MINERALOGY AND GEOCHEMISTRY OF GYPCRETE AND GYPSIFEROUS SOIL HORIZONS IN SOME NEOGENE AND QUATERNARY SEDIMENTS OF CENTRAL IRAQ

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ABSTRACT

The present work is concerned with gypcrete and gypsiferous soils in Quaternary and Neogene sediments, studied in two sections near Al-Dor and near Falluja. The study deals with lithology, mineralogy and geochemistry of these sediments and the origin of gypsum and salts. More than 20 samples were collected and studied for grain-size analysis, petrography, X-ray diffraction and chemical analysis of salts and host sediments.

The results show two genetically salt assemblages: an early diagenetic minor concentration of (Na – K – Mg – CO₃ – Cl) salts supplied from internal diagenetic solutions and a late diagenetic overwhelming concentrations of (Ca – SO₄) salts supplied from external sources. The two groups are negatively correlated. Most of the gypsum-rich soils in the studied sections are related to an in situ SO₄ enrichment from groundwater sources, whereas some are of aeolian origin and mechanically transported.

مختصر

يعد هذا البحث مراقبة القشرة الجيسية والترسب الجيسي في بعض رواسب النيوسين والعصر الرياحي في وسط العراق.

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INTRODUCTION

Gypcrete and gypsiferous soils are widely spread in Iraq. They represent the most important feature of desertification in the country and appear to develop rapidly in the recent years. Buring (1960) estimated the land coverage of gypsiferous soil in Iraq by about 20% of the total area of the country, whereas, in some more recent works the land coverage of these soils was estimated by 30% of the area (Ismail, 1994).

Gypsiferous soils represent a serious problem in many fields of human activity. They have dramatic impacts on buildings, mechanical constructions, and concrete foundations. In addition, they represent one of the poorest agricultural soils that only a few crops can survive their salinity. Furthermore, gypsum reduces the fertility of the land by decreasing its clay content. Gypsum authigenically grows within the soil on the expense of original soil components including the clay. Land deformation is another environmental impact of these soils. Gypsiferous soils are usually undulated and easily karstified. This work is a contribution to the research activities of the National Programme to Study the Specification of Gypsiferous Soils in Iraq organized by GEOSURV.

It is generally agreed that gypcrete is a secondary gypsum-rich crust within the soil, developed after sedimentation of the soil material via increased evaporation of saline and sulfate-rich groundwater in arid and warm regions. Some gypsiferous soils, however, may develop in near-shore salinas. It is usually consolidated but mechanically weak. However, gypcrete is more consolidated and may form mechanically solid crust. Gypsiferous soils retain most of the original soil components (clay, silt and sand), but impregnated by variable amounts of gypsum as nests or disseminations. Gypsum content varies in these two types from (5 – 70) %.

This work deals with study of gypsiferous soils and gypcrete in two different domains; recent sediments developed during the Holocene and ancient sediments believed to have developed during the Neogene (Injana Formation, Late Miocene). Samples were collected from two sections, one near Al-Dor (Section I) and the other near Falluja (Section II). The work includes field description, petrography, mineralogy and chemical analysis of salt constituents as well as host sediments. The main aims of this work are to compare the two gypsiferous soils in terms of mineralogy and geochemistry and to investigate the paragenesis and sources of the salt ionic constituents.

Two sections were described and sampled. The first is about 22 Km east of Al-Dor town, within the Quaternary sediments of gypcrete and gypsiferous soils. The second is located about 15 Km WSW of Falluja town, South of the Euphrates River, and encountered what is believed to be the gypsiferous paleosols and paleogypcrete horizons within the continental Injana Formation (Late Miocene) (Figs.1 and 2).

PREVIOUS WORKS

Between 1973 and 1994 several works on gypsiferous soils may be noticed:
– In 1973, Al-Berzanji studied some gypsiferous soils in several localities in Iraq.
– In 1983, GEOSURV took the initiative of preparing a map on a scale of 1: 000 000 showing the distribution of gypsum rocks and gypsiferous soils in Iraq with description and sample analysis of main localities (Mansour and Toma, 1983) (Fig.2).
– In 1984, Al-Hassani studied the characteristics of Sabkha and Shura Soils in some Iraqi regions.
– In 1986, Al-Aini studied some sabkha sediments in Western Mesopotamia with emphasis on the sedimentological, mineralogical and geochemical aspects of these sediments.
Fig.1: Location map of the studied area
Fig. 2: Distribution of gypcrete and gypsiferous soils in Central Iraq
(Mansour and Toma, 1983)
In 1986, Al-Maroof studied the sedimentology of the Injana Formation in the Habbaniya – Razzaza area.

In 1994, the National Center of Construction Laboratories (NCCL) organized a symposium on gypsiferous soils and their effect on constructions. Some of the papers delivered there are outlined here:

- Saeed (1994) studied the distribution of gypsiferous soils in Iraq and showed that there is no formal classification for these soils where gypsum may vary from (1 – 70) %.
- Razouki et al. (1994) studied the structural failures caused by gypsiferous soils in Iraq and reviewed the basic geotechnical properties of these soils.
- Al-Jumaily (1994) studied the influence of gypsum on the engineering properties of soil and mechanical impact of these properties.
- Jawad (1994) studied the problems caused by gypsiferous soils on the irrigation canals in some Middle East countries.
- Ismail (1994) studied the agricultural exploitation of gypsiferous soils and the crops suitable for various types of these soils according to their gypsum content.
- Sarsam et al. (1994) studied the karstification phenomenon in the gypsum rock of Fat'ha Formation in the Mosul area and its influence on constructions.

In 1996, Al-Baidari studied the sedimentology and geochemistry of Injana Formation in the Najaf – Kerbala area and described the gypsiferous horizons as paleogypcrete.

