MINERAL RESOURCES OF SODIUM SULFATE IN IRAQ:
AN OVERVIEW
Rafaa Z. Jassim1

Received: 23/11/2017, Accepted: 03/05/2018

Key words: Glauberite; Thenardite; Mirabilite; Shari Saltern; Sunaisla; Iraq

ABSTRACT
Sodium sulfate is an evaporite mineral that precipitates from sulfate-rich water and brines mainly in the inland salterns or sabkhas and found naturally as economic deposits in many places in the world. It is used in detergent, glass, paper, sodium silicate and some pharmaceutical industries. In Iraq, the only economic sodium sulfate deposit is found in the Shari Saltern near Samarra City. The sodium sulfate reserve in the Shari Saltern was estimated by about 22 Million tons. Other potential resources of sodium sulfate are found in the salterns of the Jazera area, but they need detailed work to estimate their economic potential. The Shari Saltern is a longitudinal closed basin originated in a subsiding N–S graben, filled with different types of sediments and solutes supplied by the ephemeral streams and seepages. The evaporite minerals found in the Shari Saltern are gypsum, glauberite, thenardite, mirabilite (in winter at low temperatures) and halite with trace amounts of bassanite, natron, trona, huntite, d’ansite and hydrated magnesium bromide. The sequential precipitation of the evaporite minerals in the Shari Saltern starts with gypsum and clay; mirabilite (in winter); gypsum, glauberite and clay; glauberite and clay; glauberite, thenardite and clay then glauberite, thenardite, halite as salt crust over the black mud slurry towards the center of the saltern and the uppermost part of the sediments column. Mirabilite crystalizes as almost pure sodium sulfate with long transparent crystals at low temperatures in winter. While glauberite precipitates by the effect of organic matter and anaerobic bacteria present in the black mud slurry which occupies the lowest part of the saltern. The mineral facies are concentric horizontally and vertically in the Shari Saltern so that the clay and gypsum facies lies below the clay and glauberite layer at depth and around it at the surface. Upward movement of groundwater from the underlying Mukdadiya Formation aquifer, formed seepages through the graben faults. These seepages feed the saltern with sulfate-rich water and precipitate gypsum, which results in a change of water composition to become suitable for glauberite precipitation. The isoconcentration maps of the Shari Saltern show the highest concentration of sodium sulfate is in the lowest part which is occupied by glauberite.

1 Expert geologist in mineralogy and geochemistry, Iraq Geological Survey (retired), Baghdad, Iraq, e-mail: rzjassim@gmail.com
Mineral Resources of Sodium Sulfate in Iraq

Rafaa Z. Jassim

INTRODUCTION

Sodium sulfate is used in Iraq in the detergent, glass, paper, sodium silicate and some pharmaceutical industries. Twenty thousand tons/year have been used in the past in the detergent and 5000 tons/year in the paper and sodium silicate industries. There is a need to restart and expand sodium sulfate production from the Shari Saltern to cover the total demand of the local market, estimated by about 44000 tons of sodium sulfate required for the detergent industry alone (Al-Ubaidi et al., 2004).

The Shari Saltern is about 20 Km long and (4 – 5) Km wide and 50 m above sea level, located about 150 Km north of Baghdad (Fig.1). The saltern lies in the area between Hemrin Mountain to the northeast, the Tigris River to the west and south and Al-Udhaim River to the east and southeast. The Shari area is characterized by hot and dry weather in summer and somewhat cold and wet climate in winter. The maximum temperature is in July and the lowest in January. The wet season starts in November and lasts till April. The estimated reserve of sodium sulfate in the Shari Saltern is about 22 million tons (Jassim, 1999a). A pilot plant for sodium sulfate production was erected in 1996 with a production capacity of 3000 tons/year. The production was marketed for detergent and glass industries. The facilities of this plant were looted in 2004 after the American invasion of Iraq and this paper is an overview of previous work carried out by Iraq Geological Survey, published papers and postgraduate research.

PREVIOUS WORK

– The early work: Bolton (1956) studied the geology, geomorphology and economic potential of the Shari Saltern and described the minerals present in the salt crust and the underlying sediments. He estimated the sodium sulfate reserve to be 250000 tons in the lake brine in winter and precipitated with the salt crust in summer. Al-Mhaidi (1968) studied the Duz and Al-Hawija salt marsh areas and mentioned the presence of some sodium sulfate concentration in the second harvest of salts.
Fig.1: Location map of the Shari Saltern

