical constituents for different crops under different soil conditions are available to check the suitability of any water for agricultural purposes. Furthermore, for studying the suitability of groundwaters for irrigation purposes the term "Sodium Absorption Ratio" (SAR) is recommended by the U.S. Salinity Laboratory Staff. This is defined by:

\[
\text{SAR} = \frac{\text{Na}^+}{\sqrt{\text{Ca}^{2+} + \text{Mg}^{2+}}}/2
\]

where all the concentrations are expressed in milli-equivalents per litre. A soil high in exchangeable sodium is very undesirable for agriculture because it can become deflocculated and tends to have a relatively impermeable crust. This condition is promoted by waters high in SAR and is reversed by waters containing a high proportion of Ca\(^{2+}\) and Mg\(^{2+}\), mainly the sodium hazard and the salinity hazard have to be considered in determining the suitability of any water for irrigation purposes.

3.0 Trace Element Chemistry

Over the past century, an extensive body of theory regarding the behaviour of dilute solution have been developed and methods of evaluating aqueous solution chemistry have attained a high degree of precision. As a result of studies made to understand the reaction between water and rock minerals, theoretical evaluations of the behaviour of some elements now are available which are in reasonable agreement with conditions observed in the field.

The Redox potential (Eh) which gives the relative intensity of oxidizing or reducing conditions in solutions is a very useful parameter in determining the various ionic species of a particular element in solutions containing oxidized and reduced ionic species at equilibrium. The stabilization of Eh brought about by equilibrium of large activities or reserves of participating species in parallel to the buffering effect observed in measuring pH value.

Even though there are some practical difficulties observed in measuring the "Eh" value in the field, the Eh-pH diagrams in studies of various species of some elements in groundwater throw light in understanding the system. This diagram is an indication of limiting conditions of and is a measure of evaluating the chemical behaviour of multivalent elements that is clear, simple and convenient (see Fig. 1). The trace elements that are generally measured to study the groundwater systems are Pb, Hg, Zn, Cu, Cr, Fe, CO, N, Y, La, Al, Sn, Ti, Sb. As they exist in very small quantities, enough care should be taken in measuring their concentrations avoiding the effects of precipitation, absorption and contamination. Usually, co-precipitation methods using organic reagents in the field and determining the concentrations using atomic absorption technique would ensure the accuracy of measurements.

4.0 Isotope Chemistry

Isotope application to groundwater study can be grouped into two types. First method is to study the groundwater flow, by artificially adding a harmless easily detectable radioactive substance to the groundwater at one point and detecting at various other points. The second method is to measure the quantity of environmental radioactive isotopes naturally present in groundwater and to gather information such as age, origin, direction of flows, mixing mechanisms and recharging areas. Furthermore, radioactive X-ray and neutron sources are used mainly for determining the density, water content and porosity of the soil.

4.1 Artificial Isotopes

Generally, in the single well method, the decrease in concentration of a radioactive trace solution added carefully into the water is measured. The infiltration velocity in an aquifer can be determined. The x-measure permeability value of the aquifer can be found if the hydraulic gradient is known. In practice Br\(^{89}\) and \(^\text{Hg}\) have been proved suitable for this purpose with their harmless properties, high sensitivity and accuracy of measurements. In fact, to find the direction of flow of
the groundwater from a well, the water column in the well is labelled with a radioactive tracer solution and allowed to flow away into the aquifer. The distribution of tracer in the ground is then measured with reference to filter tube of the well by means of a direction-sensitive detector, usually a collimated scintillation counter. For this method the recommended tracers are U-238, Cr-51 and I-131 in solution form.

In a multiple well technique, the radioactive tracer is injected in one well and the detection is carried out in the other well in the direction of the flow. From the time taken for the travel, the velocity of the flow can be computed. This is also further modified that by measuring the time taken for the tracer to reach a pumped well for the injection point, the porosity and transmissivity of an aquifer can be determined. Successfully used radioactive tracers for this purpose are Tritium, Br-82, Cr-51, I-131, and CO-58.

