

## CARBONATE CHEMISTRY AND CALCIUM CARBONATE SATURATION STATE OF RURAL WATER SUPPLY PROJECTS IN NEPAL

S. R. Panthi

Department of Water Supply and Sewerage, Kathmandu, Nepal  
E-mail: sudanraj@hotmail.com

### ABSTRACT

A mathematical model has been developed to analyze the saturation state and other condition of water, after CO<sub>2</sub> equilibrium attained with air and three phase equilibrium between dissolved carbonic species, CaCO<sub>3</sub> and CO<sub>2</sub> in the air at different temperature and measured values of alkalinity, Ca<sup>2+</sup> concentration and pH. Ionic strength can be either calculated with concentration of all cations and anions in water or just it can be approximated with help of total dissolved solids (TDS). Davies equation has been used for calculating activity coefficients. Acid-base equilibrium reactions with in water phase, CO<sub>2</sub> dissolution and exsolution reactions between atmosphere and water (Henry's law) and CaCO<sub>3</sub> dissolution and precipitation equilibrium equations have been used in the formulation of model. The model allows determining the initial and final (after gaining equilibrium between atmosphere) saturation state of water with respect to CaCO<sub>3</sub> either by calculating the Ca<sup>2+</sup> concentration needed for CaCO<sub>3</sub> saturation or by calculating theoretical pH, which gives the saturation for the measured Ca<sup>2+</sup> concentration and alkalinity values and getting Langelier Saturation Index (S.I.). The initial acidity and changed acidity due to the CO<sub>2</sub> exchange between air and water has been calculated with this model. The model also calculates the amount of CaCO<sub>3</sub> that will precipitate in one litre of water under suitable conditions. A trial and error method has been applied to calculate such three-phase equilibrium condition with a constant difference in alkalinity and Ca<sup>2+</sup> concentration. With help of this model, 36 sample water supply projects from Nepal have been studied and it is found that, there is a great potential of calcium carbonate scaling in 18 projects. It concludes that most of the water supply projects in Nepal are facing Calcium carbonate scaling problem.

**Keywords:** Calcium carbonate; Scaling; Saturation Index; CO<sub>2</sub> equilibrium

### 1. INTRODUCTION

Calcium carbonate is one of the most common scale components found in the source of drinking water in Nepal. Most of the ground water sources, which are considered safe for drinking may rich in Ca<sup>2+</sup> ion concentration. Several major limestone deposits have been identified as the natural source of the CaCO<sub>3</sub>.

Generally in ground water sources which are rich in dissolved  $\text{CO}_2$ ,  $\text{CaCO}_3$  is found in soluble form as  $\text{Ca}(\text{HCO}_3)_2$ . During the water supply system  $\text{Ca}(\text{HCO}_3)_2$  loses the excess amount of  $\text{CO}_2$  from the water and a corresponding amount of  $\text{Ca}(\text{HCO}_3)_2$  is deposited as the scale form of insoluble  $\text{CaCO}_3$  and  $\text{CO}_2$ , until the equilibrium between  $\text{Ca}(\text{HCO}_3)_2$  and the  $\text{CO}_2$  in the water is restored. Although calcium does not show any adverse effect on human health, it promotes the carbonate scale formation and that impairs water supply by blockage of valves, pumps and pipelines, imparts an alkali taste to the water and can cause other aesthetic problems. More than 50% of total drinking water supply projects in Nepal have been affected with calcium carbonate scaling problems.

Although there are many types of mechanisms to remove calcium from water, most of the projects, which are situated in the remote parts of the country, for them the conventional treatment methods are not technically and economically feasible.

In order to control a potential scale problem, it is important to know where and how much  $\text{CaCO}_3$  scale will be deposited in a water supply system. Many computer models have been developed to predict the thermodynamic tendency of precipitation, but kinetics has been neglected due to lack of reliable kinetic data (Dawe, R.A. and Zhang Yuping [2]).  $\text{CaCO}_3$  scaling is a rather forward chemical process governed by four key factors; (1) the calcium ( $\text{Ca}^{2+}$ ) concentration, (2) the concentration dissolved inorganic carbon (DIC), (3) the pH and (4) the availability of nucleation sites (Kile et al. [4]; Castanier et al. [1]). Generally the scaling inside the pipeline is not found immediately after passing the supersaturated water through it. Carbonate scale is not started to be formed even the water is supersaturated with  $\text{CaCO}_3$  until nucleation has occurred, usually by heterogeneous mechanisms (Nancollas and Reddy, [6]; Vetter, O.J., [9]). Mass exchanges across the liquid solid interface can be described by general mechanism of heterogeneous kinetics taking into account that, where as carbonate dissolution occurs in a single step, precipitation generally involves two stages, a seed formation that is a nucleation phase followed by crystal growth phase (Roques Henry, [7]). To start the seed formation it is necessary that small crystals have to be present in the supersaturated solution and the process of crystallization can be started. Once the seed crystal is there, ions leave the solution under the influence of electric field surrounding the ions already in the lattice of the seed crystal. Once the scale starts to deposit, different factors will control the growth rate.

The aim of the study is to predict the saturation state of a drinking water supply projects in Nepal and to find the potentiality of calcium carbonate scaling. For this purpose a mathematical model has been developed in excel file. This model is very easy to use and can help for a quick decision about selection of new source for a water supply system.

