CHAPTER 6

GEOCHEMICAL MODELLING AND IDENTIFICATION OF HYDROGEOCHEMICAL PROCESSES

6.1 INTRODUCTION

In order to understand the hydrogeochemistry of this area, it is essential to determine the ionic strength, activity of species, dissolved carbon-di-oxide, mineral saturation, ion complexes and degree of saturation of groundwater with respect to minerals. The entire hydrochemical data were processed by using PHREEQC (Parkhurst and Appelo 1999) for this purpose. PHREEQC is an equilibrium chemical speciation model and it is used to carry out geochemical speciation calculations which in turn helped to evaluate the geochemical processes. Groundwater chemistry of a region is generally not homogeneous and it is controlled by geochemical processes, flow and recharge processes, evaporation, evapotranspiration and possible presence of contamination sources. Identification of various geochemical processes will help to understand the causes for changes in water quality due to the interaction with aquifer material, especially in weathered rock formations. Hydrogeochemical studies assist in planning and remedial measures to protect aquifers that are contaminated by natural and anthropogenic activities. Thus, detailed knowledge on geochemical process that control groundwater chemistry is very essential to understand and deal with the groundwater related issues. The cause for the changes in groundwater quality by
anthropogenic activity like agriculture is also an important issue in arid and semiarid region. The geochemical properties of groundwater depend on the chemistry of water in the recharge area as well as on the different geological processes that take place in the subsurface. In the present study, detailed investigation of hydrogeochemical processes that are responsible for variations in groundwater chemistry was assessed.

6.2 IONIC STRENGTH

The effective concentration of a major ion in groundwater depends on the ionic strength of the water. So the ionic strength of water samples was determined before going in for equilibrium calculations. The ionic strength (I) is defined by the relation

\[ I = \frac{1}{2} \sum m_i z_{i}^2 \]  

(6.1)

where,

\[ m_i = \text{molality of species } i \]

\[ z_{i} = \text{valance or charge of the ion} \]

As only seven ionic constituents are major ions in the groundwater of this area, the equation (6.1) can be written as,

\[ I = \frac{1}{2} \left[ I\left(\text{Na}^+\right)+I\left(\text{K}^+\right)+4I\left(\text{Mg}^{2+}\right)+I\left(\text{Ca}^{2+}\right)+ \right] \]

(6.2)

\[ \left(\text{HCO}_3^-\right)+I\left(\text{Cl}^-\right)+4I\left(\text{SO}_4^{2-}\right) \]
Using this relation the ionic strength of the groundwater samples collected were determined. The ionic strength of the groundwater of this area ranges from 0.005 to 0.09 mmol/l with an average of 0.014 mmol/l.

6.3 ACTIVITY OF SPECIES

The activities of ions are important to perform the equilibrium geochemical calculations. In general there will be electrostatic attraction between cations and anions in the groundwater because of their opposite charges, and therefore the anion concentration is locally increased around each cation and vice versa (Lloyd and Heathcote 1985). Because each ion is bounded by an atmosphere of oppositely charged ions the thermodynamically effective concentration of the species is reduced. This amount of species concentration only participates in the geochemical reactions occurring in the aquifer. Therefore measured concentration of ions is to be multiplied by a factor, which is denoted as activity coefficient. Thus the reaction between the activity and molality is given by

\[ a_i = m_i \gamma_i \] (6.3)

where

\[ a_i \] - activity of solute species

\[ m_i \] – molality of solute species

\[ \gamma_i \] - activity coefficient

The activity of a solute is the same for all waters of same ionic strength. The activity coefficient (\( \gamma \)) of all the species of the groundwater
chemical data was calculated using the Debye-Huckel equation (Freeze and cherry 1979).

\[
\log \gamma = \frac{-Az^2\sqrt{I}}{1+ab\sqrt{I}}
\]  

