Formulation Of Some Mathematical Models For The Estimations Of The Most Probable Salts Derived From The Major Mineral Constituents In Natural Water

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Abstract

By extensive studies with the quantitative status of the mineral constituents of thousands of water samples, it was found that almost in all natural waters irrespective of the surface or sub–surface sources, minimum 99.5% of the total amount of the cationic constituents are generally the contributions of 3 commonly present parameters viz. Ca, Mg and Na and that of the anionic species are same and contributed by HCO_3, Cl and SO_4 only. In the field of water works, all these major mineral substances are conventionally measured as their individual ions. But till now, no reliable and generalised methods or rules have been developed for the determination of the exact kinds of the individual salt components and their amounts from these ionic constituents normally present in water. As salt content, only the TDS (Total Dissolved Solids) parameter is frequently measured by evaporation of the water sample. But TDS can tell nothing about the kinds and amounts of the individual salts present in it. Considering the analytical importance of the estimation of the mineral substances as their individual salts, some generalised mathematical models have been developed by this research which are based on the 'hypothetical order of chemical combinations' as may occur among the ionic constituents. With the help of these models, one can easily assume the most probable salts with approximate quantities derived from the ionic constituents. In addition, approximate amount of Na content can also be estimated mathematically with simultaneous verification of the correctness of the water analysis results. The models are stated in this paper with practical illustrations and descriptions of the method of applications.

Introduction

All natural waters irrespective of the surface and sub–surface sources contain various kinds of dissolved impurities, of which, the universal presence of different mineral substances such as Ca, Mg, Na, K, Fe, HCO_3, Cl, SO_4, NO_3, SiO_2 etc. are quite common. Besides, more other elements may also be present. But

they are very small in quantities and hence normally ignored in industrial water treatment field. By extensive studies on the quantitative status of the mineral substances, it was found that almost in all natural waters, minimum 99.5% of the total amount of the cationic species are the summation of only 3 particular constituents which are Ca, Mg, and Na [1]. Similarly, 99.5% of the total anionic species are the contributions of only HCO_3, Cl and SO_4 [1]. These 6 parameters are known as major minerals of natural water significantly encountered in industrial water analysis and Deionization Process [2,3]. Absence of any one of these major constituents in water analysis report is a big shortfall and for which it is difficult to ascertain the quality characteristics the water and to verify the correctness of the analytical results [4].

All dissolved mineral constituents exist in water in ionic state and which are also conventionally estimated as ions. From these ionic results, it is not easy for one to conclude – what are the exact kinds and quantities of the individual salt components present [4] ? Only TDS parameter is measured by conventional evaporation method but it can tell nothing about any individual salts and their quantities. Whereas identification of the individual salt components is a significant aspect of water analysis.

No reliable and generalised methods or rules have been developed for finding out the above. Although some attempts were taken long ago by some water analysts to solve the problem mathematically [5], the method found valid only for some specific cases. Considering the application limit of the method and analytical importance, some generalised mathematical models have been developed and formulated by this research in the light of the aforesaid quantitative status of the major minerals. The most fundamental principles of these models are based on the "hypothetical order or priority of the chemical combination" assumed to be occurred among the major ionic constituents. The

models can be used as 'thumb rules' for the following purposes of water analysis.

1. Quantitative derivation of the most probable salts.
2. Estimation of the approx. amount of Na content mathematically.
3. Verification and assurance of the correctness or accuracy of the test result of the said major mineral constituents.

Principles

(a) For Sodium (Na^+) Estimation.

Total Salts (meq/l) $= \sum M_c = \sum M_a$ .... (A)

$$\sum M_c = \sum M_a \quad .... (B)$$

$$Q_{Na} = \sum M_a - TH \quad .... (C)$$

where, M_c – major cations (i.e. Ca^{+2}, Mg^{+2} and Na^+).

M_a – major anions (i.e. HCO_3^-, Cl^- and SO_4^{-2}).

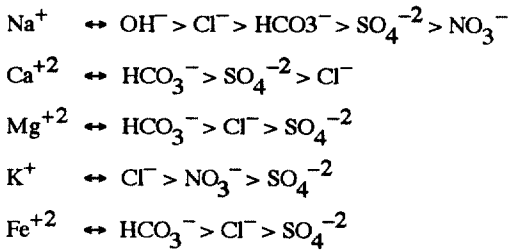TH – total hardness (i.e. $Ca^{+2} + Mg^{+2}$).

