Mineralogy and Geochemistry of Anah and Euphrates Formations and Their Suitability for Portland Cement and Noora Industry at Al-Bagh reached and Haditha Areas, Western Iraq

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Abstract
The current study including geochemical and mineralogical aspects of 12 rock samples from Anah and Euphrates formations in two outcrops, The first outcrop is at Haditha city, with 12.5 meters thickness, and the second location is at Al-Bagh reached city, with 21 meters thickness. The mineralogical study by X-ray diffraction indicated that calcite is the main mineral in the rocks of Anah Formation, while calcite and dolomite exist in Euphrates Formation, where calcite is concentrated in the lower part of Euphrates Formation, while dolomite is common in the middle and upper parts of this formation, in addition to other minor minerals such as quartz and feldspar. Geochemical study was carried out by XRF to determine the major oxides (CaO, MgO, Fe₂O₃, Al₂O₃, SiO₂, SO₃, K₂O, Na₂O, MnO) and the suitability of Anah and Euphrates rocks as raw material for Portland cement and Al-Noura (lime) cement industries. According to the results it is found that Euphrates Formation in the Al-Bagh reached and Haditha outcrops is not suitable for the Portland cement, because of high percentage of MgO as a result of the high percentage of dolomitic limestone. The chemical analysis of the samples of the Anah Formation in Haditha outcrop are suitable for the Noora cement (lime) industry according to the Iraqi standard. The high content of magnesium in the Euphrates Formation at Al-Bagh reached area used as indicator that the rocks deposited in shallow marine and warm condition, and the environment was mostly isolated with warm condition. Low Sr content indicates shallow carbonate rocks. Thus, the sedimentary environment of the Anah Formation at Haditha outcrop was relatively shallower than that of the Euphrates Formation.

Keywords: Euphrates; Anah; Mineralogy; Geochemistry; Strontium; outcrop

1. Introduction
The current study included the geochemical and mineralogical aspects of 12 rock samples from the Anah Formation (Upper Oligocene) and the Euphrates Formation (Lower Miocene) in two outcrops. The first outcrop is in the city of Haditha it is 12.5m thick, and the second outcrop is in the city of Al-Bagh reached it is 21m thick.

Samples of the present study were collected from Anah and the Euphrates formations from the Hajlan Valley outcrop in Haditha city and from the Baghdadi outcrop in Al-Bagh reached city, which is located between two latitudes 24° 05’ 34”, 36° 51’ 33” N” and longitudes 02° 22’ 42” 46° 31’ 42” E”.

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Fig. 2 represents the location of the current study and Fig. 1 represents sampling and cross section for both outcrops.

It is known that the rocks of Anah and the Euphrates limestone have wide extensions, whether in the surface or subsurface sections, and they are clearly exposed in the upper Euphrates Valley regions of Iraq. For the first time, van Bellen, (1956) described the Anah Formation at Anah city with a thickness of 49.6 m. The upper contact limit of the formation was found to be unconformable, as evidenced by the presence of a thick layer of basal conglomerates that represent the lower part of the Euphrates limestone Formation (Van Bellen et al., 1959). As for the Euphrates limestone Formation, it appears in the areas of the low folds in northern Iraq, as it alternates with Sirikakni and Al-Dhuban formations. While the thickness of the formation in the neighboring areas was found to be between 60-70 m (Buday, 1980). Radoicic (1986) discuss the contact between Anah and Azqand at KH-17/7 western Iraq while Ctyroky and Karim (1971) recognizes the contact between Baba and Anah formations. Al-Ghreri (1985) proposed an "alternative" for type section, and its location is within the boundaries of Al-Baghdadi city, due to the submergence of the old site with the waters of Haditha Dam. The lower contact boundary is characterized by a non-conformity surface, which is represented by a thick layer of basal conglomerates separating it from the limestone Anah formation. As for the upper contact boundary of the formation, none of the previous studies indicated the presence of an upper contact boundary for the formation conclusively (Ali, 2011). Through a study (Abdullah et al, 2019) Eight carbonate microfacies were identified and interpreted to have been deposited in a shallow marine environment. The Euphrates Formation passes up from deposits of restricted lagoon to shoal depositional environments. (Turki and Awadh (2023) discuss the environment of Anah and Euphrates formations using REE geochemistry, rusaltes the environment of the Anah Formation was deposited in reef for back-reef, the environment of the Euphrates Formation was deposited in open sea. The aim of this study is explaining mineralogical and geochemical studies and to determine if the raw materials in the two formations are suitable for the manufacture of cement, Al-Noura(lime) and to determine the deposited of environment condition, and deduce the sedimentary environment, and suitability of Anah and Euphrates formations for purpose of cement manufacture and al-noura.
**Fig. 1.** A- The stratigraphic columnar section; B- The stratigraphic columnar section of Al-Baghdadi’s outcrop and Haditha outcrop

