Geochemical Modeling of Groundwater in AL Teeb Area (North East Missan Governorate)

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Abstract. Geochemical model is developed to simulate the geochemical reaction with flow direction of AL Teeb area NE of Missan Governorate, south of Iraq. Geochemical model under geochemical codes, NETPATH and WATEQ4F program is used to develop a groundwater Geochemical model to interpretation of geochemical reaction. According to the conceptual model of the study area, the aquifers system within the area is subdivided into three aquifers: Quaternary deposits (unconfined aquifer), Bai Hassan (semi-confined aquifer), and Mukdadiyah (confined aquifer). Results of pumping test; by applying AQTESOLV Professional version 4.50 for pumping test analysis to determine transmissivity (T), hydraulic conductivity (K), for wells are distributed of all the studied area. The (T) value ranges from (28.17 - 613.17) m²/day and the (K) value ranges from (1.3 - 12) m/day. The groundwater quality is assessed through the analysis of the Physicochemical parameters such as pH, EC, TDS and major ions (Ca²⁺, Mg²⁺, Na⁺, K⁺, HCO₃⁻, Cl⁻, SO₄²⁻), nutrients (NO₃⁻). Two generalized flow paths were selected for the study area. These flow paths begin near the Iraq – Iran boundary to the middle of the study area from northeast to the southwest. The detailed results of the ionic strength calculations for and mineral saturation indices. All samples in the selected flow path are under saturated concerning Pco₂. The concentrations of calcium, magnesium, Bicarbonate, and sulfate increase along groundwater flow paths. All waters sampled are oversaturated concerning pure stoichiometric calcite. The SI tells us about the mineral is, in fact, present and is dissolving (SI < 0), or is, in fact, precipitating (SI > 0). The primary goal of the mass balance modeling is to define the net mass of minerals dissolved or precipitated along the flow path down gradient. There are two main flow paths reaction indicate system state for different phases CALCITE, DOLOMITE, GYPSUM, ARAGONITE, DIOPSIDE, and NaCl. The flow path 1 between wells (WS -12 and WS-23) and it is representing the lower aquifer in the study area. Where model NETPATH code checked (35) models and four models are compatible with the found concentrations of the chemical elements and selected phases of this reaction. The flow path between wells (WS-4 and WS-18) and it is representing the upper aquifer in the study area, where model NETPATH code checked (15) models and Four models are compatible with the found concentrations of the chemical elements and selected phases of this interaction reaction.

Keywords: Geochemical model, Teeb, geochemical reaction, aquifers
1. Introduction

As a result of the increasing demand for water in recent years, particularly after the emergence of drought conditions in Iraq, water policies in neighboring countries and the need to expand the uses of water for food security. There is a truly urgent need for reassessment of groundwater resources in the light of efficient modern techniques for better managing and protecting of aquifer system within the study area, which is the primary objective of this report.

2. Location and topography of the study area

The study area is located in the northeastern of Missan governorate, south of Iraq between (32° 03ˈ 25.52” – 32° 30ˈ30”) latitude and (47°05ˈ21.16” – 47°40ˈ53.52”) longitude (Fig. 1). It encompasses an area of (1856 km²). The topography elevation ranges from (7 – 230 m) (Fig. 2). The land surface is relatively flat in the central part of the area and is bounded by Hemrin hills in the northeastern and Band hill in the north close to the Al-Teeb. The surface elevations of the study area decrease from northeast to southwest. The topographic elevation is derived from the digital elevation model (DEMs) produced. The area is crossed by two streams namely, Teeb and Dewereg. The source of both is Iran territory. The bigger one is Teeb which enters the Iraqi territory at the Teeb town north of the study area and runs from north to south until it ends in Al-Sanaf marsh outside the study area.

3. Aims of the study

Figure 1: Location of the study area

Figure 2: Topography of the study area

(derived from US DEMs)
The current study aimed to determine the hydraulic parameters of groundwater in the study area. Also the study aimed to evaluate the hydrochemical characteristics of groundwater to determine water-rock interactions by processes of mineral dissolution-precipitation, by using geochemical modeling.