Q_{Na} – quantity of Na^+.

[In industrial water treatment field, Na is very often expressed as Na&K together [7] or vice versa. Since K is normally absent or trace level in water except sea source, hence it is ignored and only Na is encountered.]
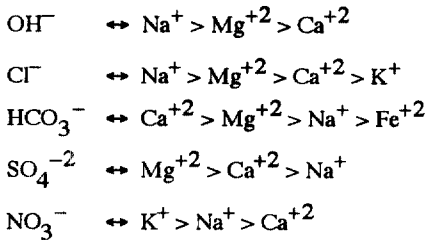
(b) For Salt Derivation.

The newly developed mathematical models for salt derivation are based on 4 fundamental principles viz.

1. Most probable priority of chemical combinations according to the following hypothetical order [5].

Cations :

$Na^+ \leftrightarrow OH^- > Cl^- > HCO3^- > SO_4^{-2} > NO_3^-$

$Ca^{+2} \leftrightarrow HCO_3^- > SO_4^{-2} > Cl^-$

$Mg^{+2} \leftrightarrow HCO_3^- > Cl^- > SO_4^{-2}$

$K^+ \leftrightarrow Cl^- > NO_3^- > SO_4^{-2}$

$Fe^{+2} \leftrightarrow HCO_3^- > Cl^- > SO_4^{-2}$

Anions :

$OH^- \leftrightarrow Na^+ > Mg^{+2} > Ca^{+2}$

$Cl^- \leftrightarrow Na^+ > Mg^{+2} > Ca^{+2} > K^+$

$HCO_3^- \leftrightarrow Ca^{+2} > Mg^{+2} > Na^+ > Fe^{+2}$

$SO_4^{-2} \leftrightarrow Mg^{+2} > Ca^{+2} > Na^+$

$NO_3^- \leftrightarrow K^+ > Na^+ > Ca^{+2}$

2. Maintenance of the ionic balance i.e. total cation concentration must be equal to total anion concentration [2,5,6] in the same unit (meq/1 or ppm as $CaCO_3$).

3. Total salinity concentration must be equal to total cation or anion concentration in the same unit.

4. No residual or negative balance of any cationic or anionic species should exist after computing for the salts resulting from the above order of the chemical combinations assumed.

(c) Rules for Salt Derivation and Estimation .

RULE – 1 (WHEN TH $\geq$ M–ALK.) :

1. Estimation of Alkali Compound as NaOH (if p–alk present in water sample).

$$Q_{NaOH} = Q_{p-alk} \cdots\cdots (1.1)$$

where, Q_{NaOH} – quantity of NaOH.

Q_{p-alk} – quantity p–alk .

Then, $R_{Na} = Q_{Na} - Q_{p-alk}$ ....(1.2)

where, R_{Na} is the residual quantity of Na which will combine with chloride (Cl) to produce NaCl either as in eq. 2.1 or 2.3.

2. Estimation of Cl–salt as NaCl.

(i) **Case–I** : when $Q_{Cl} \geq R_{Na}$.

$$Q_{NaCl} = R_{Na} \text{ or } Q_{Na} \text{ (if p–alk absent)} .. (2.1)$$

where, Q_{NaCl} is the quantity of NaCl and R_{Na} is the first residual quantity of Na after combining with p–alk as in eq. (1.2).

Then, $R_{Cl} = Q_{Cl} - R_{Na}$ .... (2.2)

where, Q_{Cl} – initial quantity of Cl^- in water sample.

R_{Cl} – first residual quantity of Cl^- after combining with R_{Na} as in eq. (2.1) and which will combine with Mg to produce $MgCl_2$ salt as in eq. (3.1) or (3.3).

(ii) **Case – II** : when $Q_{Cl} < R_{Na}$ or Q_{Na} (if p–alk absent).

$$Q_{NaCl} = Q_{Cl} \cdots\cdots (2.3).$$

Here, second residual quantity of Na after combining with Q_{Cl} is calculated as follows :

$$R'_{Na} = R_{Na} - Q_{Cl} \cdots\cdots (2.4)$$

where, R'_{Na} is the second residual quantity of Na which will now combine with SO_4 and/or NO_3 as given by eq. (9.1) and/or eq. (10).

