CHAPTER-6

GEOCHEMICAL MODELING

6.1.0 Introduction

The chemistry of the natural water is complex. Modeling of chemical constituents in aqueous system encompasses the aqueous speciation of dissolved cationic elements, among organic and inorganic anionic legends, of anionic elements. Chemical modeling includes calculation of the degree of saturation of an aqueous media with regard to meta-stable to equilibrium solids and calculation of sorption or desorption. Chemical modeling is used to describe the chemical characteristic of an aqueous system, whether lake or fluid in human digestive system, gives the required input data for the system to be modeled as well as adequate reference data (Jenne, 1978).

Simulation of physico chemical interactions in a water-rock system is based on the assumption of partial or approximate equilibrium in such systems. The principle of partial equilibrium, long known from works in chemistry and thermodynamics by Dodge (1950), Prigozhin and Defei (1966), Haaze (1967) and Karpov et al (1978)- frequently figuring in recent geochemical studies – Barton et al (1963) and Helgeson (1969,1971). The following concept of partial equilibrium is applied: usually chemical equilibrium holds true for particular chemical reaction or reactions in non equilibrium hydrogeochemical systems characterized by numerous reactions. Hence the rate of reaching chemical equilibrium in the given system
exceeds the rate of changes in external variable parameters and other reactions (Vartanyan et al 1983).

Modern ideas of chemical state of elements in groundwater and the way in which they contribute to hydrogeochemical process are the basis for the simulation of physico chemical interactions in a water-rock system. A fact of greatest importance in this connection that in groundwater which represents a multi-component system, chemical elements exists primarily not in the form of simple cations and anions but as associated compounds of different complexity and stability, i.e., as complex compounds. According to Rhyzhenko et al (1977, 1981), changes in the solubility of a solid substance in solution of another substance are considered to be a result of integration of particles of dissolving and dissolved solids.

The solubility of a solid phase has theoretically and experimentally been proved to increase proportionally to an increase in the stability constants of complex compounds formed by the solid components in a solution.

Thus in dissolution of a solid phase, e.g., CaCO₃ in pure water the expression of calcium concentration should read as follows;

$$m\sum{Ca} = m_{Ca}^{2+} + m_{CaHCO_{3}^+} + m_{CaCO_{3}^{0}} + m_{CaOH^+} + \ldots \ldots \ldots$$

In dissolving the solid phase of CaCO₃ in a solution of NaCl, association of particles of the first substance Ca²⁺, HCO₃⁻, CO₃²⁻ with those of the second, Na⁺, Cl⁻ are taken into account:

$$m\sum{Ca} = m_{Ca}^{2+} + m_{CaHCO_{3}^+} + m_{CaCO_{3}^{0}} + m_{CaOH^+} + m_{CaCl^+} + \ldots \ldots \ldots$$
Proceeding from a universal character of association of particles dissolved in water and from the Ryzhenko dissolution based theorem, concentration of any chemical component in the natural solution is regarded as originating in the equilibrium between the solid phase and adequate complex forms of an element in the aqueous phase.

It follows from the laws of thermodynamics (Gibbs, 1950) that a theoretically correct determination of an equilibrium composition of any number of components and phases can be made on the basis of the thermodynamic properties of particular substances. Construction of algorithms for computers has enabled multi-component hydro-geochemical systems with a large number of phases to be consolidated (Karpov et al 1978; Helgeson, 1969 and Sharov, 1976). In determining the equilibrium chemical composition, all potential forms of an element in the aqueous solution including components with organic matter may be considered.

A systematic use of computers for studying the hydro geochemical systems was initiated by Helgeson (1967, 1969, 1971). Recently a considerable number of algorithms and programs for calculating chemical equilibrium (Table 6.1), by using computer have been developed which introduces either of the two ways of simulating physico-chemical water rock interactions: (a) computation by using the equilibrium constants of chemical reactions, and (b) calculation by the method of free energy minimization.
<table>
<thead>
<tr>
<th>Year</th>
<th>PHREEQC</th>
<th>EQ 3/6 V8.0</th>
<th>ORCHESTRA</th>
<th>CHESS 3.0</th>
<th>CHEMSAGE</th>
<th>MINTEQA2</th>
<th>WATEQ4F</th>
</tr>
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<tr>
<td>2008</td>
<td>PHREEQC 2.14.3</td>
<td>17.12.09</td>
<td>JCHESS 2.0</td>
<td>4</td>
<td>4.03</td>
<td>2.63</td>
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</tr>
</tbody>
</table>

*Table 6.1 Evolution of different Geochemical models*
Special importance is about the potential application of the above methods to either closed thermodynamic system or open ones with rather mobile components. In this context partial pressures of CO$_2$, H$_2$S and H$_2$ can be selected to favour the evaluation of hydro geochemical systems. Therefore modeling provides possibility to control carbonate, sulphide and other equilibrium having particular significance for groundwater.

Basically there are three types of computer models in aqueous chemistry (Nordstrom et al. 1979).

1. Equilibrium
2. Mass-transfer
3. Mass-transport

The equilibrium codes are by far the most common examples, which include WATEQF, Geochem and EQ3NR. Such codes solve a simultaneous set of equations, which explains the equilibrium reactions and mass balance on dissolved elements. The output consists of theoretical distribution of aqueous species for dissolved elements. Some programs also included equation to describe ion exchange and simple linear adsorption (Parkhurst et al. 1980).