- **1970 – 1980**: Al-Rawi (1970) studied the quality and amount of NaCl salt and its chemical analysis which showed high sodium sulfate in the salt crust. El-Kiki *et al.* (1974) studied the hydrogeology of the Mukdadiya Formation aquifer in the area surrounding the Shari Saltern. Salins DU MIDI (1974) submitted a proposal for the extraction of sodium sulfate and sodium chloride from the Shari Saltern. Araim *et al.* (1976) studied the hydrogeology of the Shari Saltern and the hydrological properties of the Mukdadiya Formation aquifer, geological history and economic potential of the lake. Jajjoo *et al.* (1976) studied the possibility of separation of sodium sulfate in laboratory. Duffek (1977) gave a brief description of the lake and its hydrochemistry and suggestions on brine utilization to produce chloride and sulfate salts. Yahya (1977) studied the annual fluctuation of water level in the Shari Lake. Araim *et al.* (1978) studied the economic potential of the saltern and estimated the sodium sulfate reserve to be 20 million tons but did not specify the mineral accommodating the bulk amount.
of sodium sulfate in the sediments. The State Organization for Minerals (S.O.M., 1978) applied large scale site experiment of salt separation and collection from saltern brines. The experiment failed due to the crystallization of all salts in the same basin and the difficulty of collecting salt brines in summer.

– **1980 – 2000:** Jassim (1989) studied the hydrochemistry of the brine in the Shari Saltern and the winter and summer salt minerals deposited in the saltern and their limitations. Shakir (1989) drilled two boreholes at the eastern side of the saltern and studied the hydrochemistry of the Mukdadiya Formation aquifer. Fatih (1989) studied the hydrochemistry of the lake brines and chemistry and mineralogy of the uppermost sediments of the saltern. Jassim (1992) studied the chemistry, mineralogy and economic evaluation of the lake sediments by drilling ten boreholes inside the lake. This study revealed for the first time the presence of glauberite and the sodium sulfate reserve was estimated to be 19 million tons. A technological route for sodium sulfate extraction from the lake sediments was invented and a successful large scale field experiment to precipitate and collect hydrated sodium sulfate from the sediment’s pore brine was achieved. Al-Ubaidi et al. (1992) prepared a preliminary feasibility study outlined the material balance, technology and economic feasibility of sodium sulfate extraction from the lake sediments. Habib et al. (1992) studied the separation of sodium sulfate from the Shari lake brine. Al-Ubaidi et al. (1993) submitted a detailed feasibility study mentioning the detailed process, instruments specifications and economic feasibility to construct a plant to produce sodium sulfate from the saltern sediments. Mohammed and Jassim (1994) studied the mineralogy and possible genesis of salts and the origin of the Shari Saltern. Al-Samarrai (1995) outlined the geomorphology of the Shari Lake region using remote sensing technique. Jassim (1997) studied the mineralogy, geochemistry and origin of the Shari saltern deposit. Jassim et al. (1997) studied the role of bacteria in the formation of glauberite in the Shari saltern. Jassim (1999a) recalculated sodium sulfate reserve and distribution in the Shari Saltern. Jassim (1999b) reevaluated the salts in the Jazera salt pans and their probable source and the possibility of sodium sulfate presence in Snaisla saltern. Jassim et al. (1999) studied the mineralogy of evaporate minerals in the Shari Saltern.

– **Post 2000:** Jassim et al. (2006) studied the lineaments sets present in the Shari Saltern and adjacent area and concluded that the saltern depression is a graben. Jassim et al. (2007) studied the pollen and spores in the saltern sediments and specified the dry and rainy periods concluding that the saltern area is undergoing desertification in most of the Holocene time and according to this study, they estimated the saltern age to be 6500 years from present time. Al-Rawi et al. (2011) studied the sedimentary facies and environments of the Shari Saltern and their distribution in the depression. Jassim et al. (2014) studied the hydrochemistry of water sources and brines in the Shari Saltern and discussed the hydrochemical evolution of these sources.

**GEOLOGY OF THE SHARI SALTERN**

The western and northern sides of the Shari Saltern are represented by low hills of about 20 m high above the saltern surface. The sediments in the western side are sand, silt, clay and gravel of alluvial origin and are locally capped by secondary gypsum or gypcrete (Araim et al., 1976). The northern side of the Shari Saltern is intersected by Wadi Assam which is the most important ephemeral stream feeding the saltern. The eastern side of the Shari Saltern is mostly covered by sand dunes which are underlain by gently sloping strata towards the saltern. The sand dunes are barchans and transverse types influenced by the prevailing NW wind direction. The occasional multi directional winds have influenced the sand ripples and
dune forms. The location of the dune chains is greatly influenced by the drainage flowing from Hemrin Mountain to the Shari Saltern (Jackowski and Hasan, 1984).