4.2 Environmental Isotopes

Principal environmental isotopes namely Deuterium (H-2 or D) Oxygen -18 (-18), Tritium, (H-3) and radio carbon (C-14) provide an overall labelling of the water throughout its hydrologic cycle. Carbon 14 and Tritium occur predominantly in the upper atmosphere through the action on nitrogen atoms of neutrons generated by cosmic rays. The interplay of continuous production and decay gives rise to an equilibrium. Tritium is oxidized to water in atmosphere and reaches the earth and hence the groundwater in precipitation and in the form of water vapour. After penetrating into the soil the Tritium concentration decreased in accordance with the law of radioactive decay only. Hence it is possible to determine the age of groundwater from its Tritium content. However, after 1952, when artificially produced Tritium from nuclear weapon explosions reached the earth, the natural Tritium budget was seriously disturbed. Hence, calculated ages prior to 1952 has a meaningful value.

All living organisms on earth have been labelled in the same way with Carbon 14 which originated in the atmosphere and is subsequently converted into CO-2 through food intake and a simulation. After the death of the organism their Carbon 14 content decreases owing to the radioactive decay. While passing through the soil the groundwater receives the CO-2 of the C-14 content. Hence, it is possible to find the age of the groundwater by measuring the activity of its C-14 content. During the course of analysis it is essential to measure the C-14 content also, to correct for the exchange with biogenic CO-2. The age upto 50,000 years can be measured using C-14 dating.

It was found that isotopic ratio of water molecules such as H-2O and HD-18O is not constant but due to the reorganisation during every phase transformation e.g., condensation and evaporation, the ratio of H-2O and HD-18O fluctuates. In precipitation, the heavy isotope content decreases with increasing distance from the coast (continental effect) moreover with increasing quantities of rain there is increasing heavy isotope depletion (amount effect). Finally the heavy isotope content in pre precipitation also decreased where a moist air mass rises because of orographic elevations (altitude effect). The temperature effect in isotopic fractionation has the further consequence of seasonal changes in the isotopic content, as well as heavy isotope depletion with increasing geographical latitude (latitude effect). Hence, by measuring the deviation of Deuterium (D) and O-18 content by means of a mass spectrometer it is possible to determine the origin (time and place of precipitation) of groundwater using the magnitudes of continental effect, amount effect, latitude effect and altitude effect in controlling the above concentration of these radionuclides.

4.3 Application in Well Logging

Methods of obtaining information on the geologic formations and the water content in the formations using sealed radiation sources based on the interaction between 8-rays and neutrons and the aquifer, are popular these days. Measurement of natural 8-rays radiation down the hole gives the locations of the clay or other formations. The attenuation effect on artificially produced 8-rays depends on the thickness and the density of the layer through which the radiation is passed. Based on this principle, by measuring the 8-radiation from a radioactive source artificially introduced with the sub-soil (8-8 logging) it is possible to study the density variation down the depth. The cross sections for neutrons scattering and capture are considerably greater in the case of hydrogen than in that of most of the other elements in the subsoil. Within the aquifer, the hydrogen is in the groundwater. Measurement of the neutron flow from a neutron source artificially introduced into the sub-soil (neutron-neutron logging) would indicate the high ground water zones down the depth. Hence, combining all these three methods, it is possible to obtain the parameters such as porosity, permeability, mass density of the formations. This method has an advantage over the other well logging methods in that even in a cased well these readings can be taken.

Another recent application of isotope techniques is to measure the rate of movement of the percolating rain water into the ground (recharge) by adopting the principle that Tritium follows the movement of the water moisture. Usually, the little amount of Tritiated water is injected into the ground and its downwards movement would be periodically observed. This would enable the scientists to determine the rate and the amount of recharge.

5.0 Detrital Chemistry

The natural phenomena, harmful to the users of groundwater are the corrosion and incrustation of substances (especially with casings or screens) which are kept below the water table for a long time. It is wise to know the available corroding or incrusting elements in the groundwater and the chemistry in-
The waste disposal practices can be incineration, composting and tipping. Even though incineration is the best method, it is expensive. Similarly, composting leads to disposal of the waste in agricultural lands as fertilizer. The drainage from these agricultural lands would pollute the surface and groundwaters. Tipping the wastes in unsuitable locations and without any control cause the leachate entering the groundwater system and polluting the same. Scientists have studied the physical, chemical and biological processes that take place in forming the leachages during its travel down to the groundwater. The pollution can be minimised by adopting a compacted and controlled dry tip system and avoiding tipping in fissured geological formations such as limestones. The longer the path the leachate takes before reaching the groundwater table, the natural attenuation becomes more and thus the degree of pollution becomes low. Drainage facilities should be provided to right round the tip to prevent accumulation of water and moisture inside.