Sophisticated geochemical models have been used to describe and predict the chemical behaviour of complex natural waters and also to protect the groundwater resources from future contamination. The computerized geochemical models are powerful tools for understanding the chemical state of natural waters and for predicting the behavior of such waters under variety of such hypothetical conditions.
Helgesan et al. (1970), Plummer et al. (1976), Shannon et al. (1977), Sposito and Mattigod (1979), Wolery (1979), Runnels and Lindberg (1981), Felmy et al. (1984), Parkhurst et al. (1990) and many others have developed a variety of geochemical models for describing and deducing the chemical behavior of complex and mixed waters. A brief review of existing geochemical studies has been governed by Nordstrom et al. (1979), Jenne (1981), Plummer et al. (1983) and Runnels (1978). Several earlier workers have also used geochemical models for solubility equation study of groundwater (Wolery, 1979 and 1983; Sanford and Konikow, 1989; Plummer et al. 1990; Tamata, 1990; Deutsch, 1997; Elangovan, 1997 and Murphy and Schramke, 1998). A numerical model MINTEQAZ was tested by Hayagreeva Rao and Sekhar (2002) for solving transport calculations and geochemistry in groundwater and found oxidation of pyrite and resulting leachate concentration of groundwater.

The global problems, approaches and priorities of chemical modeling were discussed in detail by Jenne (1978). The implication of computer program in calculation of equilibrium distribution of inorganic species of major and minor elements in natural waters using chemical analysis and insitu measurements of Ec, pH were discussed in detail by Truesdell and Jones (1973). Mixing of water from the different aquifers with the water from the deep bed rock aquifer in the groundwater discharge area having an intermediate composition was explained by the dilution of Calcite precipitation using MIX2 chemical equilibrium model (Wallick, 1981), in the drainage basin of Holocene age, Canada. Simulation of
Calcite dissolution and porosity changes in saltwater mixing zone in coastal aquifers was done by Sanford and Konikow (1989). They found that there is an increasing porosity and permeability by enhanced dissolution, using geochemical model PHREEQE. The same model was used by Elangovan et al. (1999) to find out the disequilibrium indices of Calcite along with other minerals such as Aragonite, Dolomite, Hematite, Goethite, Fe (OH)$_3$ and Strontionite.

6.2.0 PHREEQC Model

PHREEQC is a computer program written in the C programming language that is designed to perform a wide variety of aqueous geochemical calculations. PHREEQC is based on an ion-association aqueous model and has capabilities for (1) speciation and saturation-index calculations, (2) reaction-path and advective-transport calculations involving specified irreversible reactions, mixing of solutions, mineral and gas equilibrium, surface-complexation reactions, and ion-exchange reactions, and (3) inverse modeling, which finds set of mineral and gas mole transfers that account for composition differences between waters, within specified compositional uncertainties.

PHREEQC is derived from the Fortran program PHREEQE, but it has been completely rewritten in C with the addition of many new capabilities. New features include the capabilities to use redox couples to distribute redox elements among their valence states in speciation calculations; to model ion-exchange and surface-
completion reactions; to model reactions with a fixed-pressure, multi-component gas phase (that is, a gas bubble); to calculate the mass of water in the aqueous phase during reaction and transport calculations; to keep track of the moles of minerals present in the solid phases and for automatic determination of the thermodynamically stable phase assemblage; to simulate advective transport in combination with PHREEQC's reaction-modeling capability; and to make inverse modeling calculations that allow for uncertainties in the analytical data. The user interface is improved through the use of a simplified approach to redox reactions, which includes explicit mole-balance equations for hydrogen and oxygen; the use of a revised input that is modular and completely free format; and the use of mineral names and standard chemical symbolism rather than index numbers. The use of C eliminates nearly all limitations on array sizes, including number of elements, aqueous species, solutions, phases, and lengths of character strings. A new equation solver that optimizes a set of equalities subject to both equality and inequality constraints is used to determine the thermodynamically stable set of phases in equilibrium with a solution. A more complete Newton-Raphson formulation, master-species switching and scaling of the algebraic equations reduce the number of failures of the numerical method in PHREEQC relating to PHREEQE.

PHRQCGRF is a separate code available for WINDOWS 95 and MS-DOS that can be used to create a variety of graphs from the data generated by PHREEQC. The output data from PHREEQC may be plotted against distance, time, or other data listed in the PHREEQC selected output file, and a series of data versus distance
graphs can be animated. PHRQCGRF can also extract the data of interest from the
PHREEQC transport results and write the data sets to an external file.

PHRQCGRF helps visualize PHREEQC transport output files generated by using the - SELECTED_OUTPUT - keyword in a PHREEQC simulation. PHREEQC does not perform any geochemical modeling, but uses these files as the starting point for its various features. Once a file is specified, several options allow the user to choose exactly how to extract the data of interest. Data may be plotted against distance at a particular time, against time at a particular distance, against other data at a particular time or distance, or several data versus distance plots can be animated within a specified time interval. Additionally, results of PHREEQC transport simulations can be compared with measured field data, or PHREEQC simulations can be compared with other PHREEQC simulations. As an alternative to graphing, the extracted data sets may be written to an external file. Except for the extracting feature, the result of PHRQCGRF’s data processing is the presentation of a graph reflecting the user’s choice.