In 2005, Sissakian and Ibrahim compiled the Geological Hazards Map, scale 1: 1000 000, showing the distribution of gypcrete and gypsiferous soils in Iraq.

In 2005, Hussain studied gypsiferous soils in Najaf, Karbala and Falluja areas. She examined the mineralogy and chemical composition of these soils, as well as the hydrochemistry of the groundwater in the studied areas.

In 2006, Yassin studied gypsiferous soils in several localities in central Iraq. He was concerned with mineralogy and hydrochemistry of soil – water extracts and geotechnical characteristics of these soils. A proposal for classification of gypsiferous soils was attempted.

**METHODS OF WORK**

Channel samples were collected from Section I at equal intervals of 0.3 m, and when change in lithology occurs in Section II. The samples were divided according to the plan shown in Fig. (3). Total number of samples was 22. Grain size analysis was carried out for all samples using wet sieving and hydrometer method following GEOSURVs Work Procedures, Part 19 (Al-Haimus, 1994). A few samples of suitable toughness were thin sectioned and the textural components were studied under the optical microscope. The clay mineralogy was studied by X-ray diffraction for all samples using first basal reflections for identification of clay minerals in the separated clay fraction (treated and natural samples) following GEOSURV's Work Procedures, Part 21 (Al-Janabi et al., 1992).

The TDS and major oxides of the water soluble salts were determined. The water extraction was carried out using 1 gm sample/ 250 ml distilled water with mechanical shaking for 1 hr, followed by filtration. The filtrate was analysed for major oxides, and it was also analysed as water for major anions and cations. The residues were dried and collective samples were prepared to include two groups in each section; the gypsum-rich and gypsum-poor samples. They were analysed for major oxides. All chemical analyses were carried out following the methods specified in GEOSURV's Work Procedures, Part 21 (Al-Janabi et al., 1992).
Gypsum and halite contents of the samples were estimated from the chemical analysis of the water extracts. The former was estimated from the SO₃ and/or CaO contents and the latter from the Na₂O and/or Cl contents. Hypothetical salt combinations were calculated using Collins (1975) procedure from the ionic composition of the water extracts. Interspecific correlation coefficients were calculated using a computer programme.

**LITHOLOGY**
- **Field Description**
  - **Section I (Al-Dor)**
    The described section is about 3 m thick, exposed in a ditch and consists of two main lithological distinct parts. The lower part (1.5 m thick) is fluvial sediment, pale brown, friable clayey soil, occasionally impregnated by gypsum as cavity, nests and vein-like filling. Gypsum showing increases upward. The upper part (1.5 m thick) is sharply emplaced, as a sheet, on the underlying clayey soil and appears as an aeolian sediment. It is more consolidated than the lower part and consists of dirty white silty gypsarenite (Fig.4).

  - **Section II (Falluja)**
    This section is about 3.8 m thick and represents part of the continental sediments of the Injana Formation in the area. It consists of green marl at base and alternations of friable gray siltstone and brown gypsiferous mudstone with three distinct gypcrete horizons, (5 – 10) cm thick each, topping the mudstones (Fig.5). The gypsum in these sediments has various forms: tabular large crystals, prismatic, fibrous and also as fine disseminations mixed with the clayey materials.
### Fig. 4: Columnar lithological succession of Section I (Al-Dor)

<table>
<thead>
<tr>
<th>Thick (cm)</th>
<th>Sample No.</th>
<th>Lithology</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>1/11</td>
<td>Whitchy brown gypsiferous, silty clayey sand (gypsarenite)</td>
<td>Whitchy brown gypsiferous, silty clayey sand (gypsarenite)</td>
</tr>
<tr>
<td>30</td>
<td>1/10</td>
<td>Whitchy brown gypsiferous, silty clayey sand (gypsarenite)</td>
<td>Whitchy brown gypsiferous, silty clayey sand (gypsarenite)</td>
</tr>
<tr>
<td>30</td>
<td>1/9</td>
<td>Whitchy brown gypsiferous, sandy clayey silt (gypsarenite)</td>
<td>Whitchy brown gypsiferous, sandy clayey silt (gypsarenite)</td>
</tr>
<tr>
<td>30</td>
<td>1/8</td>
<td>Whitchy brown gypsiferous, sandy silt (gypsarenite)</td>
<td>Whitchy brown gypsiferous, sandy silt (gypsarenite)</td>
</tr>
<tr>
<td>30</td>
<td>1/7</td>
<td>Pale brown gypsiferous, sandy clayey silt (gypsarenite)</td>
<td>Pale brown gypsiferous, sandy clayey silt (gypsarenite)</td>
</tr>
<tr>
<td>30</td>
<td>1/6</td>
<td>Pale brown gypsiferous, sandy clayey silt, friable (gypsarenite)</td>
<td>Pale brown gypsiferous, sandy clayey silt, friable (gypsarenite)</td>
</tr>
<tr>
<td>30</td>
<td>1/5</td>
<td>Pale brown silty clay, medium tough, contain gypsum</td>
<td>Pale brown silty clay, medium tough, contain gypsum</td>
</tr>
<tr>
<td>30</td>
<td>1/4</td>
<td>Whitish brown silty clay, contain gypsum</td>
<td>Whitish brown silty clay, contain gypsum</td>
</tr>
<tr>
<td>30</td>
<td>1/3</td>
<td>Pale brown silty clay, contain black stains</td>
<td>Pale brown silty clay, contain black stains</td>
</tr>
<tr>
<td>30</td>
<td>1/2</td>
<td>Pale brown silty clay, contain black stains</td>
<td>Pale brown silty clay, contain black stains</td>
</tr>
<tr>
<td>30</td>
<td>1/1</td>
<td>Pale brown clayey silt, contain black stains</td>
<td>Pale brown clayey silt, contain black stains</td>
</tr>
</tbody>
</table>