## 2. MODELING OF FRESH WATER

The water is generally considered as fresh water when mostly it has  $\text{Ca}^{2+}$  as cation and  $\text{HCO}_3^-$  as anion. The carbonic species in water is defined by five basic parameters:  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{OH}^-$  and  $\text{H}^+$ . Carbon dioxide enters the water partly direct from the atmosphere, and partly with precipitation and other inputs, but largely due to infiltration through the soil as well as by the metabolic activity of the organisms in the water. The carbon dioxide dissolved into water exist not only dissolved  $\text{CO}_2$  but also as carbonic acid,  $\text{H}_2\text{CO}_3$ , which is then dissociated to  $\text{H}^+$  and  $\text{HCO}_3^-$ .

### 2.1 Equilibrium equations

The following equilibrium has therefore to be considered:



With ionization constant,

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]} \quad (3)$$

Since a small fraction ( $\approx 0.25\%$ ) of the total  $\text{CO}_2$  dissolving into water is hydrolyzed to  $\text{H}_2\text{CO}_3$ , that fraction which is virtually unaffected by temperature and pH (Loewenthal and Marais [5]). Here we are using the concentration of carbonic acid  $[\text{H}_2\text{CO}_3^*]$ , which is the sum of the concentration of  $\text{H}_2\text{CO}_3$  and dissolved  $\text{CO}_2$  and that is given by

$$[\text{H}_2\text{CO}_3^*] = [\text{H}_2\text{CO}_3] + [\text{CO}_2] \quad (4)$$

In a similar way one can write the equilibrium for  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ .



With ionization constant

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (6)$$

The ionization of water is conventionally written as:



and the ionization constant for this reaction is given by

$$K = \frac{[H^+] \cdot [OH^-]}{[H_2O]} \quad (8)$$

From experimental work K is found to be an extremely small quantity,  $1.8 \times 10^{-16}$  moles/liters at 25°C. As K is small the fraction of H<sub>2</sub>O that ionizes is negligible compared with the unionized fraction. The unionized mass of H<sub>2</sub>O can be taken as equal to the total water mass,

$$\begin{aligned} [H_2O] &= \frac{\text{mass of 1 liter of water}}{\text{gram molecular weight}} \\ &= 1000/18 \\ &= 55.5 \text{ moles per liter} \end{aligned}$$

$$\begin{aligned} [H^+] \cdot [OH^-] &= K \times [H_2O] \\ &= 1.8 \times 10^{-6} \times 55.5 \\ &= 1.0 \times 10^{-14} \end{aligned}$$

i.e.

$$[H^+] \cdot [OH^-] = K_w = 10^{-14} \text{ at } 25^\circ\text{C} \quad (9)$$

The value of  $K_w$  is a function of temperature and ionic strength.

In pure water  $[H^+] = [OH^-] = 10^{-7}$  moles per litre at 25°C

$$\text{i.e. } \text{pH} = -\log_{10}(H^+) = 7 \text{ for pure water} \quad (10)$$

## 2.2 Influence of temperature and ionic strength

Two factors influence the equilibrium concentration of the species in the carbonic system, i.e. temperature and ionic strength.

### 2.2.1 Temperature

Ionization constants  $K_1$ ,  $K_2$ , and  $K_w$  are temperature dependent and are given by different equations as follows:

$$\text{p}K_1 = (17052/T) + 215.21 \log_{10}T - 0.12675 T - 545.56 \quad (\text{Shadlovsky \& McInnes, [8]}) \quad (11)$$

In this equation, T is in Kelvin (K) and it was determined for the range 273 K to 311 K.

$$\text{p}K_2 = (2902.39/T) + 0.02379 T - 6.498 \quad (\text{Harned \& Scholes, [3]}) \quad (12)$$

T is in Kelvin and it was determined for the range 273 K to 323 K.

$$pK_w = (4787.3/T) + 7.1321 \log_{10}T - 0.010365 T - 22.801 \quad (\text{Harned and Hamer, [2]}) \quad (13)$$

T is in Kelvin and it was determined for the range 273 K to 333 K.

### 2.2.2 Ionic strength

Increase in ionic strength reduces the activity of the species. Consequently the equilibrium equations are correct if written in terms of activity concentrations, i.e.

$$f_i [X] = (X) \quad (14)$$

where,

$f_i$  = Activity coefficient

[X] = molar concentration of X

(X) = active concentration of ion X

Activity coefficients are readily determined in terms of the ionic strength by means of Davies equation,

$$\log(f_i) = -0.5 \times Z_i^2 \left( \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.2\mu \right) \quad (15)$$

where  $\mu$  is the ionic strength is given by;

$$\mu = \frac{1}{2} \sum C_i Z_i^2 \quad (16)$$

$C_i$  = molar concentrations of  $i^{\text{th}}$  ion in solution

$Z_i$  = ionic charge of the  $i^{\text{th}}$  ion in solution.

The determination of the ionic strength by this procedure implies extensive chemical analysis, which is not practical in the field. Fortunately, the activity coefficients are not very sensitive to ionic strength so that if only an approximate estimate of ionic strength is available, the activity factors can be determined with a degree of accuracy sufficient for most water treatment problems. Langelier (1936) established experimentally that in natural water the ionic strength (moles / litre), is closely estimated from the total inorganic dissolved solids concentration (mg/l),  $S_d$ :

$$\mu = 2.5 \times 10^{-5} S_d \quad (17)$$

This relationship is only valid for values of  $S_d$  up to 1000 mg/l. For water, gases, pure solids and uncharged ion pairs and complexes the activity is considered to be 1.