PHRQCGRF also offers flexibility in how an extracted data set is displayed. For example, both the x-axis and y-axis value ranges can be specified. Various plot appearances, such as colors, symbols, and line styles, can also be set according to the user’s preference.
6.2. a Aqueous Model

PHREEQC uses ion-association and Debye-Hueckel expressions to account for the non-ideality of aqueous solutions. This type of aqueous model is adequate at low ionic strength but may break down at higher ionic strengths (in the range of seawater and above). An attempt has been made to extend the range of applicability of the aqueous model through the use of an ionic-strength term in the Debye-Hueckel expressions. These terms have been fitted for the major ions using Chloride mean-salt activity-coefficient data (Truesdell and Jones, 1974). Thus, in Sodium Chloride dominated systems, the model may be reliable to higher ionic strengths. For high ionic strength waters, the specific interaction approach to thermodynamic properties of aqueous solutions should be used (for example, Pitzer, 1979, Harvie and Weare, 1980, Harvie and others, 1984, Plummer and others, 1988). The other limitation of the aqueous model is lack of internal consistency of the data in the database. Most of the log K's and enthalpies of reaction have been taken from various literature sources. No systematic attempt has been made to determine the aqueous model that was used to develop the log K's or whether the aqueous model defined by the current database file is consistent with the original experimental data. The database files provided with the program should be considered to be preliminary. Careful selection of aqueous species and thermodynamic data is left to the users of the program.
6.2.b Ion Exchange

The ion exchange model assumes that the thermodynamic activity of an exchange species is equal to its equivalent fraction. Other formulations such as definitions of activity, mole fraction for example, or additional activity coefficients to convert equivalent fraction to activity (Appelo, 1994). No attempt has been made to include other or more complicated exchange models. In many field studies, ion-exchange modeling requires experimental data on material from the study site for appropriate model application.

6.2.c Surface Complexation

PHREEQC incorporates the Dzombak and Morel (1990) diffuse double-layer and a non-electrostatic surface complexation model (Davis and Kent, 1990). Other models, including isotherms and triple and quadruple-layer models have not been included in PHREEQC. Davis and Ken (1990) reviewed the surface-complexation modeling and note theoretical problems with the standard state for sorbed species. Other uncertainties occur in determining the number of sites, the surface area, the composition of sorbed species, and the appropriate log K's. In many field studies, surface-complexation modeling requires experimental data on material from the study site for appropriate model application. The capability of PHREEQC to calculate the composition of the diffuse layer (-diffuse layer option) is adhoc and should be used only as a preliminary sensitivity analysis.
6.2.d Convergence Problem

PHREEQC tries to identify input errors, but it is not capable of detecting some physical impossibility in the chemical system that is modeled. For example, PHREEQC allows a solution to be charge balanced by addition or removal of an element. If this element has no charged species or if charged imbalance remains even after the concentration of the element has been reduced to zero, then the numerical method will appear to have failed to converge. Other physical impossibilities that have been encountered are (1) when a base is added to attain a fixed pH, but in fact an acid is needed (or vice versa) and (2) when non-carbonate alkalinity exceeds the total alkalinity given as input.

At present, the numerical method has proved to be relatively robust. Known convergence problems--cases when the numerical method fails to find a solution to the non-linear algebraic equations--have occurred only when physically impossible equilibrium have been posed and when trying to find the stable phase assemblage among a large number (approximately 25) of minerals, each with a large number of moles (5 moles or more). It is suspected that the later case is caused due to the loss of numerical precision in working with sparingly soluble minerals (that is, small aqueous concentrations) in systems with large total concentrations (on the order of 100 moles). Occasionally it has been necessary to use the scaling features of the
KNOBS keyword. The scaling features appear to be necessary when total dissolved concentrations fall below approximately 10 to 15 moles.

6.2.e Inverse Modeling

Inclusion of uncertainties in the process of identifying inverse models is a major advance. However, the numerical method has shown some lack of robustness due to the way the solver handles small numbers. The option to change the tolerance used by the solver is an attempt to remedy this problem. In addition, the inability to include isotopic information in the modeling process is a serious limitation. Considering all these advantages in PHREEQC, this model was used to calculate the Saturation index (SI) of different minerals in the study area.

6.3.0 State of Saturation

The state of equilibrium between ground water and Calcite, Dolomite, and other minerals in the aquifer system can be evaluated by the computation of saturation indices (SI), expressed as SI mineral = log (IAP/KT), (6) where IAP is the ion-activity product of the mineral calculated from analytical data, and KT is the thermodynamic equilibrium constant at measured temperature of the water sample (Plummer and others, 1976). If the saturation index is negative, the water is undersaturated with respect to the particular mineral, and dissolution of the mineral is possible. If the saturation index is positive, the water is oversaturated with respect to the mineral, and precipitation of the mineral in the aquifer is possible. A saturation index of zero indicates that the mineral is in equilibrium with the water and that the
tendency or rates of dissolution and precipitation should be equal. Thermodynamics can only indicate the potential for such phase transfer. In reality, various kinetic factors may cause systems to behave differently than predicted (Nordstrom and Ball, 1989; Busby and others, 1991).

Saturation indices were calculated for Calcite and Dolomite by using the computer model WATEQF (Plummer and others, 1976) and chemical data for the water collected as part of this investigation. The accuracy of the saturation index for predicting equilibrium of carbonate minerals depends largely on the accuracy of the field measurements of pH and alkalinity.

Uncertainty in this and other analytical data produces an uncertainty estimate in the saturation index of + 0.1 for Calcite and + 0.2 for Dolomite (Nordstrom and Ball, 1989; Busby and others, 1991). Because the accuracy of pH measurements could not be verified for much of the historical groundwater-chemistry data, saturation indices were not calculated for historical samples.