(6.4)

where,

- \text{I} - ionic strength
- A & B - temperature dependent parameters involving universal Constants and physical properties of water (at 45° C, A= 0.5221 and B = 0.3305)
- a - ion size parameter given in Freeze and cherry (1979)
- z - Charge of the ion

The activity coefficient of seven major species in the groundwater samples of this area was calculated to convert the measured concentration to effective concentration for use in thermodynamically based equations. The calculated activity coefficients of all the species will be less than 1. The ranges of the measured concentration and the converted effective concentration by activity coefficients in a few well 1 and 4 are given in Figure 6.1. This indicates the slight variation between the actual and effective concentration of species. The effective concentration was used in the equilibrium calculations.
Figure 6.1 Variation between measured concentration and effective concentration in two groundwater samples
6.4 DISSOLVED GASES

In nature the water is exposed to gas phase, so equilibrium is established between gas and the liquid over interchange of molecules through the liquid gas interface. However, the gaseous phase is a mixture of more than one gas; equilibrium will be established for each gas. The pressure that each gas in a mixture exerts is its partial pressure. The major dissolved gases in groundwater are dissolve oxygen and carbon-di-oxide. The dissolved oxygen was not measured in this area; however dissolved carbon-di-oxide was determined by geochemical calculations. The reactions which describe the interaction between the gaseous CO$_2$ and its dissolved species in groundwater are

\[
\text{CO}_2 \text{(gas)} + \text{H}_2\text{O} \rightarrow \text{CO}_2 \text{(aqueous)} + \text{H}_2\text{O} \quad (6.5)
\]

(Freeze and cherry 1979)

\[
\text{CO}_2 \text{(gas)} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \text{(aqueous)} \quad (6.6)
\]

(Plummer and Busenberg 1982)

The recharging of water infiltrates into the partially saturated soil and it is altered chemically before it reaches the water table due to the above described reactions. Thus the CO$_2$ is an important buffering agent in the water that can contribute to both alkalinity and acidity. The carbon dioxide partial pressure (pCO$_2$) in groundwater of this area which control the and saturation index of carbonate minerals was calculated for all the samples using the following equation (Plummer and Busenberg 1982),
\[
pCO_2 = \frac{\alpha H^+ \times \alpha HCO_3^-}{KCO_2 \times K_1}
\] (6.7)

where.

\( pCO_2 \) - partial pressure of carbon dioxide

\( \alpha \) - is thermodynamic activity

\( KCO_2 \) and \( K_1 \) - Equilibrium constant

The calculated values of carbon dioxide partial pressure range from \( 10^{-1.28} \) to \( 10^{-2.24} \) with an average of \( 10^{-1.6} \); whereas atmospheric partial pressure is \( 10^{3.5} \). Thus the \( pCO_2 \) in groundwater is generally greater than the atmospheric \( pCO_2 \).

The infiltrated water in the soil is altered chemically and the major reason of alteration is the uptake of soil zone \( CO_2 \) by the water to form \( H_2CO_3, \ H_2CO_3^- \) and \( CO_3^{2-} \) by the following reactions (Plummer and Busenberg 1982).

\[
\begin{align*}
CO_2 \text{ (gas)} + H_2O & \rightarrow H_2CO_3 \text{ (aqueous)} \quad (6.8) \\
H_2CO_3 & \rightarrow H^+ + HCO_3^- \quad (6.9) \\
HCO_3^- & \rightarrow H^+ + CO_3^{2-} \quad (6.10)
\end{align*}
\]

The \( CO_2 \) is brought into solution because the \( pCO_2 \) in the partially saturated soil is generally greater than atmospheric \( pCO_2 \) as observed in this area. The higher \( pCO_2 \) pressure in the soil is caused by root and microbial respiration (Palmer and Cherry 1984) so it is the major source of carbon dioxide during recharge. Thus the carbonic acid \( H_2CO_3 \) will be formed according to the above reactions and it dissociates into \( HCO_3^- \) and \( CO_3^{2-} \). This dissociation reaction results in the increase of hydrogen ion and the pH of the
solution becomes slightly acidic so this water comes in contact with soil zone and dissolves it. These calculations were carried out before the determination of mineral saturation indexes.