The floor of the Shari Saltern consists of clay, silt and sand of alluvial origin. The uppermost clay layer contains abundant evaporite minerals (Jassim, 1992). The formations exposed in Hemrin Mountain are: Fatha Formation (Middle Miocene), Injana Formation (Upper Miocene) and Mukdadiya Formation (Upper Miocene – Pliocene) (Al-Rawi et al., 1992). The Fatha Formation is composed of cyclic alternations of marl, limestone and gypsum with some salt seams occasionally (Lateef, 1975; Buday, 1980; Fouad et al., 1992; Jassim and Buday, 2006). The Fatha Formation is overlain conformably by the Injana Formation which is composed of cyclic alternations of claystone and sandstone (Belien et al., 1959; Al-Rawi et al., 1992). The Injana Formation exhibits rapid lateral variation in thickness and lithology and has gradational contact with the overlying Mukdadiya Formation (Buday, 1980; Al-Rawi et al., 1992; Jassim and Buday, 2006). The Mukdadiya Formation consists of cyclic alternations of very thin and rare fine conglomeratic or pebbly sandstone, sandstone and mudstone. This formation is not exposed in the saltern area but it has been encountered in the boreholes drilled on the western and eastern sides of the saltern (Araim et al., 1976; Shakir, 1989). The sediments of the above mentioned formations are unconformably and discontinuously covered by variable thicknesses of flood plain sediments, valley fillings, gypseous soil and gypcrete of Quaternary age.

Hassan and A-Jawadi (1976) mentioned that the Shari Saltern occupies part of NW – SE trending synclinal structure and according to the dip directions of the Mukdadiya Formation exposures near Hemrin Mountain, the Shari Saltern is suggested to be a structural depression. While Al-Kadhimi and Ahmad (1991) mentioned that it is part of the area bounding the extension of Ajeel structure. According to Buday (1980), the Shari Saltern is located in the northern part of the Mesopotamian Zone. Buday and Jassim (1987) suggested that it is located in the Tigris Subzone and this structure is intersected by many NW – SE trending faults as well as by ENE – WSW faults following the trend of Amij – Samarra – Halabja transverse fault system at the southern part of the saltern. A geophysical study by Al-Kadhmi and Ahmad (1991) showed the presence of positive structure trending in a WNW – ESE direction and intersecting the northern part of the Shari Saltern. Jassim (1992); Jassim (1997) and Jassim et al. (2006) mentioned that the Shari Saltern is a graben formed by N – S step faults system affected at the northern part by NW – SE trending faults system parallel to Hemrin Mountain.

ORIGIN OF THE DEPRESSION

The Shari depression (holding the main body of the sodium sulfate deposit), was first developed about 6500 years from now (Jassim, 1997; Jassim et al., 2007). In the beginning, two sets of fault systems were intersected in the area, which led to the formation of seepages in a wider area than the saltern occupies now, resulting in the seepage of underground water to the surface. The N – S directed step faults initiated the subsidence of the area forming a depression. As a result, the flowing seepage water was directed inside the depression, whereas the seepages located outside the depression were abandoned (Fig.2), (Jassim, 1997; Jassim et al., 2006).
SEDIMENTOLOGY OF THE DEPOSIT

The initiated depression was simultaneously filled by sediments brought by rain runoff through drainage from the high area of Hemrin Mountain and the surrounding areas to form a seasonal lake in winter which dries up in summer forming sabkha. The coarse sediments were deposited at the mouth of the ephemeral streams forming the flood plain – alluvial fan and the finer (sand, silt and clay) were transported to fill the depression forming the sandflat. With the increase of depth due to subsidence, the sand was deposited at the depression peripheries and the finer sediments transported to the central area. Since the water fills the depression in winter and evaporates in summer, the concentration of the soluble elements increases with time leading to the precipitation of gypsum in the central part and the formation of gypsum mudflat. As the subsidence increased, the accumulation of clays and organic matter increased in the lowest part of the depression and solutes concentration increased with time. Glauberite was precipitated by the effect of anaerobic bacteria on the organic matter in the sediments forming H$_2$S which was oxidized to SO$_4^{2-}$ then combined with Na$^+$ when its concentration was enough to convert gypsum to glauberite [Na$_2$Ca(SO$_4$)$_2$] (Jassim et al., 1997; Jassim, 1997). The finer sediments, rich in organic matter, accumulated at the top forming a black mud slurry (Figs. 3, 4, 5 and 6) (Jassim, 1997; Jassim et al., 1999; Jassim et al., 2006; Al-Rawi et al., 2011).

The vertical distribution of different types of sediments and evaporate minerals are shown in Figure (6). It shows that gypsum started to precipitate at the early stage of the saltern formation, and then altered to glauberite when Na$^+$ concentration increased. Jassim (1997) and Jassim et al. (1999) projected water and brines from different sources on the ternary plot of Hardie (1968) according to their chemical composition as shown in Figure (7).