**Geological setting**

The Rocks stratum dip of uppermost Miocene and Pliocene are towards Mesopotamian plain from the foothills along the Iraqi-Iranian border on the east. These rocks are buried beneath the Mesopotamian plain by thick deposits of Pleistocene and Holocene age. Most of the study area is covered with fluviatile, lacustrine, and aeolian sediments of recent age. The Quaternary deposits represent about 72% while Tertiary sediments extend over 28% (Fig. 3) [1].

**Stratigraphic succession**

The stratigraphic column in the study area consists of the following formations;

**a. Euphrate Formation:** It is one of the most widespread formations in Iraq and belongs to the early Miocene sequence [2].

**b. Fatha Formation:** Fatha Formation is one of the most aerially widespread and economically essential formations in Iraq. The formation can be divided into two members (limestone and anhydrite or gypsum with green marl [1].

**c. Injana Formation:** The thickness of the formation is very variable due to the subsequent erosion over significant folds. The age of the formation is usually accepted as late Miocene.

**d. Mukdadiyah and Bai Hassan (lower and upper Bakhtiari) Formations:** The Bakhtiari Formation was first described in Iran. Bellen et al. (1959) [2], introduced the formation in Iraq and later divided it into the lower and upper Bakhtiari formation. Jassaim et al. (1984) [3] replaced the names of upper and lower Bakhtiari by Mukdadiya and Bai Hassan, respectively. The two formations are strongly diachronous but can be recognized throughout the foothill and high folded zones. The Mukdadiya Formation comprises up to 2000 m of fining upwards cycles of gravely sandstone, sandstone and red mudstone [1].

**Quaternary deposits;**

Most of the study area is covered with different types of Quaternary deposits mainly sand and alluvium deposits of recent and Pleistocene age. Alluvial fan, floodplain, depression fill, and aeolian deposits are the major units of the Quaternary deposits in the study area. Alluvial fans deposits comprise gravel, sand and silty sand. These sediments form a strip along the foothill zone [1]. The maximum thickness of the alluvial deposits may reach to 15 m. poorly sorted coarse deposits of pebbles and sometimes boulder occur in apical parts passing into finer grained, better sorted layered fluvial sediments, comprise layers of silty clay and clay typically 10-20 cm but sometimes up to 1m thick (Fig. 4) [1], [2].
Methodology

Chemical speciation and saturation state of the groundwater with specific mineral phases were analyzed using inverse geochemical modeling approach suggested by Plummer et al. (1982) [5]. Chemical reactions along selected flow paths at three main groups have been studied as well. All of the above processes were analyzed using geochemical codes, NETPATH developed by [5] and WATEQ4F program developed by [6].

Hydrogeology

1- According to the conceptual model of the study area (Fig.5), the aquifer system within the area is subdivided into three aquifers: Quaternary deposits (unconfined aquifer), Bai Hassan (semi-confined aquifer), and Mukdadiyah (confined aquifer). These aquifers are separated by two less permeable aquitards the hydraulic characteristics of which are unknown. The hydraulic connection between aquifer units is possible, and the confined portion of aquifer system is not fully separated. Results of pumping test; by applying AQTESOLV Professional version 4.50 for pumping test analysis to determine transmissivity (T), and hydraulic conductivity (K.) for wells are distributed of all the studied area. The (T) value ranges from (28.17 - 613.17) m²/day and the (K)value ranges from (1.3 -12 ) m/day.
2- The flow direction as inferred from the map of groundwater heads is from northeast to southwest similar to topographic elevation trend (Fig. 6). The north and northeast areas of the study area represent the recharge zone while south and southwest areas represent discharge zone. Depths to groundwater levels are shallow, whereby most of the study area having depths in the range of 1.5 to 15m. Only small parts of the study area have a depth higher than 15m.
Hydrochemistry

The groundwater quality is assessed through the analysis of the Physicochemical parameters such as pH, EC, TDS and major ions (Ca\(^{2+}\), Mg\(^{2+}\), Na\(^{+}\), K\(^{+}\), HCO\(_3^{-}\), CI\(^{-}\), SO\(_4^{2-}\)), nutrients (NO\(_3^{-}\)). The groundwater is generally alkaline with pH median ranging from 7.12 to 7.61 for two periods. The TDS values range from (612 to 14134) mg/l, and EC values range from (871-25300) µmohs/cm. The analyses indicate many variations in different places in the studied area because of intrusion of water from lower or upper aquifers due to high pumping rate. The results of the complete analyses of water samples are given in the table (1) and the locations of the water samples are shown in Fig. (6).