6.3.1 Carbonates

Calcium Carbonate exists in various solid forms that are divided into two classes: Hydrated forms and Well-known anhydrous forms of Calcite, Aragonite and Vaterite.
6.3.2 Hydrated Forms

Hydrated Forms are monohydrated Calcium Carbonate. The hexa-hydrated Calcium Carbonate is also called Ikaite, and amorphous Carbonate. Various anhydrous forms are distinguished by their crystalline structure. Calcite is thermodynamically the most stable calcareous rocks in the natural environment which are essentially composed of Calcite. The existence of hydrated forms has been debated for a long time. The first laboratory research on CaCO\textsubscript{3} hydrates dealt with the existence of mono-, di-, tri-, penta- and hexa hydrated Calcium Carbonates (Mackenzie1923). In 1963, Pauly reported the presence of hexa-hydrate form in the natural environment (Pauly 1963). He named this new mineral as Ikaite from the name of the Ika Fjord where it was discovered. The hexa hydrated Calcium Carbonate crystallizes in the mono-clinical system. At room temperature, it evolves quickly towards anhydride forms with very pronounced increase in volume (Mackenzie1923). Like Ikaite, Monohydrated Calcium Carbonate was first observed and characterized in the laboratory (Krauss et al 1930). Later it was identified in the sediments of Issyk-Koul Lake in Kirghizstan (Fleischer,1969). Monohydrated Calcium Carbonate crystallizes in the hexagonal system in little spherical shapes with a diameter close to 100 mm. The crystalline form of Monohydrated Calcium Carbonate is less compact than that of Ikaite.
6.3.3 Anhydrous Forms

However, it evolves into the anhydrous forms of CaCO₃ at 25°C, the reaction is still accompanied by an expansion of volume which depends on the new shape obtained: +7% for Aragonite and +11% for Calcite (Hull, 1973). Calcium Carbonate also exists in amorphous form. Synthesis in an aqueous medium begins with the appearance of a fluffy precipitate, strongly hydrated (Kendall, 1912). Through drying, it loses the major part of its water but preserves about one mole of water per CaCO₃ mole (Brecevic, and Nielsen, 1989). It can often be described as consisting of little spherical shapes less than 1 mm in diameter. The existence of the CaCO₃⁰ (aq) ion pair in solution was first reported by Greenwald (1941). He gave a value for the CaCO₃⁰ (aq) formation constant, βCaCO₃⁰ at 25°C. Since then, the determination of βCaCO₃⁰ has been the object of numerous (sometimes contradictory) works. Yet, CaCO₃⁰ is rarely mentioned in studies on the Calco-Carbonic system. The incoherence of the various βCaCO₃⁰ values proposed and the lack of interest in it by researchers in thermodynamics are probably the reasons. The desire to simplify calculations and the presumed relative rarity of this uncharged complex (Legrand, et al 1981 and C.Tarits, 1990) seems to explain why it sank into oblivion. Nevertheless, such an approach to the study of Calcium Carbonate formation mechanism is inadequate. Recently, a review of the CaCO₃⁰ formation constant was done (Gal., 1996 and Gache, Gal 1998). What emerges from this review is that the value proposed at various temperatures by (Plummer and Busenberg 1982) is satisfactory. Thus, it is important that not to neglect the formation in solution of the
soluble complex CaCO$_3^0$, for log $\beta_{\text{CaCO}_3}^0=3.22$ at 25ºC. According to the relation (1): $\beta_{\text{CaCO}_3}^0=\frac{\text{lCaCO}_3^0}{\text{lCa}^{2+} \times \text{lCO}_3^{2-}}$; the uncharged soluble complex CaCO$_3^0$ seems to be the precursor of the solid shape. When Calcium Carbonate solubility ‘‘S’’ is reached, the ionic activity product $\text{lCa}^{2+} \times \text{lCO}_3^{2-}$ (noted IAP) is equal to the CaCO$_3$ solubility product $K_S$: Considering relation (1) and the expression $K_{S_{\text{CaCO}_3}}=\frac{\text{lCa}^{2+} \times \text{lCO}_3^{2-}}{\text{lCaCO}_3^0}$, ‘‘S’’ must be written as (Gal et al1989 and JC.Bollinger1992) $S=\beta_{\text{CaCO}_3}^0 \times K_{S_{\text{CaCO}_3}}$ (2) The numerous studies dedicated to Calcium Carbonate agree that it is not enough to induce precipitation if the activity product of CaCO$_3$ becomes higher than the value of the Calcite solubility product. The germination stage governs the breakdown of the metastable state. A single study shows the initial formation of Ikaite in the germination stage (Venderbosch, and Overmen 1986). The similarity between ion organization in solution and in hydrated solid phase was already revealed in the case of Nitrate (Mathieu and Lounsbury.,1949). The association of hydrated ions Ca$^{2+}$ and CO$_3^{2-}$ in CaCO$_3^0$- shape can itself remain partially surrounded by water molecules (Gal et al.,1996). Adding the existence of hydrated intermediates to the Calco-Carbonic system evolution model in aqueous phase, seems judicious for the CaCO$_3^0$ precursors in solution and for the corresponding solid phases susceptible to precipitation. Pairs, thus formed, at random meetings would go and group together. Afterwards, these micelle would lose a part of their hydration cloud and would arrange according to an organization sketch close to that of less hydrated CaCO$_3$ solid form. So, step-by-step, precursors with lower hydration degrees could appear, depending on the different dehydration
reaction speeds. If the possibility of precipitating one or several solid forms has added to this evolution plan, the model (Gal et al 2002) which can then be written according to (Fig.6.1) This Calco-Carbonic system modelization leads us to consider that in fact the CaCO$_3$ complex would be a global representation of soluble forms variously hydrated. They would all have a formation constant close to that defined (Plummer and Busenberg, 1982) and associated with limited solubility ‘‘S’’ estimated by means of relation (2). As regards the various forms enumerated from left to right in (Fig.6.5), their solubility products and consequently, their respective ‘‘S’’ value decreases: $S_\alpha > S_\beta > S_\gamma > S_\delta > S_\varepsilon > S_\phi$. The values grouped at 25°C and 35°C are regrouped in (Table 6.2). The amorphous Calcium Carbonate appears as being practically 100 times more soluble than Calcite. Calcium Carbonate crystalline hydrated forms being the most soluble, their precipitation is thus possible only at high degrees of super saturation Calcium Carbonate. According to this model, as precursors of the most hydrated forms appear in solution before the last hydrated forms, their precipitation would be favored. This allows us to explain why the most hydrated solid species form first, when precipitation is caused by double decomposition of highly concentrated solutions (Ogino et al 1987, and Clarkson et al., 1992). In a more general way, hydrated forms being the most soluble forms of Calcium Carbonate, and considering that dehydration and reorganization speed of precursors can be slow, the breakdown of the metastable state is primarily through the precipitation of a hydrated form,
\[
\text{Ca}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{CaCO}_3^{\alpha}
\]