In any brine or aqueous system, the least soluble mineral is the first to precipitate (Mason and Kipp, 1997). The precipitation depends on evaporation and hence an increase in the solution concentration. Therefore, Ca$^{2+}$ bicarbonate is the first to precipitate after the carbonates followed by Mg$^{2+}$ sulfate, Ca$^{2+}$ sulfate, Ca$^{2+}$- Mg$^{2+}$ sulfate, Ca$^{2+}$ - Na$^+$ sulfate, K$^+$-Ca$^{2+}$-Mg$^{2+}$ sulfate, K$^+$-Mg$^{2+}$ sulfate - chloride, K$^+$-Mg$^{2+}$ chloride, Na$^+$ chloride and K$^+$ chloride depending on the availability of the cations Mg$^{2+}$, Ca$^{2+}$, Na$^+$ and K$^+$ and the anions HCO$_3^-$, SO$_4^{2-}$ and Cl$^-$ (Hardie, 1968).

According to Hardie (1968) it is clear that most of the system is occupied by the gypsum field and most initial liquid compositions would therefore fall within this field. Five major
areas can be recognized in this respect, each producing a certain set of phases following a certain path of crystallization as shown in Figure (7). These include:

1- Area 1. Produces, in order of crystallization, gypsum/ anhydrite; anhydrite-halite; halite-glauberite, halite-glauberite-thenardite.

2- Area 2. Gypsum; gypsum/ anhydrite-glauberite; anhydrite-halite; glauberite-halite-thenardite.

3- Area 3. Gypsum (consumed); glauberite; glauberite-halite; glauberite-halite-thenardite.

4- Area 4. Gypsum (consumed later); glauberite-gypsum (consumed); glauberite; lauberite-thenardite; glauberite-thenardite-halite.

5- Area 5. Gypsum (consumed later); gypsum-mirabilite (below 18 °C); mirabilite-glauberite; glauberite-thenardite; glauberite-halite-thenardite.

Fig. 3: Surface subenvironment map of the Shari Saltern (after Jassim, 1997)
Fig. 4: Transverse and longitudinal sections in the Shari Saltern (after Jassim, 1997)

Fig. 5: Three dimensional sections through the western part of the Shari Saltern (after Jassim, 1997)
The Geology and Economic Potential of Mineral Deposits and Occurrences of Iraq

Fig. 6: Variation of evaporite minerals with depth in the lowest part of the Shari Saltern (after Jassim, 1997)

Fig. 7: Quantitative plot of water and brines from Shari Saltern basin in the hydrous system of CaSO₄ – Na₂SO₄ – NaCl at 25 °C and 1 atm. Field boundaries are after Hardie (1968); schematized for the purpose of clarification (after Jassim, 1997)

Jassim (1997) plotted the data of the brine composition of the Shari Saltern on the system CaSO₄–Na₂SO₄–NaCl–H₂O (Fig. 7). Most of the brines in the saltern fall in areas 3 and 4. The end result of crystallization of such brine is glauberite, thenardite, and halite. The end result of the crystallization/evaporation of this brine is the salt crust which shows this expected mineral assemblage (Table 1). The brine of the black mud slurry falls in area 1, therefore the expected mineral assemblage in this case is gypsum/anhydrite, halite, glauberite and thenardite. The mineral phases found in the black mud slurry are bassanite, glauberite and thenardite (with mirabilite in winter) (Table 1), which is basically the same assemblage with bassanite representing the calcium sulfate phase. Similarly, the brine of the glauberite mudflat, which falls in area 3 (Fig. 7), is expected to yield the same mineral phases found in the glauberite-rich mud facies (Table 1), namely glauberite, thenardite and halite. The other facies (gypsum-rich mud facies and clastics substrata facies) contain only gypsum (Table 1) which is the initial phase to precipitate in almost all types of brines in this area and may survive by isolation from the concentrating solution. Most of the other brines fall in areas 1 and 2; and may contribute by mixing with the sediment pore fluids or with the saltern brines. No phases are encountered in equilibrium with these brines and therefore, they are not discussed in this respect.
Table 1: Relative abundance of evaporite minerals in the sedimentary facies of the Shari Saltern (after Jassim, 1997; Jassim et al., 1999)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Gypsum (CaSO$_4$.2H$_2$O)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bassanite (CaSO$_4$.H$_2$O)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glauberite (Na$_2$SO$_4$.CaSO$_4$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thenardite (Na$_2$SO$_4$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mirabilite (Na$_2$SO$_4$.10H$_2$O)</td>
<td>XXX in winter</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Halite (NaCl)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D’ansite [Na$_2$Mg Cl$_3$. (SO$<em>4$)$</em>{10}$]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trona (NaHCO$_3$.Na$_2$CO$_3$.2H$_2$O)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natron (Na$_2$CO$_3$.10H$_2$O)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Huntite [CaMg$_2$(CO$_3$)$_4$]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg$_2$(OH)$_3$Br.4H$_2$O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

XXX: High abundance; XX: Moderate abundance; X: Low abundance and T: Trace amount

In the early times of winter the rain fall on Hemrin Mountain and the saltern surroundings is brought to the saltern as rain runoff. The accumulated water is subjected to evaporation leading to an increase in its sulfate concentration and depositing gypsum all over the area as gypsum mudflat (Jassim, 1997). During January, the temperature drop below 18 °C resulting in mirabilite precipitation over the previously precipitated gypsum. With the elevation of temperature, mirabilite dissolves leaving a very high concentration of sodium sulfate solution which changes gypsum to glauberite (Hardie, 1968). Glauberite may be also precipitated from the final solution of the saltern lake followed by thenardite and halite.