### Fig. 5: Columnar lithological succession of Section II (Falluja)

<table>
<thead>
<tr>
<th>Thick (cm)</th>
<th>Sample No.</th>
<th>Lithology</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>2/11</td>
<td>Grey sandy siltstone, friable</td>
<td>Grey sandy siltstone, friable</td>
</tr>
<tr>
<td>100</td>
<td></td>
<td>Yellowish brown clayey siltstone, fibrous gypsum on the surface</td>
<td>Yellowish brown clayey siltstone, fibrous gypsum on the surface</td>
</tr>
<tr>
<td>5</td>
<td>2/9</td>
<td>Whitish prismatic sandy, silty gypcrete</td>
<td>Whitish prismatic sandy, silty gypcrete</td>
</tr>
<tr>
<td>30</td>
<td>2/8</td>
<td>Brown silty claystone with gypsum</td>
<td>Brown silty claystone with gypsum</td>
</tr>
<tr>
<td>30</td>
<td>2/7</td>
<td>Redish brown silty claystone rich in gypsum</td>
<td>Redish brown silty claystone rich in gypsum</td>
</tr>
<tr>
<td>10</td>
<td>2/6</td>
<td>Whitish clayey gypsum</td>
<td>Whitish clayey gypsum</td>
</tr>
<tr>
<td>10</td>
<td>2/5</td>
<td>Brownish silty claystone, motteled, contain crystals of gypsum</td>
<td>Brownish silty claystone, motteled, contain crystals of gypsum</td>
</tr>
<tr>
<td>10</td>
<td>2/4</td>
<td>Whitish prismatic sandy gypsum</td>
<td>Whitish prismatic sandy gypsum</td>
</tr>
<tr>
<td>5</td>
<td>2/3</td>
<td>Brownish silty claystone, contain whitish stains on surface</td>
<td>Brownish silty claystone, contain whitish stains on surface</td>
</tr>
<tr>
<td>40</td>
<td>2/2</td>
<td>Reddish brown clayey siltstone, motteled, very fine grained, contain rare white and black stains</td>
<td>Reddish brown clayey siltstone, motteled, very fine grained, contain rare white and black stains</td>
</tr>
<tr>
<td>40</td>
<td>2/1</td>
<td>Green marl contain white and black stains</td>
<td>Green marl contain white and black stains</td>
</tr>
</tbody>
</table>
Grain-size Analysis

All the samples collected from the two sections were subjected to grain-size analysis. The results (Table 1) show that silt-size grains are dominant in the lower part of Section I (generally > 50%). The clay fraction is second with about 40% and the sand fraction is generally less than 10%.

The sand fraction increases in the upper part of Section I up to 48%, averaging about 31%. The clay fraction decreases to about 27% on average and the silt fraction remains the dominant size fraction averaging about 42%.

Section II is dominated by siltstone and claystone; the latter is more gypsiferous. The lower part of this section (0.6 m thick) consists mostly of siltstone followed by 1.8 m thick silty claystone where the clay fraction is dominant (average > 57%). The upper part (1.30 m thick) is dominated by siltstone, where silt-size fraction exceeds 50% on average with a noticeable increase in the sand fraction reaching about 15% on average. The lower two gypcrete horizons are related to clay-size sediments, but the upper horizon is rather silty.

Table 1: Grain-size analysis of the studied samples (%)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Clay</th>
<th>Silt</th>
<th>Sand</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/1</td>
<td>43</td>
<td>55</td>
<td>2</td>
<td>Slightly gypsiferous soil</td>
</tr>
<tr>
<td>1/2</td>
<td>51</td>
<td>48</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>1/3</td>
<td>34</td>
<td>56</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>1/4</td>
<td>40</td>
<td>50</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>1/5</td>
<td>33</td>
<td>59</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>1/6</td>
<td>33</td>
<td>38</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>1/7</td>
<td>20</td>
<td>62</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>1/8</td>
<td>21</td>
<td>43</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>1/9</td>
<td>41</td>
<td>37</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>1/10</td>
<td>15</td>
<td>37</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>Top</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/11</td>
<td>31</td>
<td>33</td>
<td>36</td>
<td></td>
</tr>
</tbody>
</table>

| Bottom     |      |      |      |                              |
| 2/1        | 27   | 72   | 1    | Slightly gypsiferous paleosol |
| 2/2        | 21   | 70   | 9    |                              |
| 2/3        | 68   | 31   | 1    |                              |
| 2/4        | 61   | 22   | 17   | Paleogypcrete                |
| 2/5        | 55   | 42   | 3    | Gypsiferous paleosol         |
| 2/6        | 51   | 46   | 3    | Paleogypcrete                |
| 2/7        | 56   | 41   | 3    | Gypsiferous paleosol         |
| 2/8        | 55   | 43   | 2    | Highly gypsiferous paleosol  |
| 2/9        | 32   | 49   | 19   | Paleogypcrete                |
| 2/10       | 37   | 56   | 7    |                              |
| Top        |      |      |      | Slightly gypsiferous sediments|
| 2/11       | 27   | 51   | 22   |                              |

PETROGRAPHY

In view of the friable nature of most samples, only a few of them were suitable for thin section preparation. The lower part of Section I consists of brown mudstone with very fine disseminations of gypsum crystals (Fig.6). The overlying gypsarenite shows spindle-shaped gypsum grains with no crystal outlines, up to 1 mm long, associated with fine grained detrital quartz and embedded in a groundmass of clay and gypsum (Figs.7 and 8).