3. Estimation of Cl – salt as $MgCl_2$.

(i) **Case – I** : when $Q_{Mg} \geq R_{Cl}$.

$$Q_{MgCl_2} = R_{Cl} \cdots\cdots(3.1).$$

where, Q_{MgCl_2} – quantity of $MgCl_2$.

R_{Cl} – first residual quantity or Cl after combining with R_{Na} or Q_{Na}.

Here, the residual quantity of Mg after combining with Cl is calculated as follows.

$$R_{Mg} = Q_{Mg} - R_{Cl} \quad \text{......(3.2).}$$

where, R_{Mg} – first residual quantity of Mg which will combine with SO_4 as in eq. (4.1) or (4.3).

Q_{Mg} – initial quantity of Mg in water sample.

(ii) **Case II** : When $Q_{Mg} < R_{Cl}$.

$$Q_{MgCl_2} = Q_{Mg} \quad \text{............ (3.3).}$$

Here, the second residual quantity of Cl^- after combination with Mg is calculated as follows.

$$R'_{Cl} = R_{Cl} - Q_{Mg} \quad \text{....... (3.4).}$$

where, R'_{Cl} – second residual quantity of Cl after combination with Mg (in eq. 3.4) which now further combines with Ca to produce $CaCl_2$ (as in eq. 7). In such case, the Ca content in water would be higher than CO_3 and HCO_3 constituents (i.e. mainly HCO_3 – alkalinity).

Otherwise a 4th cationic constituent say, Fe/Cu/Al/Zn or uncommon cationic species (if any) is to be found by a quantity equivalent to that of R'_{Cl}.

4. Estimation of SO_4 – salt as $MgSO_4$.

(i) **Case – I :** When $Q_{SO_4} \geq R_{Mg}$.

$$Q_{MgSO_4} = R_{Mg} \quad \text{.................. (4.1).}$$

where, Q_{MgSO_4} – quantity of $MgSO_4$.

R_{Mg} – quantity of first residual Mg after combining with R_{Cl} as in eq. (3.2).

Here, the residual quantity of SO_4 after combine with R_{Mg} is calculated as follows.

$$R_{SO_4} = Q_{SO_4} - R_{Mg} \quad \text{.............. (4.2).}$$

where, R_{SO_4} – first residual quantity of SO_4 which will combine with Ca as in eq. (6.1) and/or (6.3).

Q_{SO_4} – the initial quantity of SO_4 constituent in the water sample.

(ii) **Case II** : when $Q_{SO_4} < R_{Mg}$.

$$Q_{MgSO_4} = Q_{SO_4} \quad \text{.............. (4.3)}$$

Here, the second residual quantity of Mg after combination with SO_4 is calculated as follows.

$$R'_{Mg} = R_{Mg} - Q_{SO_4} \quad \text{.............. (4.4)}$$

where, R'_{Mg} is the second residual quantity of Mg which will be combining with R_{HCO_3} as in eq. (81.).

5. Estimation of HCO_3 – Salt as $Ca(HCO_3)_2$

(i) **Case – I :** When $Q_{Ca} \geq$ m–alk (in absence of p–alk).

$$Q_{Ca(HCO_3)_2} = Q_{HCO_3} \quad \text{.......... (5.1)}$$

where, $Q_{Ca(HCO_3)_2}$ – the quantity of $Ca(HCO_3)_2$ salt present in the water sample.

Q_{HCO_3} – the initial quantity of m–alk. (only CO_3 & HCO_3).

Here, the residual quantity of Ca is then calculated as follows.

$$R_{Ca} = Q_{Ca} - Q_{HCO_3} \quad \text{....... (5.2).}$$

where, R_{Ca} – first residual quantity of Ca which will be combining with R_{SO_4} and/or R'_{Cl} as in eq. (6.1) and/or eq. (6.3).

Q_{Ca} – the initial quantity of Ca measured in water sample.

(ii) **Case – II** : when, $Q_{Ca} <$ m–alk (if p–alk absent).

$$Q_{Ca(HCO_3)_2} = Q_{Ca} \quad \cdots\cdots\cdots (5.3).$$

Here, the residual quantity of m–alk (only CO_3 & HCO_3) after combining with Ca is calculated as follows.

$$R_{HCO_3} = Q_{HCO_3} - Q_{Cl} \quad \cdots\cdots\cdots (5.4)$$

where, R_{HCO_3} is the first residual quantity of m–alk (i.e. CO_3 & HCO_3) which will be combine with the last residual quantity of Mg (i.e. R'_{Mg} obtained in eq. (4.4) as in eq. (8.1).