6.5 MINERAL SATURATION INDICES

In this study of geochemistry of groundwater it is necessary to represent the extent to which the water has reached chemical equilibrium with the minerals of the aquifer system. If the groundwater is saturated with respect to a mineral, that mineral will tend to precipitate, whereas if the groundwater is under saturated with respect to a mineral, then that mineral will be dissolved if it is present in the aquifer system. The saturation index (SI) of mineral was calculated using

\[ SI = \frac{\text{IAP}}{K_s} \] (Appelo and Postma, 1996)

Where IAP is the ion activity product and Ks is the solubility product of the mineral.

SI of minerals is very helpful for evaluating the groundwater chemistry and to see if it is controlled by equilibrium with solid phases (Appelo and Postma, 1996). If SI < 0, the water is under saturated, if SI = 0, the water is in equilibrium with the mineral and if SI > 0, the water is over saturated. The saturation hydrochemical data were calculated by using PHREEQC. Results of these calculations show that the groundwater chemistry of this region mainly influenced by evaporation, dissolution and precipitation. These are explained detail in later sections. The saturation index of calcite ranges from -1.05 to 1.97 with an average of 0.40 and the dolomite ranges from -1.96 to 4.15 with an average of 0.93 (Table 6.1).
Table 6.1 Summary of calculated saturation indices

<table>
<thead>
<tr>
<th>Phase</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>-1.05</td>
<td>1.96</td>
<td>1.28</td>
</tr>
<tr>
<td>Dolomite</td>
<td>1.97</td>
<td>4.15</td>
<td>2.24</td>
</tr>
<tr>
<td>Aragonite</td>
<td>-0.62</td>
<td>-0.18</td>
<td>-0.40</td>
</tr>
<tr>
<td>Gypsum</td>
<td>-0.19</td>
<td>-2.82</td>
<td>-1.5</td>
</tr>
<tr>
<td>Halite</td>
<td>-1.65</td>
<td>-3.45</td>
<td>-2.25</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>-1.73</td>
<td>-6.25</td>
<td>-3.39</td>
</tr>
</tbody>
</table>

PHREEQC was used to calculate the chemical composition of the water, when the groundwater sample of the study area with the lowest major ion concentration is evaporated Appendix I. Similarly the model was also used to determine the composition by assuming that the groundwater with highest ionic concentration is evaporated Appendix II.

6.6 EVAPORATION PROCESSES

Evaporation process would cause an increase in concentration of all mineral species in water. When evaporation takes place, the water enriches its concentration and salinity in the soil zone. During subsequent decrease in groundwater level, this enriched saline water percolates into the groundwater may be dissolved by rainfall, which increases in salinity as discussed in section 5.3. The plot of Na versus Cl (Figure 6.2) and Ca versus HCO$_3$ (Figure 6.3) of groundwater collected from the study area was compared with the evaporation line of groundwater of lowest ionic concentration (well no. 3 in November 2008), the water samples would have HCO$_3^-$ as the most abundant anion (Rogers 1989). This is because of the reaction of the feldspar minerals with the carbonic acid in the presence of water, which releases HCO$_3^-$ (Elango and others 2003). HCO$_3^-$ is the dominant anion in
groundwater of this area. A plot of Na+K/Na+K+Ca versus TDS (Fig. 6.4) also indicates the importance of rock water interaction and evaporation in this area (Gibbs 1970). These plots indicate that groundwater chemistry of this area is controlled by evaporation process. Direct evaporation of groundwater is possible as the region has many number of large diameter open wells where groundwater table occur at shallow depths.