Or according to pH:
\[
\text{Ca}^{2+} + \text{HCO}_3^- + \text{H}_2\text{O} \leftrightarrow \text{CaCO}_3^{\beta} + \text{H}_3\text{O}^- \text{ and } \text{HCO}_3^- + \text{H}_3\text{O}^+ \leftrightarrow \text{CO}_2 + 2\text{H}_2\text{O}
\]

and then:
\[
\text{CaCO}_3^{\alpha} \nleftrightarrow \text{CaCO}_3^{\beta} \nleftrightarrow \text{CaCO}_3^{\gamma} \nleftrightarrow \text{CaCO}_3^{\delta} \nleftrightarrow \text{CaCO}_3^{\delta}
\]

(amicorous) (iaikite) (Vaterite) (aragonite) (calcite)

**Fig 6.1** Crystallization sequence of CaCO$_3$

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>Calcite</th>
<th>Aragonite</th>
<th>CaCO$_3$</th>
</tr>
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<tbody>
<tr>
<td>25</td>
<td>pKs</td>
<td>8.48</td>
<td>8.35</td>
</tr>
<tr>
<td></td>
<td>s</td>
<td>5.55 x 10$^{-6}$</td>
<td>7.48 x 10$^{-6}$</td>
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<tr>
<td>35</td>
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<tr>
<td></td>
<td>s</td>
<td>6.09 x 10$^{-6}$</td>
<td>8.22 x 10$^{-6}$</td>
</tr>
</tbody>
</table>

**Table 6.2** Solubility of the CaCO$_3$ solid
at high super-saturation rates. Thus the solubility limit of the most unstable forms would limit the stability domain of Calcium Carbonate and it allows us to understand how a system is able to evolve towards a less soluble form. Let us imagine the initial precipitation of the shape α with $S_\alpha$ solubility. The solid of the corresponding form ($S_\alpha$) is then in equilibrium with its precursors in solution in $S_\alpha$ concentration. But precursors of solubility $S_\beta$ are going to appear in solution to the detriment of the earlier precursors, which are going to be replaced in solution by solid $S_\alpha$ re-dissolution. When $S_\beta$ solubility is reached, the solid $S_\beta$ begins to precipitate. Thus, by successive reactions of precipitation, re-dissolution, and new precipitation, the system will evolve gradually towards formation of Calcite crystals. Transformation from one form to another requires a passage in solution. That is why it is possible to keep intermediate forms after filtration and drying (Ogino et al., 1987). In most cases, the increasing pH due to loss of Carbon dioxide, often as a result of heating, induces Calcium Carbonate precipitation. Accordingly Gal (2002) proposes a homogeneous or a heterogeneous process. Numerous works have been published on the Calcium Carbonate precipitation caused by CO$_2$ loss, in particular the LCGE method (Roques., 1990 and Roques., et al., 1992). These works did not take into account of the existence of the CaCO$_3$ soluble complex, and the measurement interpretations were not based on the model that in all cases, the corresponding reaction was of the heterogeneous type.
Bicarbonate derived by the pressure of weathering or from other source remains in the aqueous medium trying to equilibrate with different ions like Ca, Mg, or both to attain saturation with different minerals like Calcite (SI$_c$), Aragonite(SI$_A$), Dolomite(SI$_D$) and Magnesite (SI$_m$). SI of Carbonate minerals shows under saturation to saturation state in both the seasons. The saturation state of Carbonate minerals are in the following orders SI$_D$ > SI$_c$ > SI$_m$ > SI$_a$. Saturation index of these minerals were plotted against the concentration of aHCO$_3$ during both seasons of 2007 and 2009 and found there is no pattern of variation with an increasing trend of SI is noted. The Calcite and Aragonite minerals are near the state of equilibrium with aHCO$_3$.