**Fig. 2.** The location map for this study (Ali, 2015)
2. Sampling and Methodology

Twelve rock samples were collected, Three samples from Anah Formation at Haditha outcrop, Three samples from Euphrates Formation at Al-Baghdadi outcrop, and six samples from Euphrates Formation at Al-Baghdadi outcrop, the Anah Formation not appear at Al-Baghdadi outcrop, The collected samples used for geochemical and mineralogical study. The total thickness of the Haditha outcrop is 12.5 m and the total thickness of the Baghdadi outcrop is 19 m (Fig. 1). The X-ray diffraction (XRD) technique was used to study the mineralogy of rocks and their content of calcite and dolomite. The Alizrin staining were used to differentiate between the dolomite and calcite based on the change in color. For (XRF) The rock samples were ground and crushing to powder. The geochemical analysis was carried out using the XRF device. This was done by passing the sample powder through a 200μm sieve, and then using pellets with a diameter of 32 mm, according to the working conditions of the device.

3. Results and Discussions

3.1. Mineralogy

X-ray diffraction (XRD) was used to identify the mineral nature and to recognize the constituent minerals of the Anah and Euphrates formations, Samples was selected and examined in the range 2θ=0–40 in X-ray diffraction and it was found that the main mineral of the Anah formation is calcite. while the mineral dolomite has a very small percentage in the formation. Calcite and dolomite are the two main components of the Euphrates Formation, as calcite is restricted to the lower part of the formation, while the mineral dolomite is common in the middle and upper parts of the formation. The recognized minerals which determined from XRD includes calcite, dolomite, and quartz that major minerals with minor content quartz. The percentage of calcite in high-purity limestone rocks reaches more than 98% and its percentage in impure limestone rocks is less than 85% (Kadhim and Hussein, 2016 The mineral composition of all samples is similar, as the XRD charts showed that calcite and dolomite are the major minerals in most calcareous samples as in plates A, B, C, D, E, F in Fig.3 while quartz is present in very small quantities. XRD showed that calcite is the primary mineral in all the analyzed samples, and the main peak of this mineral appears at the base reflection of the plane d space = (3.03 Å). The presence of the mineral dolomite in the limestone rocks varies from one location to another. For example, we note from the XRD charts that the model taken from the Haditha outcrop for the formation of the Euphrates is free of this mineral. d space = (2.89 Å). Quartz mineral comes in the third degree after calcite and dolomite in most calcareous forms and appears at the main base reflection d space = (3.35 Å).
Fig. 3. Curves of X-ray diffraction (XRD): Sample A. from Anah Fn., Sample B. from Euphrates Fn., Sample C. from Euphrates Fn., Sample D. from Anah Fn., Sample E. from Euphrates Fn., Sample C. from Euphrates Fn.

4. Geochemistry

Geochemistry is used to verify the determination of the geochemical composition and distinguish the transformational and sedimentary processes as well as its suitability for the cement industry for the Euphrates and Anah formations in both sections of study as geochemistry of the Anah and Euphrates formations, all geochemical study were carried out analyses in the Central Laboratories Department of the Ministry of Science and Technology / Environment and Water. The XRF method were used to determine the percentage of basic major oxides (CaO, MgO, Fe₂O₃, Al₂O₃, SiO₂, SO₃, K₂O, Na₂O, MnO). The results of the geochemical analyzes of the Anah and Euphrates formations in both sections are shown in the table below.