The gypcrete horizons of Section II contain large prismatic gypsum crystals, authigenically grown in a clay matrix (Fig.9). Interlocking of gypsum crystals, caused by recrystallization and growth, forms a mosaic texture in these horizons (Fig.10). Detrital angular quartz grains are common associate in the upper gypcrete horizon, having an average grain-size of about 0.1 mm (Fig.11).
Fig. 6: Photomicrograph of disseminated gypsum crystals (XN), sample 1/1

Fig. 7: Photomicrograph of spindle-gypsum grains (XN), sample 1/6

Q: Quartz grain
Fig. 8: Photomicrograph of spindle-shaped gypsum crystals (XN), sample 1/8

Fig. 9: Photomicrograph of euhedral tabular gypsum crystals (XN), sample 2/6
Fig. 10: Photomicrograph of interlocking gypsum crystals (XN), sample 2/9

Fig. 11: Photomicrograph of gypsum crystals associated with quartz grains (XN), sample 2/6

Q: Quartz grain
MINERALOGY

The lower part of Section I is rich in clay minerals. X-ray diffraction results show that it is dominated by palygorskite and to a lesser extent smectite and illite. Kaolinite and mixed-layer clays are present in minor amounts. Non-clay minerals are dominated by dolomite, quartz and gypsum with accessory amounts of calcite and feldspar (Table 2). The upper part contains lesser amounts of clay minerals; dominated by smectite and palygorskite. The non-clay minerals are gypsum and quartz with traces of feldspar in some samples.

The mineralogy of the sediments in Section II shows more variation than that in Section I, following the more frequent changes in lithology. However, smectite is the dominant clay mineral here, associated with palygorskite, illite, kaolinite, mixed-layer clays and rarely sepiolite. In a few samples palygorskite is dominant (samples no. 2/3 and 2/8), whereas illite is dominant among the clays in sample no. 2/7 only. The non-clay minerals are dominated by gypsum in the gypsum-rich samples (2/4, 2/5, 2/6, 2/8 and 2/9). In these samples gypsum is associated with quartz mostly. In the less gypsiferous samples, the non-clay minerals are dominated by calcite or dolomite in the marls and mudstones, or by quartz in the sandy layers (samples 2/2 and 2/11). Halite is recorded in several samples of this section (samples 2/3, 2/8 and 2/10).

Comparing the mineralogy in the two sections, it is obvious that there are many things in common. The clay minerals are dominated by smectite and palygorskite and the non-clay minerals (other than salts) are dominated by dolomite and to a lesser extent by calcite or by quartz in the sandy layers. Gypsum is the only salt detected by XRD in the Quaternary sediments, whereas gypsum and halite are recorded in the Neogene sediments. The dominant presence of palygorskite and smectite among the clay minerals reflects the arid and semi-arid climatic conditions. These clay minerals require alkaline environment and high to moderate Mg-salinity. The aridity and hot climate is obvious in the two sections, indicated by the gypsiferous soils and aeolian gypsarenite in Section I and by the gypsiferous paleosols and paleogypcrete horizons in Section II.

Gypsum and halite contents in the studied samples were calculated from chemical analysis of water extracts. Gypsum content varies in Section I from about (0.7 – 67) %. The mean value in the lower part is 5.5% and in the upper part is 65.3%.

Halite content ranges from (0.04 – 1.69) %, being higher in the less gypsiferous lower parts of the section, with a mean content of 0.8%, compared to about 0.1% mean content in the gypsum-rich upper part. The high gypsum values are related to a remarkable increase in the sand content, which demonstrates the nature of the gypsum presence in the upper part of this section, being aeolian sediments, where gypsum was transported by wind mostly as silt- and sand-size grains (gypsarenite) (Fig.12).

In the samples of Section II, gypsum ranges from (0.3 – 67) %, having a mean content of about 1.2% in the less gypsiferous horizons, whereas the mean gypsum content is about 53% in the gypsum-rich horizons. Halite shows similar tendency in this section as in Section I, being higher in the gypsum-poor part with a mean of about 2.6% and lower in the gypsum-rich parts with a mean of about 1.2%. Halite content is noticeably higher in the Neogene samples compared to the Quaternary samples. The enrichment of gypsum in Section II is generally associated with the clay-rich samples (Fig.13).
Fig. 12: Vertical distribution of TDS, grain-size, gypsum and halite in Section I

Fig. 13: Vertical distribution of TDS, grain-size, gypsum and halite in Section II
Table 2: Mineral constituents of the studied samples

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Clay minerals</th>
<th>Non-clay minerals</th>
<th>Abbreviations</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bottom</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/1</td>
<td>Sm., Mix. L., Pal. Kao.</td>
<td>D, C, Q, F</td>
<td>Sm. Smectite</td>
</tr>
<tr>
<td>1/2</td>
<td>Pal., Ill., Kao.</td>
<td>D, Q, F, G (Tr.)</td>
<td>Pal. Palygorskite</td>
</tr>
<tr>
<td>1/3</td>
<td>Pal., Ill., Kao. Sm., Mix.</td>
<td>C, Q, F, G</td>
<td>Sep. Sepiolite</td>
</tr>
<tr>
<td>1/4</td>
<td>Traces</td>
<td>D, G</td>
<td>Kao. Kaolinite</td>
</tr>
<tr>
<td>1/5</td>
<td>Ill., Pal.</td>
<td>D, G, Q, F</td>
<td>Mix. L. Mixed-layer clays</td>
</tr>
<tr>
<td>1/6</td>
<td>Sm., Mix. L.</td>
<td>G</td>
<td>Ill. Illite</td>
</tr>
<tr>
<td>1/7</td>
<td>Sm., Mix. L., Pal.</td>
<td>G, Q, (Tr.), F</td>
<td>C Calcite</td>
</tr>
<tr>
<td>1/8</td>
<td>Sm., Mix. L., Pal., Ill.</td>
<td>G, Q</td>
<td>D Dolomite</td>
</tr>
<tr>
<td>1/9</td>
<td>Sm., Mix. L., Pal. (Tr.)</td>
<td>G, Q</td>
<td>Q Quartz</td>
</tr>
<tr>
<td>1/10</td>
<td>Sm., Mix. L., Pal.(Tr.)</td>
<td>G, Q (Tr.)</td>
<td>G Gypsum</td>
</tr>
<tr>
<td><strong>Top</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/11</td>
<td>Sm., Mix. L. , Ill.</td>
<td>C, Q (Tr.)</td>
<td>H Halite</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>F Feldspar</td>
</tr>
</tbody>
</table>