MINERALOGY OF THE DEPOSIT

The closed continental basin of the Shari Saltern is largely controlled by the flood runoff, stagnation of the brine, evaporation and desiccation. These factors affect the mineral assemblage of the saltern. The mineral assemblage is characterized by the evaporite minerals crystallized from the water body by sequential crystallization as well as by the clay minerals brought to the basin by the ephemeral streams. The sequential crystallization is based on the fact that what dissolves first crystallizes last and vice versa (Tyrrell, 1975). Therefore, the following sequence of crystallization is generally valid whereby carbonates are first to crystallize followed by calcium sulfate, sodium salts, magnesium salts and then potassium salts. However, brine chemistry, concentration and temperature have an important influence on the crystallization series of salts (Eugester and Hardie, 1978; Jenson and Bateman, 1981; Sonnenfeld, 1984).

Similar to other salt lakes in the world, the Shari Saltern contains an assemblage of evaporite minerals which depends upon the chemistry of the lake and the ground water body. The evaporite minerals recognized in the Shari Saltern are mainly of sulfate and chloride types. Trace amounts of other salts were also recognized. Evaporite minerals identified by X-ray diffraction in the Shari Saltern are glauberite, gypsum, thenardite, halite, mirabilite, d’ansite, trona, natron, huntite, bassanite and hydrated magnesium bromide.
The Geology and Economic Potential of Mineral Deposits and Occurrences of Iraq

Table (1) shows the abundance and distribution of these minerals in the various facies of the saltern including the salt crust, black mud, glauberite-rich mud, gypsum-rich mud, sand-silt facies and the substrata facies (Jassim, 1997; Jassim et al., 1999).

The salt minerals related to the major cations and anions in the Shari Saltern sediments are laterally distributed in roughly concentric zones. This concentric zonation appears in the same order from bottom sediments to the top ending with the salt crust (Jassim, 1997) as follows:

\[
gypsum \rightarrow gypsum + glauberite \rightarrow glauberite \rightarrow glauberite + thenardite \rightarrow glauberite + thenardite + halite
\]

Fig. 8: X-ray diffractograms of the salt crust and the black mud samples from the Shari Saltern (after Jassim, 1997)
Fig. 9: X-ray diffractograms of the glauberite-rich mud samples from the Shari Saltern (after Jassim, 1997)
SEDIMENTARY FACIES OF THE SALT-BEARING SEDIMENTS

Four main salt-rich sedimentary facies have been recognized in the sediments of the Shari Saltern on the basis of the relative abundance of salt minerals and the type of sediments (Table 1). They include Salt Crust Facies, Black Mud Facies, Glauberite-Rich Mud Facies and Gypsum-Rich Mud Facies.

— **Salt Crust Facies:** The mineral assemblages show distinct differences between those of the Salt Crust Facies and the other facies. These differences are due to variations in the precipitation conditions and later equilibrium with the brines in the various parts of the salt pond (Jassim, 1997; Jassim et al., 1999). The Salt Crust Facies is formed by total evaporation and dryness of the surface water body. The salt crust minerals were precipitated over a wide range of concentrations during the evaporation process until total dryness. The total dryness in the desiccation stage leaves a blocky efflorescent salt crust that reaches up to 7 cm in thickness at the center of the salt pond and does not exceed a few millimeters near the periphery. Salt crust minerals are subjected annually to partial or total dissolution by the fresh water of the next winter, resulting in recycling of the solutes. The minerals are essentially thenardite, halite and glauberite as shown in the X-ray diffractogram of the salt crust (Fig. 8) (Jassim, 1997).
Mineral Resources of Sodium Sulfate in Iraq

Rafaa Z. Jassim

Black Mud Facies: It has the highest evaporite mineral variety among other facies in the Shari Saltern. The minerals identified by X-ray diffraction in this facies include glauberite \([\text{Na}_2\text{Ca(SO}_4)_2]\), thenardite \((\text{Na}_2\text{SO}_4)\), halite \((\text{NaCl})\), bassanite \((\text{CaSO}_4.\text{H}_2\text{O})\), d’ansite \([\text{Na}_2\text{MgC}_13(\text{SO}_4)_{10}]\), trona \((\text{NaHCO}_3.\text{Na}_2\text{CO}_3.2\text{H}_2\text{O})\) and \(\text{Mg}_2(\text{OH})_3\text{Br}.4\text{H}_2\text{O}\). Mirabilite \((\text{Na}_2\text{SO}_4.10\text{H}_2\text{O})\) is usually found in this facies in winter instead of thenardite (Figs. 8b and c). This is due to the fact that black mud is soaked by the highly concentrated brine in late summer which results in the precipitation of a wide variety of mineral species (Jassim, 1997).