Table 1. Results of chemical analysis of the studied samples from Anah and Euphrates formations.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sa. No.</th>
<th>CaCO₃ (CaO)</th>
<th>Na₂O</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>SO₃</th>
<th>Cl</th>
<th>K₂O</th>
<th>SrO</th>
<th>Fe₂O₃</th>
<th>MnO</th>
<th>Sr ppm</th>
<th>NiO ppm</th>
<th>TiO₂ ppm</th>
<th>ZrO₂ ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>G</td>
<td>94.635</td>
<td>0.205</td>
<td>1.756</td>
<td>0.624</td>
<td>1.848</td>
<td>0.248</td>
<td>0.113</td>
<td>0.125</td>
<td>0.047</td>
<td>0.371</td>
<td>0.029</td>
<td>470</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>H</td>
<td>97.152</td>
<td>0.110</td>
<td>0.572</td>
<td>0.436</td>
<td>1.103</td>
<td>0.153</td>
<td>0.049</td>
<td>0.089</td>
<td>0.046</td>
<td>0.289</td>
<td>460</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>I</td>
<td>87.348</td>
<td>0.728</td>
<td>6.092</td>
<td>0.861</td>
<td>2.564</td>
<td>1.027</td>
<td>0.544</td>
<td>0.212</td>
<td>0.063</td>
<td>0.303</td>
<td>630</td>
<td>0.017</td>
<td>0.060</td>
<td>0.001</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>J</td>
<td>93.885</td>
<td>0.318</td>
<td>0.742</td>
<td>0.264</td>
<td>0.980</td>
<td>3.131</td>
<td>0.078</td>
<td>0.084</td>
<td>0.067</td>
<td>0.409</td>
<td>0.042</td>
<td>670</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>K</td>
<td>96.702</td>
<td>0.217</td>
<td>0.600</td>
<td>0.484</td>
<td>1.237</td>
<td>0.193</td>
<td>0.115</td>
<td>0.107</td>
<td>0.035</td>
<td>0.266</td>
<td>350</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.1. Calcium Carbonate (CaCO₃)

Limestone is formed chemically in warm seas when the water is saturated with CaO with a low content of CO₂ (Kohlhaas, 1983 in Al-Shammari, 2010). The results of the chemical analyzes of the limestone samples in the study area showed a slight difference in the concentrations of calcium
carbonate CaCO$_3$. In the Haditha outcrop, the Euphrates Formation, it is show from Table 1 that the concentration of CaCO$_3$ in the limestone rocks is 93.885%, while in the Baghdadi outcrop, the Euphrates Formation its rate was 87.348%, while its concentration was, In Hadith outcrop Anah Formation (sample No. 5) it is 96.702%, and its concentration in Haditha outcrop, the Anah Formation (sample No. 1) is (94.635%).

**Table. 2.** Classification of the purity of carbonate rocks according to the percentage of calcium carbonate (Harrison, 1985 in Kadhim and Hussein, 2016)

<table>
<thead>
<tr>
<th>Purity</th>
<th>Percentage of CaCO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very high purity</td>
<td>&gt; 98.5</td>
</tr>
<tr>
<td>High purity</td>
<td>97.0 – 98.5</td>
</tr>
<tr>
<td>Medium Purity</td>
<td>93.5 – 97.0</td>
</tr>
<tr>
<td>Low Purity</td>
<td>85.0 – 93.5</td>
</tr>
<tr>
<td>Impure Purity</td>
<td>&lt; 85.0</td>
</tr>
</tbody>
</table>

**Table. 3.** The purity of the limestone rocks in the formations of the current study according to the percentage of calcium carbonate CaCO$_3$