## 2.3 Solubility of solids in water

When a salt is dissolves in water, the mass that can dissolve per unit volume of liquid is limited. This limited concentration is called the solubility of the salt in the particular liquid. Comparison of solubility of calcium carbonate with different salts of calcium has shown in table 1, and it can be conclude that only calcium carbonate has an extremely low solubility. The interrelation between the solubility of the calcium compounds with the various chemical constituents in the water is complex and quantitative solutions are carried out using the theory of weak acid-base equilibria and solubility.

**Table 1.** Solubilities of different calcium salts (Loewenthal & Marais, [5])

| Calcium salt        | Formula               | Solubility as ppm of CaCO <sub>3</sub> at 0°C |
|---------------------|-----------------------|---|
| Calcium bicarbonate | Ca(HCO <sub>3</sub> ) | 1620  |
| Calcium carbonate   | CaCO <sub>3</sub>     | 15  |
| Calcium chloride    | CaCl <sub>2</sub>     | 336000  |
| Calcium hydroxide   | Ca(OH) <sub>2</sub>   | 2390  |
| Calcium sulphate    | CaSO <sub>4</sub>     | 1290  |

Ionic compounds dissolve to the point where the solution is saturated and no more solid can dissolve. The concentration of the saturated solution is termed the solubility of the substance. If an excess of salt is added to a liquid, eventually a state of dynamic equilibrium is achieved between dissolution of the solid and precipitation of the ions to the solid state. The time to reach solubility equilibrium is a complex function of various factors such as:

- The degree of saturation (under or over)
- Mixing condition in water
- Charge on the crystal seed
- Availability of crystal growth sites and
- Thermodynamic properties

### 2.3.1. Effect of temperature on the solubility product of CaCO<sub>3</sub>

The equation given by Larson and Buswall (1942), gives the value of pK<sub>sp</sub> of CaCO<sub>3</sub> in different temperature.

$$pK_{sp} = 0.01183 t + 8.03 \quad (18)$$

where t is in °C. From equation (18), one can see that as temperature increases, pK<sub>sp</sub> for CaCO<sub>3</sub> increases, that is K<sub>sp</sub> decreases.

### 2.3.2. Effect of ionic strength

It is practical convenience to express the solubility product equations in term of molar concentrations instead of active concentrations.

$$f_D [Ca^{2+}] f_D [CO_3^{2-}] = K_{sp} \quad (19)$$

where the activity coefficient  $f_D$  decreases with increase in ionic strength, hence the greater the ionic strength of a liquid, the more soluble will be the dissolving substance.

### 2.3.3. Calcium carbonate saturation and saturation index

If total alkalinity, pH, and calcium concentration of water are measured, it is possible to calculate whether or not a water is saturated with respect to calcium carbonate. Where the product of the ions exceeds the solubility product ( $K_{sp}$ ), the water is oversaturated with respect to  $CaCO_3$  and  $CaCO_3$  will precipitate. Such water will exhibit a tendency to be scale forming. Where the  $K_{sp}$  is not exceeded the water is under saturated with respect to  $CaCO_3$  and such a water will tend to scale dissolving.

By measuring alkalinity and pH, concentration of carbonic species can be established. Knowing the concentration of  $CO_3^{2-}$  ions, a theoretical  $Ca^{2+}$  concentration can be calculated. If the actual  $Ca^{2+}$  concentration is less than the theoretical concentration the water is undersaturated, if greater the water is oversaturated and  $CaCO_3$  will precipitate. The degree of saturation is expressed by saturation index SI and given as:

$$SI = \log[(Ca^{2+})(CO_3^{2-}) / K_{sp}] \quad (20)$$

Instead of using the  $CaCO_3$  concentration as the measure of over- or under- saturation, Langeier calculated the theoretical pH of the water (using the measured alkalinity and calcium concentration) at which the water would be just saturated with respect to  $CaCO_3$  and called saturated pH value,  $pH_S$ . The saturation state of a water is given by the saturation index (S.I.) or the Langelier Index which is defined as the difference between actual pH of the water and  $pH_S$ , i.e.

$$S.I. = pH_{actual} - pH_S \quad (21)$$

The Saturation Index is typically either negative or positive and rarely zero. A Saturation Index of zero indicates that the water is just saturated or "balanced" and is neither scale forming or corrosive. A negative SI suggests that the water is corrosive. Corrosive water can react with the household plumbing and metal fixtures resulting in the deterioration of the pipes and increased metal content of the water. This reaction could result in aesthetic problems, such as bitter water and stains around basins/sinks, and in many cases elevated levels of toxic metals. A positive SI indicates that water may be scale forming and a probably required to overcome the problem.

## 2.4. Effect on alkalinity and acidity by adding CO<sub>2</sub> gas

### 2.4.1. Alkalinity

Proton balance equation for CO<sub>2</sub> addition:

$$\Delta H^+ = \Delta HCO_3^- + \Delta CO_3^{2-} + \Delta OH^-$$

i.e.

$$\Delta HCO_3^- + \Delta CO_3^{2-} + \Delta OH^- - \Delta OH^- = 0$$

$$\text{i.e. } \Delta \text{Alkalinity} = 0 \quad (22)$$

Thus if CO<sub>2</sub> is added to water, Alkalinity does not change.