- Glauberite-Rich Mud Facies: It is the most important facies from economic point of view. This facies is developed at the central part of the Shari Saltern together with the Black Mud Facies. Sediments and minerals of this facies are those accumulated at the bottom of the black mud slurry. Salt crystals continue to grow later by the effect of the pore brine. The most important evaporite mineral here is glauberite \((\text{Na}_2\text{SO}_4.\text{CaSO}_4)\) which may comprise 25% or even more of the volume of sediments of this facies. Thenardite \((\text{Na}_2\text{SO}_4)\) and halite \((\text{NaCl})\) are present in smaller amounts and d’ansite \([\text{Na}_2\text{MgC}_13(\text{SO}_4)_{10}]\) trona \((\text{NaHCO}_3.\text{Na}_2\text{CO}_3.2\text{H}_2\text{O})\), natron \((\text{Na}_2\text{CO}_3.10\text{H}_2\text{O})\) and huntite \([\text{CaMg}_3(\text{CO}_3)_4]\) in trace amounts as shown in the X-ray diffractograms in Figure (9) and Table (1). Gypsum is found in minor amounts at the lower transitional part of the glauberite-rich mud downward to gypsum-rich mud (Jassim, 1997; Jassim et al., 1999).

- Gypsum-Rich Mud Facies: It has gypsum as the dominant evaporite mineral which represents up to 25% by volume of the sediments of this facies. Minor amount of glauberite is found at the transitional part of this facies with the overlying Glauberite-Rich Mud Facies as a result of the increased \(\text{Na}^+\) concentration in the central part of the saltern. Similarly, Gypsum-Rich Mud Facies in the gypsum mudflat shows gypsum dominance with an inward increase of glauberite at the transition from the gypsum mudflat to the glauberite mudflat. The X-ray diffractogram of a sample from the Gypsum-Rich Mud Facies is shown in Figure (10a) (Jassim, 1997; Jassim et al., 1999).

GEOCHEMISTRY OF SOLUBLE SALTS IN THE SHARI SALTERN SEDIMENTS

The results of selective chemical analyses of the soluble salts in different types of sediments in the Shari Saltern are listed in Table (2). It can be noticed from the data presented the absence of salt minerals in the substrata sediments (column 1), then the precipitation of gypsum from the water body accumulated in the newly formed depression over the sand sheet (column 2). With time and as subsidence continued, the water current of the ephemeral streams dropped the heavy load of gravel at the mouth and then, farther more, the sand was deposited, not far from the periphery. The finer sediments of silt and clay were deposited at the center of the saltern. Gypsum precipitated first from the lake water over all the area covered by lake water (column 3). With the annual supply of solutes to the depression, \(\text{Na}^+\) concentration increased and with the progress of evaporation, the lake water became more concentrated leading to alteration of gypsum to glauberite in the presence of organic matter and anaerobic bacteria at the deepest part of the Saltern (Jassim, 1997) (column 4). The central part is filled with black mud slurry containing 2.1% organic carbon with bacteria in the fine silt and clay and some salt minerals (column 5). The black mud slurry precipitated gypsum and mirabilite in winter where the temperature is low, but when the temperature rises above 32ºC, mirabilite dissolves and \(\text{Na}^+\) and \(\text{SO}_4^{2-}\) start to alter gypsum to glauberite by the aid of bacteria. Glauberite can be formed either from the alteration of gypsum or by direct precipitation from the brine (column 5). When total evaporation of the lake water accumulated in the rain season, a salt crust is formed with increasing thickness, from few
millimeters to about 8 centimeters (column 6), from the periphery to the center of the saltern. Other salt minerals such as bassanite, natron, trona, huntite, d’ansite and hydrated magnesium bromide were also found in trace amounts in the black mud slurry (Jassim, 1997).