<table>
<thead>
<tr>
<th>Sa.No</th>
<th>Formation name</th>
<th>CaCO3</th>
<th>Limestone purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>J</td>
<td>Euphrates Formation</td>
<td>93.885%</td>
<td>Medium Purity</td>
</tr>
<tr>
<td>I</td>
<td>Euphrates Formation</td>
<td>87.348%</td>
<td>Low Purity</td>
</tr>
<tr>
<td>K,G</td>
<td>Anah Formation</td>
<td>94.635 - 96.702 %</td>
<td>Medium Purity</td>
</tr>
</tbody>
</table>

4.2. Magnesium Oxide (MgO)

Magnesium is important in determining the sedimentary environment and the cement industry. The source of magnesium in calcareous rocks is dolomite CaMg(CO$_3$)$_2$, magnesite MgCO$_3$, forsterite Mg$_2$SiO$_4$, and brucite Mg(OH)$_2$. Warkerwright CaMgFe(CO$_3$)$_2$ (Chatterjee, 2004) (Yazdin, 1990).

Chemical analysis of the limestone in the Haditha outcrop (Euphrates Formation) in Table 1 shows that the concentration of magnesium oxide MgO 0.742% does not match its concentration in the Baghdadi outcrop Euphrates Formation 6.092% and its concentration 0.600% in Haditha outcrop Anah Formation (sample 5) and its concentration 1.756% in Haditha outcrop Anah Formation (sample 1).

4.3. Silica (SiO$_2$)

Silicon oxide SiO$_2$ is one of the most abundant oxides in nature and is found in rocks (igneous, metamorphic and sedimentary) and is found in the form of a main group called (silicates), and is usually found in clay minerals and is found in the form of free silica in quartz minerals or microcrystalline silica And in the minerals Chert, Jasper, and Opal (Al-Jubouri and Al-Kawaz, 2008).

Silica oxide SiO$_2$ is present in roughly varying proportions in the calcareous rocks in the current study area. As shown in Table 1, the silica SiO$_2$ concentration of the Haditha outcrop Euphrates Formation is 0.980% and that of the Baghdadi outcrop is 0.980%. Euphrates Formation 2.564%, Haditha Outcrop Anah Formation (Sample 5) concentration is also 1.237%, Haditha Outcrop Anah Formation (Sample 1) concentration is 1.484%.
4.4. Alumina (Al$_2$O$_3$)

The average concentration of alumina oxide Al$_2$O$_3$ in the calcareous rocks of the earth's crust is 1.69% (Horn and Adams, 1966 in Al-Wandawi, 2009), and it is derived from multiple sources such as clay, shale, bauxite, and others (Hendrik, 2005). The chemical analyzes of limestone rock samples for the current study recorded similar percentages for the concentration of alumina oxide Al$_2$O$_3$ as shown in Table 1. Since its concentration in Haditha outcrop Euphrates Formation was 0.264% and its concentration in Baghdadi Outcrop Euphrates Formation was 0.861%, it was present in Haditha outcrop Anah Formation (Sample 5) is 0.484% and its concentration in the Haditha outcrop Anah formation (sample 1) is 0.624%.

4.5. Ferric Oxides (Fe$_2$O$_3$)

This oxide includes a group of minerals such as hematite, magnetite, and other minerals. Iron is widely found in the Earth's crust and is found in calcareous rocks and alluvial deposits, as well as in amphibolites and magnetites (Al-Paruany and Al-Hadithy, 2021). Which is formed as a result of the fusion of iron atoms with oxygen atoms. The chemical analyzes recorded, as shown in Table 1, the concentration of ferric oxide Fe$_2$O$_3$, Among them, its concentration in Haditha outcrop Euphrates Formation is 0.409%, and its concentration in Baghdadi outcrop Euphrates Formation is 0.303%. Its concentration was also 0.266% in Haditha outcrop Anah Formation (sample 5) and its concentration in Haditha outcrop Anah Formation (sample 1) was 0.029%.