The Aragonite and Calcite minerals show the state of equilibrium for of a HCO$_3^-$ ranging from-0.3 to -0.2, this range is depended upon the pH and log pCO$_2$ of the aquifer. In general the Dolomite and Magnesite are under saturated to near saturation, but shows increasing trend to that of a HCO$_3^-$ (Fig.6.2 a,b,c,d) In general there is an increase are fall of saturation index of the Carbonate minerals with increasing HCO$_3^-$. 
Fig 6.2a HCO₃⁻ Vs Carbonate Minerals in POM 2007
Fig: 6.2.b \( \text{HCO}_3^- \) Vs Carbonate Minerals in PRM 2007
Fig 6.2c HCO₃⁻ Vs Carbonate Minerals in POM 2009
Fig 6.2.d HCO₃⁻ Vs Carbonate Minerals in PRM 2009
6.4.0 SULFATE MINERALS

The stability relation in the system CaSO₄-H₂O are of geological interest because the minerals Gypsum (CaSO₄·2H₂O), Anhydrite (CaSO₄) and Bassanite (CaSO₄·½H₂O). The former two are common in natural marine evaporate deposits. Bassanite is rare in nature but is the principal ingredient of Plaster of Paris.

The binary system has been studied experimentally at 1 atmospheric pressure by many investigations (Partridge and White, 1929; Posnjak, 1938; Hill, 1937). Kelley et al, (1941) obtained the thermo dynamical data on the solid phases of the system at 1 atmospheric pressure. The equilibrium temperature for the Gypsum-Anhydrite transition was calculated to be at 40°C. MacDonald, (1953) calculated the effect of pressure and H₂O activity on the reaction; Gypsum=Anhydrite+H₂O (liquid). There are no experimental data on the effect of high pressure on the transition.

Previously recently Bassanite, Calcium Sulfate Hemihydrate, has been reported from a number of natural environments, for instance Bendy, (1956) reports its occurrence in Indiana Salt Beds. On the basis of experimental work and thermo chemical data (MacDonald, 1953) Bassanite is unstable relative to Gypsum and Anhydrite at 1 atmospheric pressure at all temperatures.

Equilibrium pressure-temperature curves have been determined for the following univariant reactions:
CaSO$_4$2H$_2$O$\rightleftharpoons$CaSO$_4$ ½ H$_2$O $+$ 1 ½ H$_2$O  \hspace{1cm} (1)  

Gypsum       Bassanite       H$_2$O (liquid)

CaSO$_4$ ½ H$_2$O$\rightleftharpoons$CaSO$_4$ $+$ ½ H$_2$O  \hspace{1cm} (2)  

Bassanite       Anhydrite       H$_2$O (liquid)

The stability relations of Gypsum (CaSO$_4$.2H$_2$O) and Anhydrite (CaSO$_4$) are of considerable interest because most natural marine evaporate deposits consist essentially of Gypsum and for Anhydrite inter bedded with Dolomite, Limestone and Clastic sediments (Stewart 1963). In the binary system CaSO$_4$.H$_2$O the reaction CaSO$_4$.2H$_2$O$\rightleftharpoons$CaSO$_4$ $+$ 2 H$_2$O (liq) has been studied experimentally at one atmosphere pressure by Partridge and White (1929), Toriumi and Hara (1934), Hill (1934), Posnjak (1938) and D'Ans et al (1955). Kelley et al. (1941) measured the thermo chemical properties of the solid phases of the system at atmospheric pressure and from these data calculated an equilibrium temperature for the Gypsum-Anhydrite transition. Marsal (1952), MacDonald (1953), Zer (1965) and Hardie (1965) calculated the effect of pressure on the reaction.

The conversion of Gypsum to Anhydrite, and Anhydrite to Gypsum, was studied at atmospheric pressure as a function of temperature and activity of H$_2$O (aH$_2$O) for the reaction

CaSO$_4$.2H$_2$O(g) $\leftrightarrow$ CaSO$_4$(s) $+$ 2H$_2$O (liquid in solution)

The equilibrium constant may be defined in terms of activities, as follows:
\[(K_a)_{p,T} = \frac{a\text{CaSO}_4a^2\text{H}_2\text{O}}{a\text{CaSO}_42\text{H}_2\text{O}}\]

If the standard states of the reaction components are considered to be pure H\(_2\)O liquid water, pure crystalline CaSO\(_4\) and pure crystalline CaSO\(_4\)2H\(_2\)O at one atmosphere total pressure and at the temperature of reaction, the equilibrium constant simplifies to

\[(K_a)_{T,p}^{-1} = a^2\text{H}_2\text{O}\]

It follows that the dehydration of gypsum to anhydrite, at atmospheric pressure, is a function of temperature and activity of H\(_2\)O only. Therefore, provided the solids do not change in composition, the equilibrium is independent of the components in the co-existing solution.

The saturation index of these two different minerals are represented as SI\(_{Gy}\) and SI\(_{An}\). The saturation of the Sulphate minerals were calculated for different season of the study area. It is observed that during all the seasons, the saturation index of these minerals (Fig 6.3a, b, c and d) are in the following trend SI\(_{Gy}\) > SI\(_{An}\). The SI of both the minerals are in state of Under Saturation. It is also observed that there is a linear increase in saturation index of these minerals with the increase in concentration of Sulphate during POM. The SI of these minerals increases with the Sulphate concentration in other seasons but the linearity is lesser. It may be due to the common ion effect or the interference of Na in the formation of these minerals. The effect of salt solutions on the Gypsum-Anhydrite Equilibrium at atmospheric pressure has been considered with some detail by several workers, all of whom have
verified that the transition temperature is lowered with increasing salinity. The system \( \text{CaSO}_4-\text{NaCl}-\text{H}_2\text{O} \) has been investigated experimentally by van't Hoff et al, (1903), D'Ans et al, (1955), Madgin and Swales, (1956), Bock, (1961) ; Zen (1965). MacDonald, (1953) calculated the effect of \( \text{NaCl} \) solutions on the equilibrium temperature. The transition in sea water has been studied by Toriurni et al, (1938) ; Posnjak (1940). Other pertinent laboratory studies are those of Hill and Wills, (1938) ; Conley and Bundy (1958) in the system \( \text{CaSO}_4-\text{Na}_2\text{SO}_4-\text{H}_2\text{O} \), D'Ans and Hofer, (1937) in the system \( \text{CaSO}_4-\text{H}_3\text{PO}_4-\text{H}_2\text{O} \), and Ostroff (1964), converted Gypsum to Anhydrite in \( \text{NaCl-MgCl}_2 \) solutions.