### 2.4.2. Acidity

Mass balance equation for CO<sub>2</sub> addition is developed as follows:

$$[CO_2]_{\text{added}} = \Delta [H_2CO_3^*] + \Delta [HCO_3^-] + \Delta [CO_3^{2-}]$$

and rewriting this equation in terms of equivalent concentration:

$$\{CO_2\}_{\text{added}} = \Delta \{H_2CO_3^*\} + 2\Delta \{HCO_3^-\} + \Delta \{CO_3^{2-}\}$$

and with concentrations expressed in ppm as CaCO<sub>3</sub>:

$$\begin{aligned} CO_{2\text{added}} &= \Delta H_2CO_3^* + 2\Delta HCO_3^- + \Delta CO_3^{2-} \\ \text{i.e. } CO_{2\text{added}} &= \Delta H_2CO_3^* + \Delta HCO_3^- + \Delta HCO_3^- + \Delta CO_3^{2-} \\ \text{i.e. } CO_{2\text{added}} &= \Delta H_2CO_3^* + \Delta HCO_3^- + \Delta H^+ - \Delta OH^- \\ \text{i.e. } CO_{2\text{added}} &= \Delta \text{Acidity} \end{aligned} \quad (23)$$

## 2.5. Kinetics of CaCO<sub>3</sub> scaling

To study the kinetics of CaCO<sub>3</sub>, it is necessary to know about three general types of equilibrium of carbonic species.

### 2.5.1. Single phase equilibrium

In case of single phase or aqueous equilibrium it is assumed that all chemicals are infinitely soluble and occurred only in the dissolved phase (undersaturated with respect to CaCO<sub>3</sub>). So it is assumed that no CaCO<sub>3</sub> precipitation occurs from the water and there should not be any exchange of CO<sub>2</sub> gas between water and air.

### 2.5.2. Two phases equilibrium

Two phases or solid aqueous phases equilibrium phenomena are quite important to deal with CaCO<sub>3</sub> scaling problem inside the pipelines. The most important part, that is to reduce the concentration of Ca<sup>2+</sup> ions to acceptable limit before entering the pipelines. In practice this is possible by precipitating Ca<sup>2+</sup> from water as solid CaCO<sub>3</sub>.



In this two-phase (solid and liquid) process, solubility of  $\text{CaCO}_3$  is important parameter.

### 2.5.3. Three phases equilibrium

Problems involving equilibrium between three phases occur in the various structures like intakes, service reservoirs and break pressure tanks of water supply projects, in which the water is supposed to be in contact with air (containing  $\text{CO}_2$ ).  $\text{CO}_2$  either enters or leaves the water depending on the partial pressure of  $\text{CO}_2$  in water and air (Henry's law). Total  $\text{CO}_2$  transfer will be dependent to other factors such as the degree of turbulence and the residential time of water.  $\text{CO}_2$  change affects both acidity and pH of water and could result in either oversaturation or undersaturation. In case of calcite water oversaturation with  $\text{CaCO}_3$  is result due to  $\text{CO}_2$  expelled by water and finally resulting the scaling problems in side the pipeline. Three phases equilibrium then involves equilibria reactions between the dissolved  $\text{Ca}^{2+}$  ions,  $\text{CaCO}_3$  solid and  $\text{CO}_2$  gas.

## 2.6. Equilibrium between $\text{CO}_2$ in the air and carbonic species in water

Carbon dioxide exchange between water and atmosphere takes place until the partial pressure in the two phases is equal. In the process of advancement of this equilibrium the pH in the water changes and there is a redistribution of dissolved carbonic concentrations, i.e. a change in the dissolved  $\text{CO}_2$  concentration occurs and more  $\text{CO}_2$  is exchanged with air. The pH at which the equilibrium is established depends on the alkalinity of water.

For equilibrium between dissolved and atmospheric  $\text{CO}_2$  at a particular partial pressure of  $\text{CO}_2$  ( $P_{\text{CO}_2}$ ), the concentration of dissolved  $\text{CO}_2$  is defined by Henry's Law as:

$$[\text{CO}_2] = K'_{\text{CO}_2} \cdot P_{\text{CO}_2} \quad (24)$$

$K'_{\text{CO}_2}$  is Henry's law constant which is temperature dependent and  $P_{\text{CO}_2}$  is partial pressure of  $\text{CO}_2$  in the atmosphere.

Since the ration  $[\text{H}_2\text{CO}_3^*] / [\text{CO}_2]$  is constant and temperature independent in temperature range  $0^\circ\text{C}$  to  $50^\circ\text{C}$  (Loewenthal & Maries, [5]),

$$[\text{H}_2\text{CO}_3^*] = K_{\text{CO}_2} \cdot P_{\text{CO}_2} \quad (25)$$

The constant  $K_{\text{CO}_2}$  is temperature dependent and given by two linear functions (Loewenthal & Maries, [5]);

$$pK_{\text{CO}_2} = 1.12 + 0.0138 \cdot t \quad \text{for the range } 0^\circ\text{C} \text{ to } 35^\circ\text{C} \quad (26)$$

$$pK_{\text{CO}_2} = 1.36 + 0.0069 \cdot t \quad \text{for the range } 35^\circ\text{C} \text{ to } 80^\circ\text{C} \quad (27)$$

For CO<sub>2</sub> equilibrium between atmosphere and water, alkalinity is directly related to pH (Weber and Stumm, 1963). Well known Modified Caldwell-Lawrence Diagrams give a nomogram of pH against alkalinity for CO<sub>2</sub> equilibrium between air and water. During this work, for the purposes of analysis the available range of the diagrams are not sufficient, further more for different temperatures and ionic strengths, a large numbers of diagrams are needed which is not convenient to use. For the entire reasons a mathematical model in Excel has been developed.