6. Estimation of the SO_4 – salt as $CaSO_4$.

(i) **Case – I** : When $R_{Ca} \geq R_{SO_4}$.

$$Q_{CaSO_4} = R_{SO_4} \quad \cdots\cdots\cdots (6.1).$$

$$\text{or,}$$
$$= R_{Ca} \text{ (if } R_{SO_4} = R_{Ca})$$

where, Q_{CaSO_4} – quantity of $CaSO_4$
R_{SO_4} – first residual quantity of SO_4 after combination with Mg (obtained in eq. 4.1).

Here, the second residual quantity of Ca is calculated as follows.

$$R'_{Ca} = R_{Ca} - R_{SO_4} \quad \cdots\cdots\cdots (6.2).$$

where, R' is the second residual quantity of Ca which will be combining with R'_{Cl} (obtained in eq. 4.4) as in eq. 7.

(ii) **Case – II** : When $R_{Ca} < R_{SO_4}$

$$Q_{CaSO_4} = R_{Ca} \quad \cdots\cdots (6.3).$$

where, R_{Ca} is the first residual quantity of Ca as obtained in eq. (5.2).

Here, the second residual quantity of SO_4 is to be calculated as follows.

$$R'_{SO_4} = R_{SO_4} - R_{Ca} \quad \cdots (6.4).$$

where, R'_{SO_4} is the second residual quantity of SO_4 which will be combining with R'_{Na} (obtained in eq. 2.4) as in eq. 9.1

7. Estimation of Cl–salt as $CaCl_2$.

$$Q_{CaCl_2} = R'_{Cl} - R'_{Ca} \quad \cdots\cdots (7).$$

where, Q_{CaCl_2} – quantity of $CaCl_2$.

R'_{Cl} – second residual quantity of Cl as left in eq. (3.4).

R'_{Ca} – second residual quantity of Ca as obtained in eq. (6.2).

8. Estimation of HCO_3–salt as $Mg(HCO_3)_2$

(i) **Case – I** : $R_{HCO_3} = R'_{Mg}$.

$$Q_{Mg(HCO_3)_2} = R'_{Mg} = R_{HCO_3} \quad \cdots\cdots\cdots (8.1).$$

where, R'_{Mg} – second residual quantity of Mg as obtained in eq. 4.4.

R_{HCO_3} – first residual HCO_3 as left in eq. (5.4).

(ii) **Case – II** : When $R_{HCO_3} > R'_{Mg}$.

In such case, the second residual HCO_3 would be--

$$R'_{HCO_3} = R_{HCO_3} - R'_{Mg} \quad \cdots\cdots\cdots (8.2).$$

where, R'_{HCO_3} is the second residual HCO_3.

If second residual HCO_3 is found to left in any water sample analysis, then this will be combining with Na as in eq. (4.2) of Rule – 2. For such type of water, it is not suggested to apply Rule–1 but to be followed Rule–2.

9. Estimation of SO₄–salt as Na₂SO₄

(i) **Case–I** : When $R'_{SO_4} = R'_{Na}$.

$$Q_{Na_2SO_4} = R'_{Na} = R'_{SO_4} \quad \cdots\cdots\cdots (9.1).$$

where, $Q_{Na_2SO_4}$ – quantity of Na_2SO_4.

R'_{Na} – the second residual quantity of Na as obtained in eq. (2.4).

R'_{SO_4} – the second residual quantity of SO_4 as obtained in eq. (6.4).

(ii) **Case – II** : When $R'_{SO_4} < R'_{Na}$.

$$Q_{Na_2SO_4} = R'_{SO_4} \quad \cdots\cdots\cdots (9.2).$$

But in such case, the third and last residual quantity of Na is calculated as follows.

$$R''_{Na} = R'_{Na} - R'_{SO_4} \quad \cdots\cdots\cdots (9.3).$$

where, R''_{Na} is the third and last residual quantity of Na which will be finally combining with NO_3 or other minor anionic species (if any) as in eq. (10).