The activity of \( \text{H}_2\text{O} \) of the solutions co-existing with Gypsum or Anhydrite was varied by adding \( \text{Na}_2\text{SO}_4 \) or \( \text{H}_2\text{SO}_4 \) (Hardie et al,1967): these were chosen because the Gypsum=Anhydrite conversion rates were found to be relatively rapid in sodium sulfate or sulfuric acid solutions. In the system \( \text{CaSO}_4-\text{Na}_2\text{SO}_4-\text{H}_2\text{O} \) neither Gypsum nor Anhydrite can co-exist with a solution of \( \text{Na}_2\text{SO}_4 \) concentration greater than that fixed by the one atmosphere isothermally invariant assemblage Gypsum (or) Anhydrite + Glauberite (\( \text{CaSO}_4.\text{Na}_2\text{SO}_4 \)) +Solution + Vapour. The \( a\text{H}_2\text{O} \) of the invariant solutions varies from about 0.90 at 25ºC to about 0.96 at 70ºC. This limits the very dilute solutions, a considerable disadvantage because many natural Calcium Sulphate deposits must have formed in brines with activities of \( \text{H}_2\text{O} \) at least as low as 0.75, as defined by the assemblage Gypsum (or Anhydrite) + Halite + Solution + Vapour in the "haplo-evaporite" (Zen, 1965) system \( \text{CaSO}_4-\text{NaCl}-\text{H}_2\text{O} \). In the system \( \text{CaSO}_4-\text{H}_2\text{SO}_4-\text{H}_2\text{O} \), however, the stability fields of
Gypsum and Anhydrite are not limited by double-salt formation. Due to the increase of Na during both pre and post monsoons, the increase of salinity and the formation of the CaSO$_4$ salts are hindered.
Fig: 6.3.a SO$_4^{2-}$ Vs Anhydrite, Gypsum POM2007
Fig: 6.3.b SO$_4^{2-}$ Vs Anhydrite, Gypsum PRM2007
**Fig: 6.3.c SO$_4^{2-}$ Vs Anhydrite, Gypsum POM2009**
SO4 Vs Anhydrite, Gypsum PRM 2009

Fig: 6.3.d SO4 $^{2-}$ Vs Anhydrite, Gypsum PRM2009
6.5.0 Relationship of pCO$_2$ to State of Saturation

Partial pressure of CO$_2$ plays a significant role in the state of saturation of Carbonate minerals. Considering the above fact and extra placed relationship between log pCO$_2$ and Saturation Index graph was plotted.

During Pre-Monsoon (Fig.6.4 b,c) it is observed that pCO$_2$ ranges from -4 to -1. Few samples show saturation with respect to Calcite and low pCO$_2$ condition. This may be due to the availability of Ca and Mg in the Alluvial aquifer during both pre monsoon seasons. Post-Monsoon shows (Fig.6.4 a,d) higher pCO$_2$ condition increases found less saturation in Dolomite and Magnesite and more saturation increases in less pCO2.

The fact that, at in constant Ω (rate of Crystallization) a greater DOC concentration is required to block the active sites on the Calcite crystals with increasing pCO$_2$ which may be due to combination of at least three factors: (1) the increase in negative charge on the Calcite surface with increasing pCO$_2$ (Charlet et al 1990), (2) the decrease of bonding capacity of the fulvic acid with decreasing pH of the solution (Engebretson et al 1996) and (3) the decrease in the specific volume of DOC due to increase in ionic strength of the solution (Benedetti et al 1996).
Fig:6.4 a Log pCO$_2$ Vs Carbonate Minerals POM 2007
Fig 6.4 b Log pCO₂ Vs Carbonate Minerals PRM 2007
**Fig 6.4 c** Log pCO₂ Vs Carbonate Minerals PRM 2009
Fig. 6.4 Log pCO$_2$ Vs Carbonate Minerals POM 2009
The ground water pH decreases when pCO$_2$ increases. The degree of dissociation of the organic matter and functional groups depends largely on the pH of the solution. At higher pH, the mutual repulsion of the negatively charged sites causes the molecule with multiple functional groups to adopt a stretched configuration. As the pH of the solution is lowered and some of the charged sites are neutralized, a reduction in intra-molecular repulsion is predicted, resulting in a contraction of the polymer chain. Engebretson et al (1996) defined an association index for humic acids using fluorescence anisotropy. This association index is a quantitative parameter for estimating the polymer contraction. They found that the association index increases with decreasing pH, consistent with a structural contraction of the humic acid molecules. Another factor affecting the characteristics of DOC is the ionic strength. Murphy and Zacharia (1995) and Benedetti et al (1996) found that the specific volume of humic substances is strongly depending on the ionic strength. Several attempt have been made to model electrostatic interactions of the humic substances with organic ligands and cations (Tipping and Hurley, 1992; Marinsky and Ephraim, 1986; De wit et al., 1990, 1993; Bartschart et al., 1992; Barak and Chen, 1992; and Milne et al., 1995)
6.6.0 INVERSE MODELLING

A model is a subject of the selected phases that satisfies all the selected constraints. The model is of the form.