## 2.7. Description of the model

The necessary input data for the model are: temperature, pH, alkalinity, Ionic strength and calcium ion concentration. If all cation and anion concentrations are known, one can calculate the ionic strength using the model. The calculation procedure is an interactive one involving the following successive steps:

- Total species concentrations can be used to calculate the initial ionic strength and the starting activity coefficients were calculated with equation (15).
- First the dissociation constant pK<sub>1</sub> has been calculated with the help of equation (11), and then the value of K<sub>1</sub> is adjusted for activity coefficient effects (K<sub>1</sub>'), dividing by square of activity co-efficient. Generally alkalinity and carbonic species are expressed as ppm CaCO<sub>3</sub> unit, hence in this case one can modified the value of K<sub>1</sub> as,

$$K_1' = \frac{H^+ / (5 * 10^4) \times HCO_3^- / (5 * 10^4)}{H_2CO_3^* / 10^5}$$

i.e.,

$$\frac{H^+ \cdot HCO_3^-}{H_2CO_3^*} = K_1' * 2.5 * 10^4 = K_{c1}' \quad (28)$$

Similarly the dissociation constant, K<sub>2</sub> and K<sub>w</sub> and the solubility product K<sub>s</sub> are converted to effective values as K<sub>2</sub>', K<sub>w</sub>' and K<sub>s</sub>' by taking into consideration of active concentrations. Further more if units of all the carbonic species are in ppm as CaCO<sub>3</sub>, these concentrations can be rewritten as:

$$K_2' = \frac{H^+ / (5 * 10^4) \times CO_3^{2-} / 10^5}{HCO_3^- / (5 * 10^4)}$$

$$\frac{H^+ \cdot CO_3^{2-}}{HCO_3^-} = K_2' * 10^5 = K_{c2}' \quad (29)$$

Similarly,

$$K_w' = H^+ / (5 * 10^4) \times OH^- / (5 * 10^4);$$

$$H^+ \cdot OH^- = K_w' * 25 * 10^8 = K_{cw}' \quad (30)$$

$$K_s' = CO_3^{2-} / 10^5 \times Ca^{2+} / 10^5$$

$$Ca^{2+} \cdot CO_3^{2-} = K_s' * 10^{10} = K_{cs}' \quad (31)$$

(c) Henry's constant for CO<sub>2</sub>, K<sub>co2</sub> is given by the equations (26) or (27), for a given temperature. When the concentration of H<sub>2</sub>CO<sub>3</sub> is expressed as ppm CaCO<sub>3</sub>

$$H_2CO_3^* = K_{co2} \cdot P_{co2} * 10^5 = K_{cco2} \cdot P_{co2} \quad (32)$$

There will be three different stages of calculations as followings:

### 2.7.1 Before equilibrium with air (stage I)

According to simple definition as;

$$[\text{Alkalinity}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \quad (33)$$

When concentration expressed in equivalent concentrations or as ppm CaCO<sub>3</sub>,

Then,

$$\text{Alkalinity} = \text{HCO}_3^- + \text{CO}_3^{2-} + \text{OH}^- - \text{H}^+ \quad (34)$$

$$\text{Acidity} = \text{H}_2\text{CO}_3^* + \text{HCO}_3^- + \text{H}^+ - \text{OH}^- \quad (35)$$

By substituting the concentration of species in term of H<sup>+</sup>, K'<sub>cs</sub>, K'<sub>c2</sub>, K'<sub>cw</sub> and Ca<sup>2+</sup> it follows;

$$\text{Alkalinity} = \frac{H^+ \cdot K'_{cs}}{K'_{c2} \cdot Ca^{2+}} + \frac{K'_{cs}}{Ca^{2+}} + \frac{K'_{cw}}{H^+} - H^+$$

$$Ca^{2+} = \frac{K'_{cs} \left[ \frac{H^+}{K'_{c2}} + 1 \right]}{\text{Alkalinity} - \frac{K'_{cw}}{H^+} + H^+} \quad (36)$$

If the actual Ca<sup>2+</sup> concentration is higher than this calculated value, the water is oversaturated with respect to CaCO<sub>3</sub>, otherwise undersaturated. One can calculate the theoretical pH, i.e., pH<sub>s</sub> and the Langelier Saturation Index described by equation (21).