Table (1): hydrochemical parameters for groundwater in the studied area

| Well NO | ID well | Easting | Northing | Na  | K   | Ca  | Mg  | Cl  | HCO\(_3^{-}\) | SO\(_4^{2-}\) | NO\(_3^{-}\) | TDS | EC  |
|---------|---------|---------|----------|-----|-----|-----|-----|-----|-------------|-----------|-----------|------|-----|
| WQ01    | 701164  | 355904  | 41.05    | 0.105 | 25.13   | 25.11 | 30.62 | 9.085 | 38.89       | 0.987 | 10792 | 2790 | 10493 |
| WQ02    | 703032  | 359150  | 15.23    | 0.179 | 18.30   | 17.96 | 24.82 | 11.8   | 16.10       | 0.085 | 4760   | 7080 |       |
| WQ03    | 706290  | 358075  | 29.61    | 0.070 | 3.428   | 0.788 | 17.50 | 6.717 | 24.93       | 0.145 | 4140   | 6470 |       |
| WQ04    | 701836  | 358179  | 24.73    | 2.381 | 16.64   | 13.18 | 15.14 | 7.892 | 20.18       | 0.218 | 7000   | 8590 |       |
| WQ05    | 703153  | 357573  | 13.64    | 0.268 | 16.52   | 13.65 | 14.96 | 6.898 | 12.71       | 0.113 | 5890   | 4650 |       |
| WQ06    | 707710  | 357320  | 52.42    | 2.853 | 43.41   | 44.81 | 44.59 | 12.82 | 68.21       | 0.13  | 5000   | 3200 |       |
| WQ07    | 705510  | 355050  | 22.27    | 2.813 | 15.92   | 12.36 | 15.04 | 8.012 | 25.02       | 0.064 | 3610   | 9630 |       |
| WQ08    | 73910   | 355049  | 33.63    | 1.128 | 27.46   | 19.05 | 35.90 | 12.38 | 40.49       | 0.062 | 6500   | 1480 |       |
| WQ09    | 705036  | 355180  | 24.76    | 2.405 | 18.63   | 13.25 | 19.27 | 8.05   | 24.93       | 0.068 | 4500   | 7380 |       |
| WQ10    | 703709  | 354339  | 24.71    | 2.378 | 18.67   | 13.25 | 19.21 | 8.045 | 24.92       | 0.062 | 5500   | 7770 |       |
| WQ11    | 74807   | 355002  | 25.71    | 0.471 | 16.97   | 13.42 | 18.01 | 8.013 | 20.04       | 0.019 | 4890   | 5120 |       |
| WQ12    | 703036  | 358002  | 2.994   | 0.028 | 2.329   | 2.329 | 5.964 | 1.466 | 4.664       | 0.064 | 912    | 871  |       |
| WQ13    | 718311  | 356593  | 10.42    | 0.281 | 8.47    | 0.037 | 15.20 | 2.687 | 6.502       | 0.016 | 2100   | 2740 |       |
| WQ14    | 705034  | 356064  | 18.21    | 6.664 | 19.1    | 8.713 | 14.43 | 5.075 | 16.01       | 0.04 | 4450   | 6850 |       |
| WQ15    | 71801   | 355834  | 5.235    | 2.924 | 30.63   | 25.17 | 37.95 | 16.69 | 49.67       | 0.083 | 7777   | 11903 |      |
| WQ16    | 71802   | 355834  | 2.994   | 0.281 | 2.329   | 2.329 | 5.964 | 1.466 | 4.664       | 0.064 | 912    | 871  |       |
| WQ17    | 702470  | 357423  | 16.51    | 0.089 | 11.37   | 8.877 | 15.5  | 5.076 | 16.08       | 0.067 | 6680   | 2670 |       |
| WQ18    | 707742  | 357799  | 25.25    | 1.003 | 17.68   | 14.41 | 19.47 | 8.331 | 32.33       | 0.085 | 5990   | 7380 |       |
| WQ19    | 711800  | 359239  | 25.71    | 4.809 | 17.52   | 13.91 | 18.85 | 8.327 | 31.73       | 0.023 | 2590   | 6900 |       |
| WQ20    | 707814  | 354043  | 43.33    | 2.831 | 60.28   | 465.4 | 168.0 |       |            |       | 15300  |      |       |
| WQ21    | 712512  | 358049  | 60.54    | 1.825 | 46.62   | 30.86 | 62.62 | 22.16 | 47.29       | 0.049 | 10600  | 16330 |       |
| WQ22    | 708551  | 357810  | 24.77    | 1.561 | 16.65   | 12.53 | 15.14 | 5.814 | 22.21       | 0.065 | 3100   | 6680 |       |
| WQ23    | 712517  | 358560  | 21.33    | 6.156 | 7.225   | 2.829 | 12.7  | 6.005 | 12.04       | 0.016 | 1980   | 2400 |       |
| WQ24    | 728079  | 357042  | 47.24    | 1.841 | 28.63   | 25.83 | 43.28 | 14.97 | 43.43       | 0.05  | 5030   | 5790 |       |
| WQ25    | 733903  | 356240  | 44.52    | 2.807 | 36.61   | 25.16 | 37.61 | 16.1  | 49.21       | 0.029 | 5000   | 8650 |       |