**Figure 6.2** Na Vs Cl along with evaporation line of groundwater with lowest ionic concentration

**Figure 6.3** Ca Vs HCO₃ along with evaporation line of groundwater with lowest ionic concentration
6.7 ION EXCHANGE

In order to evaluate the ion exchange process in this region, a plot of Na–Cl versus Ca + Mg –HCO₃ – SO₄ was prepared (Figure 6.5). If ion exchange is the dominant process in the system which can be explained by the following reaction (6.11) (Rajmohan and Elango, 2004), the points should form a line with a slope of -1.

\[
\text{Ca}^{2+} (\text{Mg}^{2+}) + \text{Na}^+ \text{Clay} \rightleftharpoons 2 \text{Na}^+ + \text{Ca} (\text{Mg}) \text{Clay}
\]  

(6.11)

Similar results were observed for the groundwater of this area. The plot shows that the points give a line with a slope of -0.8794. This confirms that Ca²⁺, Mg²⁺ and Na⁺ concentrations are interrelated through ion exchange (Rajmohan and Elango, 2004, Elango et al., 2003 and Fisher and Mullican, 1997). In addition to ion exchange processes occurring in this region also
confirmed by the two indices of Base Exchange (IBE), also known as chloro alkaline indices (CAI 1 and CAI 2); it explains detail in following reactions

$$\text{CAI 1} = \text{Cl} - \frac{(\text{Na}+\text{K})}{\text{Cl}}$$

$$\text{CAI 2} = \text{Cl} - \frac{(\text{Na}+\text{K})}{\text{SO}_4^2+\text{HCO}_3^-+\text{CO}_3^-+\text{NO}_3^-} \text{ (Scholler 1965)}$$

When there is an ion exchange between Na, Ca and Mg in the aquifer system. In this area CAI values of groundwater vary with respect to time and groundwater level fluctuation (Figure 6.6). Usually they are positive when the groundwater level is high and become negative with its lowering of water level. Thus water level is high, reverse ion exchange is dominant and the water level is low ion exchange is dominant (Rajmohan and Elango 2004). In our study area the CAI values is high when water level is low, simultaneously water level is high the CAI values are low, Hence it shows that the ion exchange is dominant.

Figure 6.5 Relationship between Na–Cl and Ca+Mg–HCO$_3$–SO$_4$
Figure 6.6 Relation between groundwater fluctuation and chloroalkaline indices (CIA) values
6.8 SILICATE WEATHERING

Silicate weathering is one of the major processes that release Na and K in groundwater in aquifers of plutonic rocks. This process is likely to be the major processes that contribute Na and K to the groundwater. Na vs Cl scatter diagram (Figure 6.7) shows that most of the sample points below 1:1 line indicating that they are derived by silicate weathering (Stallard and Edmond 1983). Similarly Ca + Mg Vs Total cations (TC) scatter diagram (Figure 6.8) indicate that most of the samples lie below the 1:1 line. This also indicates that the contribution of Na and K to groundwater by silicate weathering may be explained by the following weathering reaction (2) though the silicate weathering is found to be the major causes for alkalies in the aquifer of this type the results obtained also support this process. Similar processes of weathering of pyroxene, amphibole and calcic feldspar minerals, which are common in basic rocks and easily weatherable, controlled the concentration of these ions in groundwater in certain other parts of southern India and in Himalayan river basin (Jacks, 1973; Bartarya, 1993).

\[
2\text{NaAlSi}_3\text{O}_8 + 2\text{H}_2\text{CO}_3 + 9\text{H}_2\text{O} \Rightarrow \text{Al}_2\text{Si}_2\text{O}_5 (\text{OH})_4 + 2\text{Na}^+ + 4\text{H}_4\text{SiO}_4 + 2\text{HCO}_3^- \quad (6.12)
\]

(Albite) (Silicate weathering) (Kaolinite)

Figure 6.7 Relationship between Na and Cl with 1:1 line
6.9 DISSOLUTION OF MINERALS