Calculation of pH<sub>s</sub>

Solving equation (36) for H<sup>+</sup>

$$H^+ = \frac{1}{2 * (K_{cs} / K_{c2} * Ca^{2+} - 1)} [(Alk - K_{cs} / Ca^{2+}) + \sqrt{((Alk - K_{cs} / Ca^{2+})^2 - 4 * (K_{cs} / K_{c2} * Ca^{2+} - 1) * K_{cw})}] \quad (37)$$

Calculation of acidity

When two parameters; alkalinity and pH are measured, acidity can be calculated using equilibria relationships.

$$\text{Acidity} = HCO_3^- + H^+ \cdot HCO_3^- / K'_{c1} + H^+ - OH^-$$

This equation gives,

$$HCO_3^- = \frac{\text{Acidity} - H^+ + K'_{cw} / H^+}{1 + H^+ / K'_{c1}} \quad (38)$$

From equations (29) and (34)

$$\text{Alkalinity} = HCO_3^- + K'_{c2} \cdot HCO_3^- / H^+ + OH^- - H^+$$

Substituting equation (30), into this equation and solving for HCO<sub>3</sub><sup>-</sup>:

$$HCO_3^- = \frac{\text{Alkalinity} - K'_{cw} / H^+ + H^+}{1 + K'_{c2} / H^+} \quad (39)$$

Equating equations (38) and (39),

$$\text{Acidity} = \left[ \frac{1 + H^+ / K'_{c1}}{1 + K'_{c2} / H^+} \right] \times (\text{Alkalinity} - K'_{cw} / H^+ + H^+) + H^+ - K'_{cw} / H^+ \quad (40)$$

**2.7.2. After equilibrium with atmosphere (Stage II)**Alkalinity

Loss or gain of CO<sub>2</sub> by water does not change the alkalinity.

Calculation of pH

Substituting the equations (28), (29), (30) and (32) in equation (33),

$$\text{Alkalinity} = \frac{K_{cCO_2} \cdot P_{CO_2} \cdot K'_{c1}}{H^+} \left(1 + K'_{c2} / H^+\right) + K'_{cw} / H^+ - H^+ \quad (41)$$

$$H^+ = \frac{1}{2 \cdot \text{Alk}} \left[ P_{CO_2} \cdot K_{cCO_2} \cdot K'_{c1} + K'_{cw} + \sqrt{(P_{CO_2} \cdot K_{cCO_2} \cdot K'_{c1})^2 - 4 \cdot \text{Alk} \cdot P_{CO_2} \cdot K'_{c1} \cdot K'_{c2}} \right] \quad (42)$$

### Calculation of acidity

Acidity is calculated with same equation (40), with new pH Value. CO<sub>2</sub> exchange between air and water is exactly the same as the change in acidity, as explained by equation (23). An increase in acidity means, CO<sub>2</sub> is absorbed by the water. Acidity will decrease when CO<sub>2</sub> is expelled from the water to the air.

When CO<sub>2</sub> is exchanged with the atmosphere, the acidity changes resulting into a new equilibrium point with new pH value. For this point, the Ca<sup>2+</sup> concentration required for CaCO<sub>3</sub> saturation may differ from the initial one and a new saturation state will appear. The calcium concentration required for saturation can be calculated with help of equation (36).

#### **2.7.3. During precipitation is occurring (Stage III)**

When oversaturated water starts to precipitation of CaCO<sub>3</sub>, the alkalinity starts to decrease and the water is no longer in equilibrium with the CO<sub>2</sub> in the air. The water attains a state of three-phase equilibrium between dissolved carbonic species, precipitated CaCO<sub>3</sub> and CO<sub>2</sub> in air. After three phase equilibrium, new values of alkalinity, Ca<sup>2+</sup> concentration, acidity and pH can be calculated with a trial and error method. Because the difference between alkalinity and Ca<sup>2+</sup> concentration remains constant, and one can select a set of alkalinity and Ca<sup>2+</sup> concentration so that the difference (Alk-Ca<sup>2+</sup>) remains the same as it's initial value. Final values of alkalinity and Ca<sup>2+</sup> concentration are those values, for which the pH given by the equation (42), and selected alkalinity will give a Ca<sup>2+</sup> concentration required for saturation equal to the selected one. Total CaCO<sub>3</sub> precipitated is given by the change in either alkalinity or calcium concentration.

### **3. Results and discussion**

The program developed in this work was applied to 36 projects at different temperatures to perform saturation state of rural drinking water supply projects. Table 2 shows the result after analysis.