\[
\text{Initial water + “Reactant Phases”} \rightarrow \text{Final Water + “Product Phases”}
\]

The modeling assumes that the selected initial water mix is of some proportion, with or without further mineral water reactions. The fraction of each initial water mixed to produce the final water is displayed in a mixing case. In this pathway 28 is considered as the initial and 29 as the final solution. For data input to PHREEQC, identifiers in the INVERSE_MODELING data block were used for the selection of aqueous solutions 28 to 29, default uncertainty limits was selected, reactant phases include Halite, Calcite, Aragonite, dolomite, magnesite, anhydrite and gypsum. The phases were selected after deriving the SI of the groundwater with respect to these minerals. Range calculations were determined to 1000(-range) and minimal models were opted. Aqueous solution compositions are defined with the SOLUTION, SOLUTION_SPREAD, data block and reactants were defined with PHASES or EXCHANGE_SPECIES data blocks.

The output of the run has evolved nine different types of models giving their respective solution fractions and Phase mole transfer.
6.7.0 Models

Among the samples of post monsoon 2009; 28 was take as the initial solution and sample 29 as the final solution. The results of these models were then compared with the saturation index tables of the initial and final solution (Table 6.3). The study of the SI of minerals indicates that there is addition of phase moles noted in minerals like, Aragonite, Calcite, Dolomite, Gypsum and Anhydrite. The order of the dominance of Saturation is in the following order Dolomite $>$ Calcite $>$ aragonite $>$ Gypsum $>$ anhydrite. The saturation index table shows dissolution of all the mineral phases though certain of them are in the positive saturations. Depending upon the significant dissolutions the Saturation index of different phases, the constraints and uncertainties were determined.

The six models were obtained Table 6.4 are calibrated to achieve the apt field model by establishing the relationships. The addition and removal are considered as dissolution and precipitation of the phases from the system. This is derived by the positive and negative symbols respectively, in the phase mole transfer. Hence, dissolution is noted by positive values in phase mole transfer. Thus examining the models all the models have positive phase mole transfer but the higher amount of phase mole transfer was noted in Dolomite and Anhydrite and these two were represented in the model 4. Hence, model 4 is believed to be the most apt model form the list obtained.
<table>
<thead>
<tr>
<th>Phase</th>
<th>Solution 1</th>
<th>Solution 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anhydrite</td>
<td>-2.44</td>
<td>-2.25</td>
</tr>
<tr>
<td>Aragonite</td>
<td>1.07</td>
<td>1.16</td>
</tr>
<tr>
<td>Calcite</td>
<td>1.22</td>
<td>1.31</td>
</tr>
<tr>
<td>Dolomite</td>
<td>2.64</td>
<td>2.95</td>
</tr>
<tr>
<td>Fluorite</td>
<td>-3.99</td>
<td>-3.91</td>
</tr>
<tr>
<td>Gypsum</td>
<td>-2.22</td>
<td>-2.03</td>
</tr>
<tr>
<td>Halite</td>
<td>-5.11</td>
<td>-5.11</td>
</tr>
</tbody>
</table>

**Table: 6.3 Models comparison**
<table>
<thead>
<tr>
<th>Model 1</th>
<th>Model 2</th>
<th>Model 3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Phase Mole Transfers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anhydrite CaSO₄</td>
<td>1.774e-004</td>
<td>Anhydrite CaSO₄</td>
</tr>
<tr>
<td>Calcite CaCO₃</td>
<td>1.153e-004</td>
<td>Aragonite CaCO₃</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Model 4</th>
<th>Model 5</th>
<th>Model 6</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Phase Mole Transfers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anhydrite CaSO₄</td>
<td>2.488e-004</td>
<td>Gypsum CaSO₄·2H₂O</td>
</tr>
<tr>
<td>Dolomite CaMg(CO₃)₂</td>
<td>4.380e-005</td>
<td>Calcite CaCO₃</td>
</tr>
</tbody>
</table>

**Table: 6.4** Six type of Models
<table>
<thead>
<tr>
<th>Input</th>
<th>Initial solution (in moles)</th>
<th>Modeled solution (in moles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.400e+000</td>
<td>8.422e+000</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>9.838e-003</td>
<td>1.004e-002</td>
</tr>
<tr>
<td>C(4)</td>
<td>9.545e-003</td>
<td>9.660e-003</td>
</tr>
<tr>
<td>Ca</td>
<td>1.365e-003</td>
<td>1.658e-003</td>
</tr>
<tr>
<td>Cl</td>
<td>1.879e-002</td>
<td>1.874e-002</td>
</tr>
<tr>
<td>F</td>
<td>2.637e-006</td>
<td>2.637e-006</td>
</tr>
<tr>
<td>K</td>
<td>5.189e-004</td>
<td>5.189e-004</td>
</tr>
<tr>
<td>Mg</td>
<td>2.597e-003</td>
<td>2.597e-003</td>
</tr>
<tr>
<td>Na</td>
<td>2.144e-002</td>
<td>2.144e-002</td>
</tr>
<tr>
<td>S(6)</td>
<td>6.258e-004</td>
<td>8.433e-004</td>
</tr>
</tbody>
</table>

**Table: 6.5** Comparison of Modeled Solution
Any model run requires a validity and in order to check the validity of the model, the composition of the solution 2 is plotted as a bar diagram against the modeled value. The variations in the major and minor ions with the original solution 2 and that of the modeled value are minimal. The total error percentages were calculated to be 0.61% (the difference in the TDS/Sum of TDS of both the solutions).