Geochemical Modeling

Geochemical models are tools that aid in the interpretation of geochemical reaction. Models can be used for a variety of purposes, including determination of the common geochemical reaction, quantification of the extent to which these reactions occur, prediction of the inorganic contaminants and estimation of the direction and rates of groundwater flow [7].

Geochemical speciation modeling

Speciation models calculate thermodynamic properties of the solutions including the molalities and activities of the aqueous solution and saturation indices of the mineral phases. Chemical analysis of the water samples was used to calculate different parameters such as ionic strength, saturation indices of specific mineral phase and the partial pressure of CO\(_2\) gas using a WATEQ4F program developed
by [6]. The law of mass action is fundamental to any description of equilibrium in water; it states that for a reaction of the generalized type:

\[ aA + bB \leftrightarrow cC + dD \]

Where:
- \( a, b, c \) and \( d \) are the stoichiometric fractions of the chemical constituents \( A, B, C \) and \( D \), respectively, at equilibrium. The mass action equation for this example is

\[
K_{eq} = \frac{[C]^c \, [D]^d}{[A]^a \, [B]^b}
\]

where: \( K_{eq} \) is the equilibrium constant, which is a function of the temperature and pressure [8]. The activity of the chemical species can be calculated using the following equation:

\[
[i] = \gamma_i \, (i)
\]

Where:
- \([i]\): activity of the chemical species
- \((i)\): is the molality of species \( i \)
- \( i \): is the activity coefficient

We can calculate the activity coefficient for ions from one of several different activity models. The simplest is based on the Debye–Huckel equation:

\[
\log \gamma_i = \frac{-A_i z_i^2 (I)^{0.5}}{1 + B_i (I)^{0.5}}
\]

Where:
- \( A_i \) and \( B_i \): are temperature-dependent constants
- \( ai \): is the radius of the hydrated ions in centimeters
- \( zi \): is the ion charge
- \( I \): ionic strength

Ionic strength, as sum parameter for strength, is calculated according to the following equation [10]:

\[
I = 0.5 \sum m_i z_i^2
\]

Where:
- \( I \): ionic strength, \( m_i \): molal concentration of the species, \( Z_i \): charge of the species. The primary purpose of the chemical speciation is to calculate mineral saturation indices, which are indicators of the saturation state of the solution with the specific mineral phases. The saturation index is defined as:

\[
SI = \log \left( \frac{IAP}{KT} \right)
\]

Where:
- \( SI \): saturation index.
- \( IAP \): is the ion activity product of the mineral–water reaction
- \( KT \): is the thermodynamic equilibrium constant.

SI value of zero indicates that the water is in equilibrium or saturated concerning the mineral phase, a value less than zero, indicates under saturated (mineral dissolution is possible) and value greater than zero, indicates oversaturated (mineral precipitation is possible) [5]. The partial pressure of carbon dioxide (PCO2) is an important factor controlling the precipitation and is solute ion of carbonates. PCO2 can be calculated by the following equation [11]:

\[
\log PCO2 = \log K + \log a_{HCO} - 3 + \log a_{H} - \log a_{H2O}
\]

Where:
- \( K \): is the constant equilibrium
- \( a \): is the species activity

Groundwater Flow Paths

Two generalized flow paths (Fig. 6) were selected for the Study area. These flow paths are in areas where the Mukdadiyah (confined aquifer) is outcrop in the north of study area and is above by Bai Hassan (semi-confined aquifer) and Quaternary deposits (unconfined aquifer), as shown in (Fig. 7).