**Table 2.** Calcium carbonate scaling situation in 36 sample projects

| S.N. | Project's Source name      | Temp (°C) | Total hardness (CaCO <sub>3</sub> mg/l) | Ca <sup>2+</sup> (CaCO <sub>3</sub> mg/l) | Alkalinity (CaCO <sub>3</sub> mg/l) | pH  | SI Initial | SI Final | Type* | Ca <sup>2+</sup> preci. mg/l | Final Alk. (CaCO <sub>3</sub> mg/l) |
|------|----------------------------|-----------|---|---|-------------------------------------|-----|------------|----------|-------|------------------------------|-------------------------------------|
| 1    | Deep tube well-1, Attaria  | 24.5      | 185                                     | 141                                       | 213.2                               | 7.4 | -0.02      | 1.43     | C     | 116                          | 97.2                                |
| 2    | Deep tube well-2, Attaria  | 20.5      | 313                                     | 241                                       | 324.6                               | 6.9 | -0.18      | 1.9      | C     | 215.3                        | 109.3                               |
| 3    | Deep tube well-3, Attaria  | 21        | 327                                     | 245                                       | 329.9                               | 7   | -0.06      | 1.94     | C     | 220.2                        | 109.7                               |
| 4    | Shallow tube well, Attaria | 21        | 373                                     | 335                                       | 375.6                               | 6.9 | 0.03       | 2.18     | B     | 292.6                        | 83                                  |
| 5    | Geru Khola, Bandipur       | 21        | 14                                      | 9   | 17.8                                | 6.4 | ~          | ~        | A     | 0                            |                                     |
| 6    | Jupra Khola, Surkhet       | 23        | 31                                      | 21  | 33                                  | 7   | -2.17      | -1.11    | A     | 0                            |                                     |
| 7    | Latikoilee, Surkhet        | 29        | 101                                     | 61  | 81.2                                | 6.8 | -1.32      | 0.38     | C     | 18.1                         | 63.1                                |
| 8    | Itram Khola, Surkhet       | 24.5      | 100                                     | 69  | 93.9                                | 7.9 | -0.19      | 0.43     | C     | 23.1                         | 70.8                                |
| 9    | Doctor Khola-Fikkal, Illam | 20        | 11                                      | 6   | 17.8                                | 7.5 | ~          | ~        | A     | 0                            |                                     |
| 10   | Bagbire-Fikkal, Illam      | 21        | 6                                       | 3   | 10.1                                | 7.8 | ~          | ~        | A     | 0                            |                                     |
| 11   | Dug Well, Parsa-Chitwan    | 27.5      | 52                                      | 38  | 36.3                                | 6   | -2.73      | -0.59    | A     | 0                            |                                     |
| 12   | Shallow TW-1, Chitwan      | 27.5      | 330                                     | 207                                       | 313.4                               | 7.1 | 0.08       | 2.00     | B     | 193.2                        | 120.2                               |
| 13   | Shallow TW-2, Chitwan      | 27.5      | 78                                      | 55  | 80.3                                | 6.4 | -1.8       | 0.28     | C     | 13.1                         | 67.2                                |
| 14   | Shallow TW-3, Chitwan      | 25        | 124                                     | 62  | 126.9                               | 6.8 | -1.19      | 0.65     | C     | 35.1                         | 91.8                                |
| 15   | Shallow TW-4, Chitwan      | 25        | 226                                     | 128                                       | 199.4                               | 7.3 | -0.84      | 0.68     | C     | 103.3                        | 96.1                                |
| 16   | D. Well, Ratna N.-Chitwan  | 25        | 221                                     | 119                                       | 202                                 | 6.9 | -0.6       | 1.33     | C     | 97.8                         | 104.2                               |
| 17   | Bijayapur Khola, Kaski     | 21        | 140                                     | 79  | 130                                 | 8.3 | 0.34       | 0.66     | B     | 41.6                         | 88.4                                |
| 18   | Khudi, Kaski               | 24        | 13                                      | 6   | 20.4                                | 6.4 | ~          | ~        | A     | 0                            |                                     |
| 19   | Baruwa Khola Udayapur      | 29        | 192                                     | 98  | 180.2                               | 7.9 | 0.34       | 1.26     | B     | 80.2                         | 100                                 |
| 20   | Gaighat rvt., Udayapur     | 32        | 187                                     | 98  | 177.7                               | 7.9 | 0.4        | 1.33     | B     | 82                           | 95.7                                |
| 21   | Gaighat-mul, Udayapur      | 20        | 222.2                                   | 121                                       | 181.8                               | 8.5 | 0.85       | 1.11     | B     | 86.5                         | 95.3                                |
| 22   | Bagale pani, Belghundi     | 23        | 169.7                                   | 101                                       | 161.6                               | 8.3 | 0.59       | 1.01     | B     | 70.1                         | 91.5                                |
| 23   | Dadikat, Bejhundi          | 23        | 232.3                                   | 101                                       | 218.2                               | 8   | 0.42       | 1.26     | B     | 85.8                         | 132.4                               |
| 24   | Gwang, Sindhulimadhi       | 13        | 102                                     | 54  | 68                                  | 7.7 | -0.9       | -0.3     | A     | 0                            |                                     |
| 25   | Boring 1, Dhalkebar        | 25        | 80.8                                    | 51  | 86.9                                | 7.4 | -0.85      | 0.24     | C     | 11.6                         | 75.3                                |
| 26   | Boring 2 (JADP), Dhalkebar | 25        | 72.7                                    | 43  | 74.7                                | 7.6 | -0.79      | 0.03     | C     | 1.4                          | 73.3                                |
| 27   | Dhedu Khola, Nijgadh       | 14        | 252                                     | 124                                       | 256                                 | 8.1 | 0.48       | 1.24     | B     | 103.5                        | 152.5                               |
| 28   | Boring-1, Nijgadh          | 14        | 120                                     | 80  | 120                                 | 6.7 | -1.45      | 0.40     | C     | 26.9                         | 93.1                                |
| 29   | Boring-2, Nijgadh          | 14        | 124                                     | 80  | 124                                 | 6.6 | -1.53      | 0.43     | C     | 28.9                         | 95.1                                |
| 30   | Boring-3, Nijgadh          | 14        | 81                                      | 80  | 128                                 | 6.8 | -1.32      | 0.46     | C     | 30.9                         | 97.1                                |
| 31   | Patan-Source, Tanahu       | 24        | 310                                     | 275                                       | 285                                 | 7   | -0.01      | 1.95     | C     | 219.6                        | 65.4                                |
| 32   | Patan-Reservoir, Tanahu    | 26        | 300                                     | 270                                       | 225                                 | 7.9 | 0.82       | 1.8      | B     | 117.9                        | 47.1                                |
| 33   | Ramjakot- Source, Tanhu    | 21        | 252                                     | 232                                       | 204                                 | 7   | -0.29      | 1.52     | C     | 146.3                        | 57.7                                |
| 34   | Ramjakot-Reservoir, Tanhu  | 27        | 222                                     | 204                                       | 195                                 | 7.8 | 0.56       | 1.59     | B     | 140.1                        | 54.9                                |
| 35   | Atitar-Source, Puythan     | 24        | 339                                     | 312                                       | 370                                 | 7.1 | 0.26       | 2.22     | B     | 281.3                        | 88.7                                |
| 36   | Atitar-Reservoir, Puythan  | 27        | 291                                     | 268                                       | 321                                 | 7.5 | 0.59       | 2.12     | B     | 238.7                        | 82.3                                |