4.6. Sulphate (SO$_4$)

Sulphate oxide SO$_4$ is present in sedimentary rocks in the form of pyrite and sometimes in the form of marxite (Schafer, 1987). Sulfur is found in calcareous rocks in the form of SO$_4$, and (Soroka, 1979) indicated that its concentration in calcareous rocks ranges between 0.1-0.5%.

The calcareous rocks in the study area contain different percentages of SO$_4$ concentrations as shown in Table 1. Their concentration in the Haditha outcrop Euphrates Formation is 3.131%, and in the Baghdadi outcrop Euphrates Formation is 1.027%, Haditha outcrop Anah Formation (sample 5) concentration is also 0.193%, Haditha outcrop Anah Formation (sample 1) concentration is 0.248%.

4.7. Sodium Oxide (Na$_2$O)

The salts are the main source of sodium oxide Na$_2$O, the calcareous rocks in the study area contain different percentages of concentration Na$_2$O, as shown in Table 1, where its concentration was in the Haditha outcrop Euphrates Formation 0.318%, and its concentration was in the Al-Baghdadi outcrop Euphrates Formation 0.728%, and its concentration was also in the Haditha outcrop Anah Formation (sample 5) 0.217%, and its concentration was in the Haditha outcrop Anah Formation (sample 1 ) 0.205%.

4.8. Potassium Oxide (K$_2$O)

Salts are the main source of potassium oxide K$_2$O. The calcareous rocks in the study area contain different percentages of K$_2$O concentration, as shown in Table 1, where its concentration in the Haditha outcrop Euphrates Formation was 0.084%. Its concentration in the outcrop of Al-Baghdadi Euphrates Formation was 0.212%, and its concentration was also in the outcrop of Haditha Anah Formation (sample 5) 0.107%, and its concentration in the Haditha outcrop Anah Formation (sample 1) was 0.125%. 

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4.9. Manganese Oxide (MnO)

Limestone rocks in the study area contain different percentages of MnO concentration, as shown in Table 1, where its concentration was in the Haditha outcrop Euphrates Formation 0.042%, and its concentration was in the Baghdadi outcrop Euphrates Formation (0.000%). Its concentration was also in Haditha outcrop Anah Formation (sample 5) (0.000%), and its concentration in Haditha outcrop Anah Formation (sample 1) was 0.029%. Manganese is considered as an indicator of the ancient climate, as low MnO contents indicate to an dry climate in the source area during sedimentation (Kadhim and Hussein, 2016).

4.10. Chloride (Cl)

It can arise from groundwater or from halite during the evaporation of sea water (Al-Dabbas and et al, 2013). The chloride Cl appears in the samples of the current study as in Table 1, where its concentration was in the Haditha outcrop Euphrates Formation 0.078%, and its concentration was in the Al-Baghdadi outcrop Euphrates Formation 0.544%, and its concentration was also in the outcrop of Haditha Anah Formation (sample 5) 0.115%, and its concentration was in the Hadithah outcrop Anah Formation (sample 1) 0.113%.

4.11. Strontium (Sr)

The content of strontium in the Haditha outcrop of the Euphrates formation is 670 ppm, while in the Baghdadi outcrop of the Euphrates formation of 630 ppm, while in the Baghdadi outcrop of the Anah formation 350 ppm as in Table 1. Aragonite allows a large amount of Sr to be incorporated into the crystal lattice (Al-Dabbas et al., 2013). The global average carbonate ranges from 425 to 765 ppm (Bausch, 1968). It seems that the strontium content in the Al-Baghdadi Formation is lower than the global carbonate, while in the Haditha and Al-Baghdadi Formation the Euphrates Formation is within the global carbonate limit. This is generally attributed to the digenesis processes that converted aragonite to calcite. Sr is present in high concentrations in the deep environment (Flugel 1982). (Bausch, 1968) indicated that low Sr content is indicative of shallow carbonate rocks. The Sr content is a good indication of the shallow sedimentation environment. Thus, the sedimentational environment of the Anah Formation in the Baghdadi outcrop Formation was relatively shallower than in the Euphrates Formation.