10. Estimation of NO₃–salt as NaNO₃

$$Q_{NaNO_3} = R''_{Na} = Q_{NO_3} \quad \cdots\cdots\cdots (10)$$

where, Q_{NaNO_3} is the quantity $NaNO_3$ subjected to the presence of NO_3 in the analysed water sample. Which has been termed as Q_{NO_3}.

RULE–2 (WHEN TOTAL HARDNESS < M–ALK)

1. Estimation of Alkali Compound as NaOH (if p–alk present in water sample).

$$Q_{NaOH} = Q_{p-alk} \quad \cdots\cdots\cdots (1.1)$$

where, Q_{NaOH} is quantity of NaOH.

Then, $R_{Na} = Q_{Na} - Q_{p-alk} \quad \cdots\cdots\cdots (1.2)$

where, R_{Na} – residual quantity of Na which will be combining with HCO_3, Cl and SO_4.

Q_{p-alk} – quantity p–alk.

2. Estimation of HCO₃–salt as Ca(HCO₃)₂.

(i) **Case – I** : When $Q_{HCO_3} \geq Q_{Ca}$.

$$Q_{Ca(HCO_3)_2} = Q_{Ca} \quad \cdots\cdots\cdots (2.1).$$

where, $Q_{Ca(HCO_3)_2}$ – quantity of $Ca(HCO_3)_2$.

Q_{Ca} – initial quantity of Ca as in water sample.

Here, the residual quantity of HCO_3 may be calculated as follows.

$$R_{HCO_3} = Q_{HCO_3} - Q_{Ca} \quad \cdots\cdots\cdots (2.2).$$

where, R_{HCO_3} – first residual quantity of HCO_3 left after combination with Ca and which will be combining with Mg, R_{Na} and Fe (if any more HCO_3 is present). However, the residual HCO_3 will first combine with Mg as in eq. (3.1).

Q_{HCO_3} – initial quantity of HCO_3 in water.

(ii) Case – II : When $Q_{HCO_3} < Q_{Ca}$.

$$Q_{Ca(HCO_3)_2} = Q_{HCO_3} \ \cdots\cdots\cdots (2.3).$$

Here, the residual quantity of Ca is calculated as follows.

$$R_{Ca} = Q_{Ca} - Q_{HCO_3} \ \cdots\cdots\cdots (2.4).$$

where, R_{Ca} is the first residual quantity of Ca which will be then combining with Cl and SO_4 shown later on.

3. Estimation of HCO_3 salt as $Mg(HCO_3)_2$

(i) Case – I : When $R_{HCO_3} \geq Q_{Mg}$.

$$Q_{Mg(HCO_3)_2} = Q_{Mg} \ \cdots\cdots\cdots (3.1).$$

where, $Q_{Mg(HCO_3)_2}$ – quantity of $Mg(HCO_3)_2$ salt.

Q_{Mg} – initial quantity of Mg in water sample.

Here, the second residual quantity of HCO_3 is calculated as follows.

$$R'_{HCO_3} = R_{HCO_3} - Q_{Mg} \ \cdots\cdots\cdots (3.2).$$

where, R'_{HCO_3} – second residual quantity of HCO_3 left after combination with Mg which enters into further combination with R_{Na} and Fe.

(ii) Case – II : $R_{HCO_3} < Q_{Mg}$.

$$Q_{Mg(HCO_3)_2} = R_{HCO_3} \ \cdots\cdots\cdots (3.3).$$

where, R_{HCO_3} is the first residual quantity of HCO_3 remaining in excess as in eq. (2.2).

Here, the residual quantity of Mg is calculated as follows.

$$R_{Mg} = Q_{Mg} - R_{HCO_3} \ \cdots\cdots\cdots (3.4).$$

where, the R_{Mg} is the first residual quantity of Mg left after combination with the residual HCO_3 as in eq. (3.4) and which will be combining with Cl and SO_4 later on.

4. Estimation of HCO_3 salt as $NaHCO_3$.

(i) Case – I : When $R_{HCO_3} \geq R_{Na}$.

$$Q_{NaHCO_3} = R_{Na} = Q_{Na} \text{ (if p–alk absent)}..... (4.1).$$

where, Q_{NaHCO_3} – quantity of $NaHCO_3$ salt.

R_{Na} – first residual amount of (Na) as in eq. (1.1).

Q_{Na} – initial quantity Na in water sample.