**GEOCHEMISTRY**

The geochemistry of the gypsiferous soils and sediments was investigated using three routes. Water-extracts were analysed (in Wt. %) for major oxides and TDS. They were also analysed, as water, for major cations and anions and these analyses were used to derive hydrochemical formulas and hypothetical salt combinations. Furthermore, the host sediments were analysed, after salt extraction, for major oxides.

- **Major Oxides Composition of the Water Extracts**
  - **Quaternary Samples (Section I)**

Two parts can be clearly defined; the lower part (slightly gypsiferous soil, 1.5 m thick) where TDS is < 20%, and show increase of CaO and SO₃ contents from bottom to top. This part is relatively rich in Na₂O and Cl, generally forming together > 40% of the TDS constituents. The MgO, K₂O and CO₃ contents are generally low, as compared to the other constituents, but they are noticeably higher in this part than the overlying aeolian gypsum gypsarenite (Table 3).

Gypsum and halite contents were estimated from chemical analysis; the former ranges from about (0.7 – 12.7) % whereas the latter ranges from about (0.5 – 1.7) %. Together they make more than 70% of the TDS constituents; gypsum being the dominant salt. The upper part (aeolian gypsum, 1.5 m thick) contains > 60% salts of which gypsum represents > 90%. Na₂O, Cl and other constituents are highly reduced in this part.
Table 3: Chemical composition, TDS, gypsum and halite contents of the water extracts (Section I) (Wt. %)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>SO₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>Cl</th>
<th>CO₃</th>
<th>TDS</th>
<th>Gypsum</th>
<th>Halite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/1</td>
<td>0.86</td>
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<td>0.38</td>
<td>0.01</td>
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<td>0.05</td>
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</tr>
<tr>
<td>1/2</td>
<td>0.32</td>
<td>0.22</td>
<td>0.07</td>
<td>0.27</td>
<td>&lt; 0.01</td>
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<td>2.00</td>
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<td>0.51</td>
</tr>
<tr>
<td>1/3</td>
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<td>0.09</td>
<td>0.33</td>
<td>0.01</td>
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<td>66.95</td>
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<td>0.08</td>
<td>59.35</td>
<td>63.73</td>
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</table>

Neogene Samples (Section II)

The major oxide composition of the water-extracts in this section is more heterogeneous relative to Section I samples. However, this section can be divided into three parts on the basis of TDS content. A lower part (0.1 m thick) contains < 10% TDS dominated by Na₂O and Cl and to a lesser extent by CaO and SO₃, indicating more halite than gypsum in this part. The other oxides are minor or trace (Table 4).

In the middle part, the TDS increases to (33 – 64) % of the sediment constituents dominated by CaO and SO₃, whereas the other constituents are of relatively minor importance. However, within this gypsum-rich part there are two horizons (0.7 m and 0.3 m thick), where the TDS is relatively low (about 33%), show relative increase in Na₂O and Cl.

In the upper part the TDS is reduced and so are CaO and SO₃, which account for < 40% of the TDS constituents. Na₂O and Cl are relatively enriched at the base of this part and, together, they represent about 72% of the leachate constituents.

Table 4: Chemical composition, TDS, gypsum and halite contents of the water extracts (Section II) (Wt. %)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>SO₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>Cl</th>
<th>CO₃</th>
<th>TDS</th>
<th>Gypsum</th>
<th>Halite</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.02</td>
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<td>0.43</td>
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<td>0.02</td>
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<td>3.10</td>
<td>0.34</td>
<td>1.50</td>
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<td>0.16</td>
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<td>0.04</td>
<td>9.00</td>
<td>4.25</td>
<td>3.40</td>
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<td>21.10</td>
<td>&lt; 0.01</td>
<td>0.01</td>
<td>&lt; 0.01</td>
<td>0.04</td>
<td>0.02</td>
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<td>0.70</td>
<td>0.02</td>
<td>1.59</td>
<td>0.02</td>
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<td>0.01</td>
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<td>0.02</td>
<td>58.50</td>
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<td>0.04</td>
<td>11.20</td>
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<td>5.30</td>
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</tbody>
</table>

The major oxides composition and the derived gypsum and halite contents show similar behavior in both sections (Table 5); CaO and SO₃ are negatively correlated with the other constituents of the water extracts and gypsum is inversely related to halite. The increase in CaO and SO₃ and consequently of gypsum is taking place on the expense of other salt constituents. This may suggest that gypsum enrichment in these sediments had taken place in a relatively younger stage of diagenesis than the other salts.
Table 5: Mean chemical composition of the water extracts, grain-size, gypsum and halite contents (Wt. %)