Table 2: Chemical analyses of soluble salts in the Shari Saltern sediments and calculation of salt minerals

<table>
<thead>
<tr>
<th>Ion or Mineral (%)</th>
<th>1 Clastics of the Substrata</th>
<th>2 Sand of Sand Flat</th>
<th>3 Gypsum Rich Mud</th>
<th>4 Glauberite Rich Mud</th>
<th>5 Black Mud Slurry</th>
<th>6 Salt Crust</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>0.28</td>
<td>4.61</td>
<td>3.51</td>
<td>8.78</td>
<td>10.76</td>
<td>27.3</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.02</td>
<td>0.06</td>
<td>0.06</td>
<td>0.07</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.32</td>
<td>4.95</td>
<td>6.24</td>
<td>5.8</td>
<td>4.87</td>
<td>2.1</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.01</td>
<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
<td>0.08</td>
<td>10</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.43</td>
<td>5.60</td>
<td>4.23</td>
<td>3.95</td>
<td>7.31</td>
<td>11.77</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.73</td>
<td>13.81</td>
<td>16.1</td>
<td>27.72</td>
<td>24.75</td>
<td>46.1</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.59</td>
<td>9.23</td>
<td>6.86</td>
<td>6.58</td>
<td>12.05</td>
<td>22.26</td>
</tr>
<tr>
<td>Na₂SO₄·CaSO₄ (Glauberite)</td>
<td>--</td>
<td>3.24</td>
<td>2.37</td>
<td>28.22</td>
<td>--</td>
<td>17.53</td>
</tr>
<tr>
<td>Na₂SO₄ (Thenardite)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>5.19</td>
<td>Winter</td>
<td>36.4</td>
</tr>
<tr>
<td>Na₂SO₄·10H₂O (Mirabilite)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>Summer</td>
<td>--</td>
</tr>
<tr>
<td>CaSO₄·2H₂O (Gypsum)</td>
<td>0.79</td>
<td>18.38</td>
<td>24.22</td>
<td>7.52</td>
<td>Winter</td>
<td>42.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Summer</td>
<td>17.81</td>
</tr>
</tbody>
</table>

The bacteria present in the black mud were identified by microscopic study of bacteria grown on a growth medium (Agar). Some salt tolerant species of bacteria and biota, whose activity extend over a wide range of concentrated brines, were found in Shari Saltern. The presence of *Atremia* algae, which produces red pigments coloring the brine, was readily identified. Culture growth of bacteria from the Black Mud Facies in the laboratory revealed the presence of the following bacteria: *Pseudomonas aerugenosa*, *Bacillus subtilis*, *Staphylococcus saprophyticus* and *Staphylococcus aureus*. Decomposition of the cellulose of the plant remains produces H₂S which is in turn oxidized to SO₄²⁻ by *Pseudomonas aerugenosa* and *Staphylococcus aureus* aerobic oxidizing bacteria (Jassim *et al.*, 1997).

Sodium sulfate is an important constituent in the water and brines feeding the Shari Saltern. The brine of the saltern was studied by many authors (as mentioned in the previous work) and the last was by Jassim *et al.* (2014). Samples from different sources in the saltern were collected (Fig.11) and analyzed. The chemical analyses of water and brines from the saltern are shown in Table (3) and their hydrochemical types are shown in Table (4).
Fig.11: Location of water and brine samples collected from the Shari Saltern (after Jassim et al., 2014)

Table 3: Analysis of water and brines of different sources from the Shari Saltern (after Jassim, 1997)