These flow paths begin near the Iraq – Iran boundary to the middle of the study area from northeast to the southwest. North and North West of the study area especially in Iraq – Iran boundary discharge occurs by artesian flow from wells and other wells by pumping, the water chemistry of
water in Mukdadiyah (confined aquifer) reflects that of water unaffected by local recharge from the overlying shallow aquifers. Two-thirds of the wells sampled are monitoring wells or low-capacity wells for domestic, irrigation, or water supply use. Other wells sampled are water-supply production wells, the artesian wells sampled are located in up gradient parts of the study area, where downward leakage predominates. Well-construction data are summarized in Table (1). Cross sections were constructed along the two generalized flow paths based on geologic data of a recent study in 2014.

Temperature, pH, major, minor elements for eight wells samples (four wells in Bai Hassan aquifer and Quaternary deposits aquifer and four wells in Mukdadiyah aquifer) in the study area were used as input data to the computer software WATEQ4F. The detailed results of the ionic strength calculations for and mineral saturation indices (SI=log IAP/K, where IAP is the ion activity product for the reaction and K is the equilibrium constant) were calculated using aqueous model for the carbonate system as implemented in WATEQ [5]. Under these conditions, an uncertainty of ±0.05 SI is assigned to calcite and ±0.1 SI to dolomite, due to uncertainties in measurements and stoichiometric effect on saturation indices. The average charge balance of analyses (calculated relative to the sum of the equivalents of the cations and anions) is 0.1±1.5 percentage. The major- and minor-element chemistry is summarized in Table (2) along with calculated mineral saturation indices.

Figure 7: Hydrogeological sections of study area along flow paths 1 and 2, showing well locations and depths.
Results and Discussion

Chemical evolution along flow paths

All samples are undersaturated concerning Pco₂ (Table 2). In addition to, Pco₂ of groundwater is lower than that of atmospheric CO₂ pressure (3.5-10 bar). A highly significant positive relationship between ionic strength (mol/Kg) and TDS (mg/l) in both flow path (Fig. 8).

Figure 8: Relationship between Ionic Strength and TDS

Table 2: Chemical composition of groundwater samples

| Well ID no. | T (°C) | pH    | TDS (mg/l) | Ionic Strength |
|-------------|--------|-------|------------|---------------|
| Flow path 1 | 25     | 7.2   | 3724.3     | 8.4E-02       |
|             | 26     | 7.35  | 4060       | 7.2E-02       |
|             | 26     | 7.2   | 3925.5     | 7.1E-02       |
|             | 27     | 7.12  | 2353.4     | 4.5E-02       |
| Flow path 2 | 25     | 7.16  | 538.1      | 1.2E-02       |
|             | 26     | 7.44  | 1662.8     | 1.0E-02       |
|             | 27     | 7.15  | 2086       | 3.7E-02       |
|             | 26     | 7.1   | 3161.6     | 5.8E-02       |

Table 3: Chemical Species of groundwater samples

| Species       | Flow path 1 | Flow path 2 |
|---------------|-------------|-------------|
| HCO3⁻         | 6.9E-03     | 6.3E-03     |
| H₂CO₃         | 6.4E-04     | 6.2E-03     |
| Ca²⁺          | 6.7E-09     | 5.7E-09     |
| CaCO₃         | 1.9E-05     | 3.0E-05     |
| Ca²⁺O₃        | 1.0E-04     | 2.1E-04     |
| CaSO₄         | 2.1E-03     | 2.3E-03     |
| CaHSO₄        | 7.9E-10     | 6.1E-10     |
| Mg²⁺O₇        | 1.1E-07     | 1.7E-07     |
| MgCO₃         | 6.5E-06     | 1.3E-05     |
| Mg²⁺O₃        | 1.4E-04     | 1.4E-04     |
| MgSO₄         | 1.9E-03     | 2.1E-03     |
| NaOH          | 2.0E-09     | 2.3E-09     |
| Na²⁺O₃        | 1.0E-06     | 2.6E-06     |
| Na₂CO₃        | 6.5E-05     | 7.0E-05     |
| Na²⁺SO₄       | 4.1E-04     | 4.5E-04     |
| KCO₃⁻         | 5.4E-05     | 1.1E-04     |
The concentrations of calcium, magnesium, Bicarbonate, and sulfate increase along groundwater flow paths (data for flow paths 1 and 2 in Table 1), of the horizontal component of the distance of groundwater flow. This compositional behavior is consistent with the classic dedolomitization reaction. Calcite precipitation driven by dissolution of gypsum (or anhydrite) and dissolution of dolomite [12]. About carbonate speciation all water samples have pH values between 7 to 7.5; most carbonate is in the bicarbonate form, HCO$_3$-.