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Section I</th>
<th>Section II</th>
</tr>
</thead>
<tbody>
<tr>
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<td>(1)</td>
<td>(2)</td>
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<tr>
<td>SO₃⁺</td>
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</tr>
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<td>CaO</td>
<td>1.81</td>
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</tr>
<tr>
<td>MgO</td>
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</tr>
<tr>
<td>K₂O</td>
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<td>0.01</td>
</tr>
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<td>Cl⁻</td>
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</tr>
<tr>
<td>CO₃⁻</td>
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<td>0.03</td>
</tr>
<tr>
<td>TDS</td>
<td>8.51</td>
<td>63.51</td>
</tr>
<tr>
<td>Clay</td>
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<td>26.83</td>
</tr>
<tr>
<td>Silt</td>
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<td>41.67</td>
</tr>
<tr>
<td>Sand</td>
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<td>31.50</td>
</tr>
<tr>
<td>Gypsum</td>
<td>5.55</td>
<td>65.27</td>
</tr>
<tr>
<td>Halite</td>
<td>0.81</td>
<td>0.12</td>
</tr>
</tbody>
</table>

(1) Gypsum-poor samples  
(2) Gypsum-rich samples

- **Hydrochemistry Of Water Extracts**

The water extracts were analysed, as water, for major cations and anions in order to study the hydrochemistry of the salt-bearing solutions that caused the post-depositional enrichment of these sediments with gypsum and other salts (Table 6). The processing of the hydrochemical data included correlation coefficient (Tables 7 and 8), hydrochemical formulas (Tables 9 and 10) and hypothetical salt combination (Table 11).

Ca²⁺ and SO₄²⁻ dominate the ionic composition of the water extracts in Section I. Na⁺ is the second cation in all samples, whereas Cl⁻ or CO₃²⁻ is the second anions. The latter is more dominant than the former, especially at the upper parts of Section I. However, Na⁺, CO₃²⁻ and Cl⁻ show higher concentrations in the lower parts, where Ca²⁺ and SO₄²⁻ decrease. The water type varies in Section I extracts from Na−Ca−Cl−sulfate to Na−Ca−CO₃−sulfate in the less saline samples of the lower part, but changes to Ca−sulfate as the salinity increases upwards.

The hydrochemistry of the water extracts of the Neogene samples (Section II) shows some differences compared to the Quaternary samples. Na⁺ and Cl⁻ dominate the lower meter of the section, Ca²⁺ and SO₄²⁻ or Ca²⁺ and CO₃²⁻ come second. In the following 1.5 m (the middle of the section), SO₄²⁻ and Ca²⁺ dominate the ionic composition, followed by Na⁺ and Cl⁻. In the upper part (1.3 m thick) Na⁺ and Cl⁻ or Na⁺ and CO₃²⁻ return again as major ions. Hence, the water type varies from Ca−Na−CO₃−chloride to Ca−Na−SO₄−chloride in the less saline lower part. It changes to Ca−sulfate in the highly saline middle part, and to Ca−Na−chloride or Ca−Na−Cl−carbonate in the upper part, where salinity is reduced again.

The ionic constituents may be grouped in the samples of both sections into two groups on the basis of interionic correlations (Tables 7 and 8). Group I includes the positively correlated Na⁺−K⁺−Mg²⁺−CO₃²⁻−Cl⁻ and Group II includes Ca²⁺−SO₄²⁻−TDS. These two groups are negatively correlated with each other. This type of relation suggests two salt-mineralization episodes in these sediments: An early diagenetic mobilization of the ions from host minerals due to diagenetic alteration of some unstable minerals (like feldspar), ion exchange in the clay minerals and/ or early diagenetic dolomitization or dedolomitization leading to a limited formation of chloride-and carbonate-type salts.

A later episode of SO₄²⁻-rich solution have penetrated and affected the sediments by physical growth and chemical corrosion, leading to the formation of a highly gypsiferous soils or gypcrete horizons. The source of these solutions is external and most probably is a highly saline groundwater. However, this model does not include the upper part of Section I, which is physically derived to the site by wind transportation (aeolian sediments).
### Table 6: Ionic composition of the water extracts

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Na(^+)</th>
<th>Mg(^{2+})</th>
<th>Ca(^{2+})</th>
<th>K(^+)</th>
<th>SO(_4)(^{2-})</th>
<th>Cl(^-)</th>
<th>CO(_3)(^{2-})</th>
<th>TDS</th>
</tr>
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<tbody>
<tr>
<td><strong>Bottom</strong></td>
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<td></td>
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<td></td>
</tr>
<tr>
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### Table 7: Interionic correlation coefficient of the water extracts (Section I)

(significant value = 0.6)

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<th>Cl</th>
<th>SO(_4)</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
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</tr>
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<td>K</td>
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<td>−0.77</td>
<td>0.98</td>
<td>0.97</td>
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<td></td>
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<tr>
<td>SO(_4)</td>
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<td>−0.93</td>
<td>0.75</td>
<td>−0.90</td>
<td>0.89</td>
<td>0.86</td>
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<td>−0.69</td>
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<td>CO(_3)</td>
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<td>−0.92</td>
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### Table 8: Interionic correlation coefficient of the water extracts (Section II)

(significant value = 0.6)

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<th>SO(_4)</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
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<td>0.80</td>
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<td>K</td>
<td>0.94</td>
<td>−0.97</td>
<td>0.94</td>
<td>0.89</td>
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<tr>
<td>SO(_4)</td>
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<td>0.99</td>
<td>0.99</td>
<td>−0.91</td>
<td>0.97</td>
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<td>−0.95</td>
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<tr>
<td>CO(_3)</td>
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<td>−0.86</td>
<td>0.85</td>
<td>−0.85</td>
<td>0.87</td>
<td>−0.92</td>
<td>−0.80</td>
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Table 9: Hydrochemical formula and water-type of the water extracts (Section I)