The industrial effluents should be treated to bring down the chemical and biological composition to a minimum level before entering the groundwater system. Regular monitoring of the quality of drinking water is very essential in industrial areas.

Because the major component of the artificial fertilizers which are popularly applied by the farmers is the nitrate, a remarkable extent of pollution due to excessive nitrate in the groundwater has been observed in many agricultural lands in the world. Nitrate when it is above 50 mg/litre in groundwater the bottle-fed babies suffer from the disease "METHAMOglobinaemia" causing the reduction of oxygen flow and leads to death. High nitrates are found in recharge areas and not discharge areas. The sources of nitrate are fertilizer, animal feedlots and sewage. It was observed that in Winchester, U.K. the movement profile of Tritium coincided with that of Nitrate down through the unsaturated zones of the chalk formation.

Care should be taken to ensure that the groundwater supply is located at a minimum distance from the source of pollution, considering the geology of the formation, soil characteristics, the extent of catchment area and the details of well construction.

7.0 Case Histories

Attempts are made here to cite a few case histories to illustrate the use of chemistry in groundwater studies.

(a) In North-Eastern Jordan where the geological formations were chalks, limestones, sandstones with marl bands creating distinct aquifer systems, Dr. Lloyd was able to show that the groundwaters from each geological formation had fallen into one group and its changes along the
The sandstone waters (Fig. 3) had an average TDS of 1050 ppm but the values increased in the direction of flow. Also it could be observed that there was a relationship between the altitude and the position in the metasomatic order.
Maps showing the distribution of total hardness, TDS and salinity (chloride) were prepared. The first two maps indicated a general groundwater flow to the South. Salinity contours implied the existence of two faults. (See Fig. 6).

High values of Tritium (100 T.U.) were determined from groundwater and samples around the Warwick area (recharge area) indicating modern water. Water samples from wells outside this area had a low Tritium content of 0-0.5 T.U. indicating no modern recharge had occurred. Using Carbon 14 isotope method the ages of waters were obtained (see fig. 7). The saline water IV was observed to be the oldest water, whereas Group II waters were of modern age.

In this case the chemistry had given clues to understand the groundwater system whereas the actual drilling would have taken a longer time and cost a substantial amount.

(c) Fig. 9 illustrates an investigation carried out near Antalya, Turkey the aim of which was to ascertain the catchment area (source) of several springs. (Payne 1967). The deviations of Deuterium and O18 content from that of the standard were observed for the spring water, the precipitation and few nearby lakes. When these were plotted, it was established unequivocally that the springs are not fed by submarine discharges from the lakes.
(d) In the chalk aquifer in Winchester area in U.K., high concentrations of Nitrate in the interstitial water from the unsaturated zones have been observed during 1970-1972. A quantity of Nitrate equivalent up to 50% of the total fertilizer application over the last three decades has been recorded in the unsaturated zones. A qualitative relationship between higher levels of Nitrate leaching from arable soils and low levels from pastures and leys have been postulated. (Young 1976). The hypothesis has been extended to the correlation of peak concentrations in the unsaturated zone with episodes of ploughing the leys. Two possible mechanisms of solute movement through the chalk have been considered. Available evidence suggested that recharge takes place through the fissures rather than through the chalk matrix. But the issue is under research programme. Also denitrification was found to occur within the unsaturated zone due to biological activity which appeared to vary with depth. Computer models are purchased to study this Nitrate pollution in order to predict the future dangers of this pollution.

8.0 Conclusion

From the facts and evidences given above, it can be seen that chemistry can be used as a powerful tool in groundwater investigation works especially in understanding the flow mechanism, the recharging source, the existence of geological features in the aquifer, the evaluation of aquifer characteristics, the quality of groundwater and the pollution of groundwater.

9.0 References