These relationships follow directly from the dissociation reaction (Fig. 9),

$$
\text{H}_2\text{CO}_3 = \text{HCO}_3^- + \text{H}^+ ; k = 10^{-6.37}
$$

Figure 9: Molalities of H$_2$CO$_3$, bicarbonate, and carbonate ions as a function of pH

All waters sampled are oversaturated concerning pure stoichiometric calcite. Waters from the initial points on flow path 1 is under saturated concerning dolomite, and become oversaturated relative to stable crystalline dolomite with a distance of flow path 2. The saturation indices (Table 2, Fig.10, and Fig.11) of calcite and dolomite are consistent with the dedolomitization reaction if the reacting dolomite is less stable than pure stoichiometric dolomite. The gypsum saturation index increases with the distance of flow but remains under saturated along all flow paths (Table 2, Fig.10, and Fig.11).

Chloride concentrations are low in most waters, but they increase in some areas with a Na/Cl ratio near. Most of the waters contain hydrogen sulfide. The SI tells us about the mineral is, in fact, present and is dissolving (SI < 0), or is, in fact, precipitating (SI > 0), the histograms below explain that in selected paths in the study area and shows the deferent between the upper aquifer and lower aquifer.

Figure 10. Saturation Indices for minerals in flow path 1.
Mass-Transfer Models

The chemical data were interpreted using NETPATH for geochemical reactions [5]. The NETPATH code uses equations of chemical mass balance to define all possible net geochemical reactions between the initial and final water along a flow path. The geochemical reactions are constrained to occur among reasonable reactant and product minerals and gases, and they are consistent with the observed chemical data of the groundwater. Each geochemical reaction model is then solved as a chemical -evolution problem [13]. Inverse geochemical modeling based on the principle of mass balance between the reactant and product phases in which mass transfer of certain mineral phases can be calculated according to the following equation.

Initial water + reactant phases → Final water + product phases

The primary goal of the mass balance modeling is to define the net mass of minerals dissolved or precipitated along the flow path down gradient. Table 4 (A, B) describes the magnitude of mass transport for choosing mineral phases. There are two main flow paths reaction indicate system state for different phases CALCITE, DOLOMITE, GYPSUM, ARAGONITE, DIOPSIDE, and NaCl. The flow path 1 between wells (WS-12 and WS-23) and it is representing the lower aquifer in the study area fig. (7), where model NETPATH code checked (35) models and Four models are compatible with the found concentrations of the chemical elements and selected phases of this reaction table 4 (A, B), fig. 12, 13. The flow path between wells (WS-4 and WS-18) and it is representing the upper aquifer in the study area fig. (7), where model NETPATH code checked (15) models and Four models are compatible with the found concentrations of the chemical elements and selected phases of this interaction reaction table four (A, B), fig. 12, 13.

Table 4 (A): Flow path 1 models of the study area.
Figure 12: Histogram Flow path 1 models of the study area

Table 4 (B): Flow path 2 models of the study area.

|MODELS IN FLOW PATH 2 |
|-----------------------|

Figure 13: Histogram Flow path 2 models of the study area
Conclusion

All waters sampled are oversaturated concerning with calcite. Waters from the initial points on flow path 1 is under saturated concerning dolomite, and become oversaturated relative to stable crystalline dolomite with a distance of flow path 2. The saturation indices of calcite and dolomite are consistent with the dedolomitization reaction. The gypsum saturation index increases with the distance of flow but remains under saturated along all flow.

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