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<th>Hydrochemical formulas (mg eq/l) (%)</th>
<th>Water type</th>
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<td>Na – Ca – CO$_3$ – Sulfate</td>
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<tr>
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<td>2.31</td>
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<td>1/11</td>
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Table 10: Hydrochemical formula and water-type of the water extracts (Section II)

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Table 11: Hypothetical salts combination (meq %) of the water extracts

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<th>MgSO₄</th>
<th>MgCl₂</th>
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<th>Na₂SO₄</th>
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<td>2/10</td>
<td>6.75</td>
<td>8.86</td>
<td>12.53</td>
<td>–</td>
<td>–</td>
<td>13.78</td>
<td>–</td>
<td>–</td>
<td>57.52</td>
<td>0.56</td>
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<td><strong>Section II</strong></td>
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<td>2/11</td>
<td>37.38</td>
<td>–</td>
<td>2.80</td>
<td>–</td>
<td>10.80</td>
<td>24.51</td>
<td>23.58</td>
<td>0.93</td>
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</table>

**Hypothetical Salts Combination**

The hypothetical salts were derived from the hydrochemical formulas using Collins (1975) principles and are presented in meq/1% units. The results (Table 11) show that all the Quaternary samples contain CaSO₄, CaCO₃, NaCl and KCl hypothetical salts in varying amounts. CaSO₄ is dominant in the gypsarenite samples (upper part), whereas CaCO₃, CaSO₄ and NaCl dominate the soil samples of the lower part. Na₂SO₄ and MgSO₄ occur in the lower part only, suggesting more SO₄²⁻ anions than Ca²⁺ can take to form CaSO₄. MgCl₂ is found in the lowermost part indicating excess Cl⁻ relative to Na⁺. The presence of Na₂SO₄ in a specific horizon in the gypsarenite (sample 1/10) may suggest the Shari saltern as an occasional source area for this aeolian sediments.

All the Neogene samples contained CaCO₃, NaCl and KCl as hypothetical salts. CaSO₄ is missing in the lower and upper parts, but it is the dominant hypothetical salt in the middle part. Na₂SO₄ is found in considerable amounts (≈ 20 – 25%) in some samples at the lower and upper parts suggesting excess Na⁺ and deficiency in Ca²⁺ in the diagenetic solutions of these parts of the section. MgCl₂ is found in reasonably high amounts in some samples of the lower and upper parts suggesting Na⁺ deficiency relative to Cl⁻. This deficiency is also expressed in the middle part (gypsum-rich), where CaCl₂ is found in many samples. In the uppermost part of the section a unique occurrence of Na₂CO₃ and MgCO₃ is recorded together with considerably high amounts of Na₂SO₄, NaCl and CaCO₃ and absence of CaSO₄. This trend reflects a highly carbonated water where the CO₃²⁻ anion is present in excess of the available Ca²⁺, which may be attributed to short or occasional rainy episodes, where rain water is usually rich in HCO₃⁻. It may also reflect an excess of Na⁺ in the solution.
**Geochemistry of Host Sediments**

The analysis of the sediments associated with gypsum in the studied sections (after salts extraction) is shown in Table (12). The analysis reflects the mineral heterogeneity of the sediments, being of multisource and mechanically driven to the depositional site. Most of the chemical constituents may be related to four mineral species:

- Carbonates (calcite and dolomite): CaO, MgO and L.O.I.
- Clay minerals (smectite, palygorskite and illite): SiO₂, Al₂O₃, Fe₂O₃, MgO, K₂O and Na₂O.
- Quartz: SiO₂.
- Feldspar: SiO₂, Al₂O₃, K₂O, Na₂O and CaO.

Group 1 of samples is high in CaO, MgO and L.O.I., suggesting high carbonate content (mostly dolomite). It is also rich in Al₂O₃ but low in SiO₂, which suggest high clay minerals content but little quartz. The feldspar content seems low as suggested by the relatively low K₂O and Na₂O.

| Table 12: Chemical analysis (Wt %) of the host sediments (after salts extraction) |
|---------------------------------|---------------------------------|----------------|----------------|----------------|
| (1) SiO₂                         | (2) SiO₂                         | (1) SiO₂     | (2) SiO₂     | (3) SiO₂     |
| 33.66                            | 58.30                            | 39.6         | 37.3         | 46.98        |
| Fe₂O₃                            | 3.75                             | 3.68         | 4.76         | 5.80         | 3.44         |
| Al₂O₃                            | 8.26                             | 9.57         | 11.33        | 12.04        | 10.15        |
| CaO                              | 17.36                            | 9.66         | 15.96        | 9.56         | 3.16         |
| MgO                              | 11.90                            | 6.44         | 6.0          | 13.78        | 6.80         |
| Na₂O                             | 0.73                             | 1.61         | 0.73         | 0.43         | 1.64         |
| K₂O                              | 0.87                             | 1.44         | 1.22         | 1.26         | 1.01         |
| L.O.I.                           | 23.02                            | 7.54         | 18.94        | 19.74        | 15.21        |

Group 2 of samples represents most of the non-gypsiferous impurities of the aeolian gypsarenite in Section I, as most of the constituents in this part of the section are gypsum. It is high in SiO₂ content suggesting considerable amounts of quartz. It is also high in Al₂O₃, MgO, K₂O and Na₂O indicating high contents of clay minerals as well as feldspars. Carbonates are low indicated by the very low content of L.O.I.

The host sediments of Section II are represented by three composite samples. Groups 1 and 2 of samples are relatively rich in Al₂O₃, Fe₂O₃ and K₂O suggesting high clay minerals content. The carbonate content is high as suggested by the high CaO, MgO and L.O.I. being more dolomite than calcite in Group 2 of samples, as shown by high MgO content in this group of samples. The SiO₂ is low suggesting little quartz. Group 3 of samples represents the upper part of Section II. It is relatively high in SiO₂ and low in Al₂O₃, MgO, Fe₂O₃ and CaO, as compared to Groups 1 and 2 of samples, suggesting lower carbonates and clay minerals and higher quartz contents in the upper part.