Table 4. Limits of the chemical composition of limestone rocks used in the Portland cement industry (Duda, 1985)

<table>
<thead>
<tr>
<th>Permissible Limits in Raw Material (Wt%)</th>
<th>The ingredients</th>
</tr>
</thead>
<tbody>
<tr>
<td>≥ 45.0</td>
<td>CaO</td>
</tr>
<tr>
<td>≤ 2.0</td>
<td>MgO</td>
</tr>
<tr>
<td>≤ 1.5</td>
<td>SO₃</td>
</tr>
<tr>
<td>≤ 6.75</td>
<td>SiO₂</td>
</tr>
<tr>
<td>≤ 0.66</td>
<td>Fe₂O₃</td>
</tr>
<tr>
<td>≤ 2.0</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>≥ 38.0</td>
<td>L.O.I</td>
</tr>
<tr>
<td>≤ 0.28</td>
<td>Na₂O</td>
</tr>
<tr>
<td>≤ 0.1</td>
<td>K₂O</td>
</tr>
</tbody>
</table>
5. Conclusions

- Through the results of the analyzes and in comparison with the limits of the chemical composition of the limestone rocks used in the manufacture of Portland cement (Duda, 1985).

- It was found that the rocks of the Euphrates Formation in Al-Baghdadi outcrop are not suitable for the manufacture of Portland cement because the proportions of unwanted oxides in the cement industry were too high for the permissible limit, as the percentage (MgO = 6.092%) and the permissible limit (≤2.0), and the percentage (Na₂O = 0.728%) and the accepted limit (≤0.28). The percentage (K₂O = 0.212%) and the accepted limit (≤0.1), and the rocks of the Euphrates Formation in Haditha outcrop were also not suitable for the Portland cement industry because the proportions of unwanted oxides in the cement industry were very high than the accepted limit in the international standard chemical specification for limestone rocks used in the cement industry, where the ratio was (SO₃ = 3.131%) and the allowable limit was (≤1.5), and the ratio was (Na₂O = 0.318%) and the allowable limit was (≤0.28) (Duda, 1985). As for the rocks of Anah formation in a Haditha outcrop, they are considered good raw materials in the Portland cement industry, because the percentages of oxides is within the acceptable range for the Portland cement industry, according to the standard specifications set by (Duda, 1985), as shown in Table.1.

- The standard specification for the Al-Noura industry in the Al-Noura cement factory in Karbala Governorate (CaCO₃ = 96%) (Al-Faraji, 2021). In comparison with the data of the chemical analyzes of the current study samples, it was found that only the formation Anah in a Haditha outcrop is suitable for the Al-Noura cement industry, as it is within the permissible range At Al-Noura Cement Factory in Karbala.

- The high content of magnesium in Euphrates Formation at Al-Baghdadi outcrop (MgO = 6.092%), is an indication that the water is shallow and warm. while the percentage of (MgO) in the Haditha outcrop (Anah Formation) was low (MgO = 0.600%), and this is an indication that the environment was also isolated and warm.

- The concentration of Na₂O and K₂O increased in Euphrates Formation more than the Anah Formation, and this is evidence of a greater increase in the deposition of salts, and the low content of manganese oxide MnO, whose percentage was low in the Haditha outcrop Euphrates Formation (MnO = 0.042%), and the disappearance of manganese oxide from the Haditha outcrop Formation of it and Al-Baghdadi outcrop Euphrates Formation, This is also an indication that the marine environment was shallow, which may have its origin from aragonite deposited in a shallow marine environment, and the low manganese oxide MnO content indicates an dry climate in the source area during sedimentation (Kadhim and Hussein, 2016).

- High content of Sr in Euphrates Formation at Haditha outcrop is 670 ppm, and this is an indication that the water is deep, and the concentration of Sr in Euphrates Formation at Baghdad outcrop is 630 ppm The concentration of Sr in Anah Formation at Al-Baghdadi outcrop was 350 ppm. Low Sr content indicates shallow carbonate rocks. Thus, the sedimentary environment of the Anah Formation in the Haditha outcrop was relatively shallower than it that of the Euphrates Formation.

References


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