Here, the third residual quantity of HCO_3 is calculated as follows.

$$R''_{HCO_3} = R'_{HCO_3} - R_{Na} \ \cdots\cdots\cdots (4.2).$$

where, R''_{HCO_3} – the third residual amount of HCO_3 constituent which will be combining with Fe and will be balanced at this stage.

R'_{HCO_3} – the second residual HCO_3 as left after combination with Mg as in eq. (3.2).

(ii) **Case – II** : When $R'_{HCO_3} < R_{Na}$.

$$Q_{NaHCO_3} = R'_{HCO_3} \quad \text{............. (4.3).}$$

where, R'_{HCO_3} is the second residual quantity of HCO_3 as in eq. (3.2).

Here, the second residual amount of Na is calculated as follows.

$$R'_{Na} = R_{Na} - R'_{HCO_3} \quad \text{............. (4.4).}$$

where, R'_{Na} is the second residual amount of Na which will be combining with Cl and SO_4 given in eq. (5.1 or 5.3) and eq. (10.1 or 10.3). The residual amount (if any may combine with NO_3 as shown in eq. (11).

5. Estimation of Cl–salt as NaCl.

(i) **Case – I** : When $Q_{Cl} \geq R'_{Na}$.

$$Q_{NaCl} = R'_{Na} \quad \text{............. (5.1).}$$

where, Q_{NaCl} – probable quantity of NaCl salt.

Q_{Cl} – initial quantity of Cl in water sample.

R'_{Na} – the second residual quantity of Na according to eq. (4.4).

Here, the residual quantity of Cl is calculated as follows.

$$R_{Cl} = Q_{Cl} - R'_{Na} \quad \text{................. (5.2).}$$

where, R_{Cl} is the first residual amount of Cl which will be combining with R_{Mg} as left in eq. (3.4).

(ii) **Case – II** : When $Q_{Cl} < R'_{Na}$.

$$Q_{NaCl} = Q_{Cl} \quad \text{.......... (5.3).}$$

Here, the third residual quantity of Na is calculated as follows.

$$R''_{Na} = R'_{Na} - Q_{Cl} \quad \text{.............. (5.4).}$$

where, R''_{Na} is the third residual quantity of Na which will be combining with R'_{SO_4} as left in eq. (9.2) according to either of eq. (10.1) or (10.2).

6. Estimation of Cl – salt as $MgCl_2$.

(i) **Case – I** : When $R_{Mg} \geq R_{Cl}$.

$$Q_{MgCl_2} = R_{Cl} \quad \text{................. (6.1).}$$

where, R_{Cl} – first residual amount of Cl as obtained in eq. (5.2).

Q_{MgCl_2} – quantity of $MgCl_2$ salt.

Here, the second residual quantity of Mg is calculated as follows.

$$R'_{Mg} = R_{Mg} - R_{Cl} \quad \text{.............. (6.2).}$$

where, R'_{Mg} is the second residual quantity of Mg which will be combining with R_{SO_4} (obtained in eq. 7.2) as shown in the eq. (9.2).

(ii) **Case – II** : When $R_{Mg} < R_{Cl}$.

$$Q_{MgCl_2} = R_{Mg} \quad \text{........ (6.3).}$$

where, R_{Mg} is the first residual quantity of Mg as in eq.(3.4).

Here, the second residual amount of Cl is calculated as follows.

$$R'_{Cl} = R_{Cl} - R_{Mg} \quad \text{............. (6.4).}$$

where, R'_{Cl} is the second quantity of Cl which will be combining with R'_{Ca} (as in eq. 7.4) according to eq. (8.1) or (8.2).

7. Estimation of SO_4-salt as $CaSO_4$

(i) **Case – I** : When $Q_{SO_4} \geq R_{Ca}$.

$$Q_{CaSO_4} = R_{Ca} \quad \text{...............} \quad (7.1).$$

where, Q_{CaSO_4} – quantity of $CaSO_4$ salt .

Q_{SO_4} – initial quantity of SO_4 in water .

R_{Ca} – first residual quantity of Ca as in eq. (2.4).

Here, the residual quantity is calculated as follows.

$$R_{SO_4} = Q_{SO_4} - R_{Ca} \quad \text{..........} \quad (7.2).$$

where, R_{SO_4} is the first residual quantity of SO_4 which will be combining with R_{Mg} (as in eq. 6.2). and R_{Na} (as in eq. 5.4) according to eq. (9.1) and (10.1).