The analysis of these sediments shows no clear affinity of gypsum to certain chemical composition. However, Section II may show some tendency of gypsum enrichment in the clay-rich part of the section (Group 2 of samples), which is rich in Al₂O₃, MgO, Fe₂O₃ and K₂O. The MgO content is especially high here, which points towards dolomite and palygorskite. The latter could be partly authigenic as aridity and salinity favour the formation of this clay mineral by neo-formation or alteration of other clay minerals.
SOURCE AND PARAGENESIS

Salts precipitation follow a rule that depends highly on the salinity, temperature as well as on the ionic composition of the solution. Generally, carbonates precipitate first, followed by sulfates and finally by the chlorides, within each of these salt assemblages there are sequential precipitation series that depends on the cations and anions involved, the interaction of the ionic constituents and on temperature (Collins, 1975).

Long period of aridity under hot climate and shallow groundwater sources, increase the salinity of the soil water by increased evaporation, leading to the formation of salt crusts on the surface (Fig.14). The composition of the salts in these crusts depends mostly on the composition of the soil-water. They are mostly composed of gypsum and/or halite as main salts, with minor amounts of other salts.

The development of these salt crusts in thickness requires stability of the conditions such as aridity, groundwater sources and lack of sedimentation or erosion. Wind erosion of primary gypsum beds or secondary gypcrete horizons may lead to the formation of gypsiferous sand dunes or sand sheets (Fig.14).

Most of the ionic constituents participating in the post depositional generation of the salt minerals may be supplied from groundwater sources. Hence, the hydrochemistry of these waters may play the main role in determining the composition of the evaporites formed.

Groundwater may be divided into two genetic types (Ivanov et al., 1968):

Meteoric water: Rain water that penetrates the earth surface and recharges the shallow aquifers with fresh water. In the mean time, it works on the dissolution of many soil and rock components. Such waters are usually rich in Ca$^{2+}$ and SO$_4^{2-}$ in arid and semi-arid regions.

Ancient marine waters: These are normal marine waters entrapped within the sediments during precipitation, but were mobilized during compaction into subsurface traps or aquifers. These waters are usually enriched in Na$^+$ and Cl$^-$ depicting sea-water composition. However, their composition may be altered when mixed with ground waters of meteoric origin.

Internal sources of cations and anions may be also supplied from within the sediments by ionic exchange and alteration of parent minerals during diagenesis. Sodium, potassium, calcium and to some extent magnesium are common exchangeable cations in clay minerals.
(Grim, 1968). They can be generated into a mobile form and influence the diagenetic fluids of the sediments. Another important source of Na⁺ and K⁺ is the alteration of feldspars and micas by hydrolysis. The former may be also mobilized after aragonite transformation to calcite or by the dolomitization of calcite.

Sulfate may be generated into a mobile form following the oxidation of sulfides present in sediments, especially pyrite. Magnesium may be also mobilized following dolomitization process. The carbonate anion (CO₃²⁻) may be derived from atmospheric CO₂ or degradation and dissociation of organic matter in the sediments.

Hence, there are many possible sources for the ionic constituents forming the salt minerals, in the studied sections. However, the overwhelming sulfate-type minerals suggest meteoric near-surface ground waters of very high salinity with respect to Ca²⁺ and SO₄²⁻ resulting from the dissolution of primary gypsum deposits of the Fat'ha Formation in the Folded Zone and Jeziра area. The increased salinity also indicates hot and arid climate, which have characterized the Holocene time and seems to have periodically prevailed during the Late Miocene times.

The development of gypcrete horizons in the Injana Formation reflects non-depositional episodes and aridity juxtaposed with hot climate. The gypsarenite horizon in Section I is an aeolian sediment, transported by wind erosion from near-by older gypcrete horizons, or even from the erosional products of the exposed primary gypsum beds of the Fat'ha Formation in the Jeziра area and the near-by Hemreen and Makhoul Ranges.

The less gypsiferous horizons, in both sections, may be attributed to the continuity of fluvial sediments (semi-arid climate) preventing crustification and development of gypcrete horizons. The main source of salts in these horizons may be internal diagenetic solutions.

CONCLUSIONS

- Gypcrete and gypsiferous soils are common in the Injana Formation and Quaternary sediments and appear to have developed in certain episodes of arid and warm climatic conditions during the Neogene. In both cases the host sediments are of continental origin.
- Gypsum is enriched in the upper parts of the soil by upward migration of SO₄²⁻-rich ground waters induced by arid and hot climates. It replaced the original soil components physically and chemically.
- Two types of mineralizing solutions can be distinguished causing salts formation in soil. An early diagenetic internal source rich in (Na – K – Mg – CO₃ – Cl) ions, which is of minor concentration resulting from the mobilization of these ions from the soil mineral components. The second is a later stage, where external sources of Ca – SO₄ rich solutions invade the soil by capillary action and precipitate gypsum. The two types are negatively correlated.
- Gypsum may by transported by wind from the erosion of the primary and secondary gypsum deposits to form gypsiferous sand dunes and sand sheets composed mostly of gypsarenite.
- Gypcrete and gypsiferous horizons require certain conditions to develop vertically and laterally including the stability of the climate (hot and dry), availability of the source (SO₄-rich and near-surface ground waters), lack of deposition or erosion (aridity, no floods and low lands) and permeable sediments as host.
- Considering the available facts, gypcrete and gypsiferous soils will continue to develop in Iraq as long as the present conditions prevail, and it forms one of the most serious problems of desertification in the country.
REFERENCES