\*Type A = A saturated or unsaturated water, in which no CaCO<sub>3</sub> is precipitated.

B = A saturated water, in which CaCO<sub>3</sub> is precipitated.

C = An unsaturated water becomes oversaturated with respect to CaCO<sub>3</sub> and precipitated.

Saturation description and the theoretical recommendation are given in Table 3 and it shows that treatment is needed only for 18 projects. In fact the field situation is completely different. Three projects, with saturation index more than 2 have been stopped to run due to severe scale formation. The projects with SI more than 0.5 are also suffering a lot from scaling. In the case of polythene pipe using as the distribution system, the problem of scaling depends on the smoothness of joints between two pieces of pipe. Butt joints of polythene pipe featuring having excess material melted,

certainly helps to fasten scaling of  $\text{CaCO}_3$ . Thus, for small drinking water supply projects having polythene pipe or GI pipe as distribution system, theoretical classification recommended as in table 3, may not work. For such small projects it may need of re-classification of SI, their effects and recommendation for necessary treatment.

**Table 3.** Status of drinking water supply projects according to SI- classification

| S. No. | S.I.         | No. of projects | Description    | General recommendations        |
|--------|--------------|-----------------|----------------|--------------------------------|
| 1      | <-1.00       | 5               | Corrosion      | Treatment should be considered |
| 2      | -0.5 - -1.00 | 1               | Mild corrosion | Treatment should be considered |
| 3      | 0 - -0.50    | 1               | Mild corrosion | Treatment probably not needed  |
| 4      | 0.00         | -               | Balanced       | Treatment typically not needed |
| 5      | 0.00-0.50    | 8               | Faint Coating  | Treatment typically not needed |
| 6      | 0.50-1.00    | 3               | Faint Coating  | Some aesthetic problems        |
| 7      | 1.00-2.00    | 15              | Mild scale     | Treatment should be considered |
| 8      | 2.00-3.00    | 3               | Moderate scale | Treatment should be considered |

#### 4. Conclusion

More than 80% ongoing projects have potential to be failure by scaling problem. In the context of Nepal, many water supply agencies including department of water supply and sewerage are not in position to use other costly software due to lacking of technical manpower. The developed model is very simple to use and will be useful to treat existing projects and to select new sources for water supply purpose. Solubility equilibrium is a complex function of other a few more factors such as, mixing condition, concentrations of different ions, charge on the crystal seed and availability of crystal growth sites etc, which is not considered in this model. Furthermore when precipitation is occurring the ionic strength is also changing continuously, which has not been taken into account during the calculation, nevertheless quite reasonable results have been obtained by the model.

#### REFERENCES

- [1] Castanier S, Le Metayer-Levrel G & Perthuisot JP. Carbonate precipitation and limestone genesis- the microbiological point of view. *Sediment. Geology*, PP. 126 (1-4); 9-23, 1999.

- [2] Dawe, R.A. and Zhang Y., Kinetics of calcium carbonate scaling using observation from glass micromodels. Journal of Petroleum Science & Engineering, 18, PP. 179-187, 1997.
- [3] Harned, H.S., and Hamer, W.J. The first ionization constant of  $\text{HCO}_3^-$ , Journal of the American Chem. Soc., PP. 51, 2194, 1933.
- [4] Harned, H.S., Scholes, S.R. The first ionization constant of  $\text{HCO}_3^-$ , Journal of the American Chem. Soc., PP. 63, 1706, 1941.
- [5] Kile D.E., Eberl D.D., Hoch A.R. & Reddy M.M. An assessment of calcite crystal growth mechanisms based on crystal size distributions. *Geochem. Cosmochim. Acta* 64(17); PP. 2937-2950, 2000.
- [6] Loewenthal R.E., Marais G.V.R. Carbonate chemistry of aquatic systems; Theory and application, Ann Arbor Science Publishers, Inc, Michigan USA, 1976.
- [7] Nancollas, G.H., Reddy, M.M. The kinetics of crystallization of scale forming minerals. *Journal of Petroleum Science & Engineering*, PP. 117-126, 1974.
- [8] Roques Henry. Chemical water treatment principle and practice, 1996.
- [9] Shadlovsky, T. and McInnes, D. The first ionization constant of  $\text{HCO}_3^-$ , Journal of the American Chem. Soc., PP. 59, 2304, 1935.
- [10] Vetter, O.J., Calcium carbonate scale in oilfield operations. SPE 16908, 62<sup>nd</sup> Ann. Tech. Conf. Dallas, Texas, Sept., 27-30, 1987.