(ii) **Case – II** : When $Q_{SO_4} < R_{Ca}$.

$$Q_{CaSO_4} = Q_{SO_4} \quad \text{.............} \quad (7.3).$$

Here, the second residual quantity of Ca is calculated as follows.

$$R'_{Ca} = R_{Ca} - Q_{SO_4} \quad \text{................} \quad (7.4).$$

where, R'_{Ca} is the second residual quantity Ca which will be combining with R'_{Cl} (obtained eq. 6.4) as shown in eq. (8.1) or (8.2).

8. Estimation of Cl-salt as $CaCl_2$.

(i) **Case –I** : When $R'_{Cl} > R'_{Ca}$.

$$Q_{CaCl_2} = R'_{Cl} = R'_{Ca} \quad \text{................} \quad (8.1).$$

At this stage of combination, both of the Ca and Cl constituents would be exhausted and balanced.

(ii) **Case – II** : When $R'_{Cl} > R'_{Ca}$.

$$Q_{CaCl_2} = R'_{Ca} \quad \text{..............} \quad (8.2).$$

where, Q_{CaCl_2} is the quantity of $CaCl_2$ salt in water.

Here, the third residual quantity of Cl is calculated as follows.

$$R''_{Cl} = R'_{Cl} - R'_{Ca} \quad \text{..............} \quad (8.3).$$

where, the R''_{Cl} is the third residual quantity of Cl which will be combining with Fe or any undetected trace cationic constituent. But possibility of such case is very rare.

9. Estimation of SO_4-salt as $MgSO_4$.

When $R_{SO_4} \geq R'_{Mg}$:

$$Q_{MgSO_4} = R'_{Mg} \quad \text{..............} \quad (9.1).$$

where, Q_{MgSO_4} – quantity of $MgSO_4$ salt in water.

R'_{Mg} – second residual quantity of Mg (as in the eq. 6.2).

Here, the second residual quantity of SO_4 is calculated as follows.

$$R'_{SO_4} = R_{SO_4} - R'_{Mg} \quad \text{..........} \quad (9.2).$$

where, R'_{SO_4} is the second residual quantity of SO_4 which will be finally combining and balancing with R_{Na} (obtained in eq. 5.4) according to eq. (10.1 and 10.3).

10. Estimation of SO_4-salt as Na_2SO_4

(i) **Case – I** : When $R'_{SO_4} = R''_{Na}$.

$$Q_{Na_2SO_4} = R''_{Na} = R'_{SO_4} \ \cdots\cdots (10.1).$$

where, $Q_{Na_2SO_4}$ – quantity of Na2SO4 salt assumed.

R''_{Na} – the second residual quantity of Na.

(ii) **Case – II** : When $R'_{SO_4} < R''_{Na}$.

$$Q_{Na_2SO_4} = R'_{SO_4} \ \cdots\cdots (10.2).$$

Here, the 4th residual quantity of Na is calculated as follows.

$$R'''_{Na} = R''_{Na} - R'_{SO_4} \ \cdots\cdots (10.3).$$

where, the R'''_{Na} is the 4th and last residual quantity of Na which will be combining with NO_3 (if any) according to eq. (11).

(iii) **Case – III** : When all the quantity of Ca and Mg are exhausted by prior combining with HCO_3 and Cl constituents, in such case,

$$Q_{Na_2SO_4} = Q_{SO_4} = R''_{Na} \ \cdots\cdots (10.4).$$

11. Estimation of NO_3-salt as $NaNO_3$.

Satisfying the major anionic constituents (HCO_3^-, Cl^- and SO_4^{-2}) if any further residual quantity of Na is left, then that quantity may be considered for combining with NO_3^- constituent (if present) and the probable quantity of the salt is calculated from the relationship as follows.

$$Q_{NaNO_3} = R'''_{Na} \ \cdots\cdots (11).$$

where, Q_{NaNO_3} is the quantity of $NaNO_3$ salt present in water sample analysed.

Experiments And Results

Verification of the Validity of the Models by Analytical Results of Typical Water Samples.

Example–1

Water analysis (Type : TH > m–alk).