Mineral equilibrium calculations for groundwater are useful in predicting the presence of reactive minerals in the groundwater system and estimating mineral reactivity (Deutsch 1997). The SI of all minerals was calculated using PHREEQC by assuming that the groundwater of lowest concentration of ions is evaporated. It was found that the SI of calcite and dolomite increases to more than zero when water is evaporated by 40 % and 70 % respectively (Figure 6.9). All the other minerals do not reach saturation level even after 100% of evaporation. It is expected that calcite and dolomite may have been deposited in the soil zone and well sections due to evaporation. Presence of such calcareous material was noted in the well sections of this area and also in the neighbouring watershed of similar geological condition by Reddy et al (2010). The CaCO$_3$% of 26 soil samples collected from this area ranges from 0.4% to 27.3%.

Figure 6.8 Relationship between Ca + Mg and TC with 1:1 line
Jacks and Sharma (1995) also reported the occurrence of dolomitic carbonates in this area. They also observed preferential formation of calcite in the chromusters while dolomite occurs only in the Rhodustals. The soils in the Nalgonda region are of moderately to gently sloping Ustrothents and Rhodustals (Gajbhiye and Mandal, 2000). Hence, it is reasonable to assume that these minerals are reactive in groundwater environment and they can control solution concentration. The SI of calcite and dolomite of groundwater of this area vary with time. During recharge of rainfall, the groundwater level increases and SI of calcite and dolomite decreases (Figure 6.10). During dry periods, when the groundwater level decrease, the SI of these minerals increases which indicates the processes of evaporation. That is, the recharge of rainwater dissolves these minerals deposited during the preceding dry months in the soil zone takes into the groundwater, which increases the SI of minerals in groundwater. If the rainfall continues for more time, the saturation levels of minerals decrease in groundwater. Similar observation was made in a few other regions of south India (Elango and Ramachandran 1991, Rajmohan and Elango 2004). Saptial variation of saturation index of calcite and dolomite (Figures 6.11 and 6.12) in groundwater are oversaturated in the central part of the area and undersaturated in the northern and southern part of the area. This spatial variation also supports evaporation processes and dissolution of minerals. As it is arid dry land where irrigation is practised both use surface and groundwater, the water used for irrigation undergoes evaporation leading to increase the concentration of ions. This evaporation enriched irrigated water enters the groundwater zone as recharge, which is pumped again for irrigation. Thus pumping of groundwater for irrigation and its evaporation from the irrigated area lead to increase in concentration of salts especially carbonates in the soils. Modeling of evaporation processes by
PHREEQC also indicates that the water reaches the saturation level only for the minerals of Calcite and Dolomite (Rajesh et al 2012)

The study of the Ca/Mg ratio of groundwater from this area also supports the dissolution of calcite and dolomite (Figure 6.13). That is, if the ratio Ca/Mg=1, dissolution of dolomite should occur, whereas a higher ratio is indicative of greater calcite contribution (Maya and Loucks, 1995; Jacks and Sharma, 1995). Higher Ca/Mg molar ratio (>2) indicates the dissolution of silicate minerals, which contributes calcium and magnesium to groundwater. In this plot, the points closer to the line (Ca/Mg=1) indicate the dissolution of dolomite. Most of the samples which having a ratio between 1 and 2 indicate the dissolution of calcite. Those with values greater than 2 indicate the effect of silicate minerals (Figure 6.13).

![Figure 6.9 Calculated changes in SI of minerals during evaporation of groundwater](image)

**Figure 6.9** Calculated changes in SI of minerals during evaporation of groundwater
Figure 6.10 Temporal variations in rainfall (mm), groundwater level (m) and mineral saturation index
Figure 6.11 Spatial variation of saturation index of calcite in groundwater during November 2009

Figure 6.12 Spatial variation of saturation index of dolomite in groundwater during November 2009
In general the groundwater chemistry of this area is principally controlled by evaporation, ion exchange, silicate weathering and dissolution of minerals.

Figure 6.13 Relationships between Ca/Mg and total cations (TC)