Cations, meq/l		Anions, meq/l	
Ca^{+2}	: 7.0	p–alk	: 00
Mg^{+2}	23.0	m–alk	: 3.4
TH	30.0	Cl^-	: 130.9
* Na^+	: 112	SO_4^{-2}	: 7.7
M_c	= 142	M_a	= 142

Example–2

Water analysis (Type : TH < m–alk).

Cations, meq/l		Anions, meq/l	
Ca^{+2}	: 1.5	p–alk	: 00
Mg+2	: 2.3	m–alk	: 8.5
TH	: 3.8	Cl^-	: 3.7
* Na^+	: 8.7	SO_4^{-2}	: 0.3
M_c	= 12.5	M_a	= 12.5

* [Here, Na^+ has been determined mathematically according to eq. (C) i.e. $Na^+ = M_a - TH$
i.e. 142–30 = 112 ;   12.5–3.8 = 8.7].

Table-1 : *Substitution of the analytical results of Example-1 in appropriate equations of Rule-1 and derivation of the salts.*

Most probable Salt assumed	Equation applied for calculation	Quantity of salt assumed (meq/l)	Proportion of the assumed salt (%)
NaCl	$Q_{NaCl} = Q_{Na}$ (eq. 2.1)	112	78.87
MgCl$_2$	$Q_{MgCL_2} = R_{Cl}$ (eq. 3.1)	18.9	13.31
MgSO$_4$	$Q_{MgSO_4} = R_{Mg}$ (eq. 4.1)	4.1	2.89
Ca(HCO$_3$)$_2$	$Q_{Ca(HOC_3)_2} = Q_{HCO_3}$ (eq. 5.1)	3.4	2.39
CaSO$_4$	$Q_{CaSO_4} = R_{SO_4}$ (eq. 6.1)	3.6	2.54

Table-2 : *Substitution of the analytical results of Example-2 in appropriate equations of Rule-2 and derivation of the salts.*

Most probable Salt assumed	Equation applied for calculation	Quantity of salt assumed (meq/l)	Proportion of the assumed salt (%)
Ca(HCO$_3$)$_2$	$Q_{Ca(HCO_3)_2} = Q_{Ca}$ (2.1)	1.5	12
Mg(HCO$_3$)$_2$	$Q_{Mg(HCO_3)_2} = Q_{Mg}$ (3.1)	2.3	18.4
NaHCO$_3$	$Q_{NaHCO_3} = R_{HCO_3}$ (3.2)	4.7	37.6
NaCl	$Q_{NaCl} = Q_{Cl}$ (5.3)	3.7	29.6
Na$_2$SO$_4$	$Q_{Na_2SO_4} = Q_{SO_4}$ (10.4)	0.3	2.4

Discussion

The probable salt derivation and estimation may be done by 2 ways of calculation designated as Rule-1 and Rule-2. Each rule consists of a series of correlative equations termed as 'models' which have been derived from the successive residual quantities of the mineral constituents. Any one of the rules should be followed. Right rule is selected for a particular water sample according to the following quantitative status of the total hardness (TH) and m-alkalinity (normally HCO$_3^-$ constituent).

TH>m-alk.

TH=m-alk.

TH<m-alk.

In the case of **TH ≥ m-alk, Rule-1 to be applied and when TH < m-alk, then Rule-2 is applicable.** The other criteria for the derivation of each individual salts have been explained in the respective equations of the models.

For the application of appropriate models in finding out the most probable salts and their concentrations, the following factors must always be considered.

1. Right rule should be selected first according to the above quantitative relation between TH and m-alkality.

2. Individual equations of the respective selected rule to be applied.

3. Appropriate successive equations should be selected and systematically applied according to the equation serial and residual quantitative position of the available ionic concentration.

4. During determination of a specific salt component, the condition of predominance between the two constituents taking part in combination must be noted carefully.

After the completion of calculations, if any small residual cationic or anionic constituents still remain(s) surplus, that should be discarded in view of the combination of the undetected trace constituents of opposite charges.

In the equations of Rule–1, the last residual HCO_3^- (after combining with Ca^{+2} would have to be balanced with Na^+ to produce $NaHCO_3$ and with Fe^{+2} to form $Fe(HCO_3)_2$. Such cases frequently occur when m–alk > TH in any water [8,9].

The experimental results of the two typical water sample analyses (Example–1 & 2) have proved the validity of the models. Table–1 and Table–2 give the guide lines for the application procedure of the appropriate Rule and its respective models.

Acknowledgment

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