<table>
<thead>
<tr>
<th>Source</th>
<th>Sample No.</th>
<th>Na⁺ (mg/L)</th>
<th>K⁺ (mg/L)</th>
<th>Ca²⁺ (mg/L)</th>
<th>Mg²⁺ (mg/L)</th>
<th>Cl⁻ (mg/L)</th>
<th>SO₄²⁻ (mg/L)</th>
<th>CO₃²⁻ (mg/L)</th>
<th>HCO₃⁻ (mg/L)</th>
<th>T.D.S. mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perennial spring (23rd April)</td>
<td>V5</td>
<td>27.3</td>
<td>0.23</td>
<td>26.0</td>
<td>16.7</td>
<td>7.0</td>
<td>60.0</td>
<td>0.6</td>
<td>2.74</td>
<td>5108</td>
</tr>
<tr>
<td>Pore brine from sandflat (23rd April)</td>
<td>V4</td>
<td>1864.6</td>
<td>3.29</td>
<td>25.5</td>
<td>345.9</td>
<td>1230</td>
<td>1000</td>
<td>1.4</td>
<td>7.9</td>
<td>139690</td>
</tr>
<tr>
<td>Seepage brine (21st May) (22nd May)</td>
<td>8NSP3</td>
<td>1142.4</td>
<td>2.8</td>
<td>47.0</td>
<td>52.94</td>
<td>1030</td>
<td>217</td>
<td>1.02</td>
<td>1.98</td>
<td>75300</td>
</tr>
<tr>
<td></td>
<td>6NSP1</td>
<td>827.3</td>
<td>2.74</td>
<td>45.5</td>
<td>2.2</td>
<td>705</td>
<td>210</td>
<td>.36</td>
<td>2.42</td>
<td>57420</td>
</tr>
<tr>
<td>Lake brine (28th December) (19th March)</td>
<td>L12</td>
<td>1800.9</td>
<td>5.93</td>
<td>33.6</td>
<td>37.6</td>
<td>1275</td>
<td>600</td>
<td>1.8</td>
<td>2.46</td>
<td>120912</td>
</tr>
<tr>
<td></td>
<td>L95/12</td>
<td>2849.6</td>
<td>8.95</td>
<td>32</td>
<td>63.78</td>
<td>1500</td>
<td>1450</td>
<td>1.8</td>
<td>2.5</td>
<td>197790</td>
</tr>
<tr>
<td>Mukdadiya Formation aquifer (21st March)</td>
<td>WS5/S</td>
<td>37.4</td>
<td>0.12</td>
<td>25.4</td>
<td>19.6</td>
<td>29.0</td>
<td>52.5</td>
<td>0.12</td>
<td>1.34</td>
<td>5846</td>
</tr>
<tr>
<td>Brine from black mud slurry (20th May)</td>
<td>D1/100</td>
<td>2191.9</td>
<td>8.13</td>
<td>43.4</td>
<td>88.1</td>
<td>2150</td>
<td>80</td>
<td>0.6</td>
<td>1.0</td>
<td>156080</td>
</tr>
<tr>
<td>Brine from glauberite-rich mud (2nd July)</td>
<td>Sh2/B</td>
<td>5881</td>
<td>25.47</td>
<td>15</td>
<td>275</td>
<td>4865</td>
<td>1325</td>
<td>3.6</td>
<td>3.0</td>
<td>470950</td>
</tr>
</tbody>
</table>
Table 4: Hydrochemical types of water and brines from the Shari Saltern (after Jassim, 1997)

<table>
<thead>
<tr>
<th>Water type</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺ – Cl⁻ – SO₄²⁻</td>
<td>Saltern lake brine, water from one of the western and eastern ephemeral streams and from the flood plain-alluvial fan.</td>
</tr>
<tr>
<td>Na⁺ – SO₄²⁻ – Cl⁻</td>
<td>Western ephemeral streams water, water from well in the sand dune field and few saltern lake brines.</td>
</tr>
<tr>
<td>Na⁺ – Cl⁻</td>
<td>Pore brine from the glauberite-rich mud and seepages inside the saltern.</td>
</tr>
<tr>
<td>Na⁺ – Mg²⁺ – SO₄²⁻ – Cl⁻</td>
<td>Water from ephemeral stream at the northern edge of the saltern.</td>
</tr>
<tr>
<td>Na⁺ – Ca²⁺ – Mg²⁺ – SO₄²⁻ – Cl⁻</td>
<td>Ground water of Mukdadiya Formation aquifer.</td>
</tr>
<tr>
<td>Ca²⁺ – Mg²⁺ – SO₄²⁻ – Cl⁻</td>
<td>Water seeping from the sand dunes at the eastern side of the saltern</td>
</tr>
<tr>
<td>Ca²⁺ – SO₄²⁻</td>
<td>Water from a branch of a perennial stream at the northern edge of the saltern</td>
</tr>
<tr>
<td>Ca²⁺ – Na⁺ – SO₄²⁻</td>
<td>Water from the other branch of a perennial stream at the northern edge of the saltern.</td>
</tr>
<tr>
<td>Na⁺ – Ca²⁺ – SO₄²⁻</td>
<td>Water from the main perennial stream at the northern edge of the saltern and the perennial spring water.</td>
</tr>
</tbody>
</table>

SPATIAL DISTRIBUTION OF SODIUM SULFATE IN THE SHARI SALTERN

Jassim (1997) collected and analyzed 624 samples from the saltern sediments, calculated the percentage of glauberite, total sodium sulfate and constructed an isoconcentration maps to show their distribution and zonation in the Shari Saltern (Figs. 12 and 13). These figures show that glauberite and most of Na₂SO₄ are present in the middle part of the saltern, especially in the center and the western side, while sodium chloride salt is covering the entire middle part of the saltern and extends to the north and south. It has been noticed that the area rich in glauberite is the same area covered by the black mud slurry which support the idea of Jassim (1997) and Jassim et al. (1997) about the role of bacteria present in the black mud slurry in the glauberite formation and precipitation.

GENESES OF EVAPORITE MINERALS

In the early stages of development of the Shari Saltern depression, annual ponding and evaporation of the surface water and the ascending brines through weakness zones resulted in increased solutes concentration with time. Evaporite minerals in the sediments were precipitated from the Shari Lake water body. Some of these minerals remained unchanged as they became isolated from the brine as a result of lake water regression due to evaporation, whereas those remained in direct contact with the brine could have changed into new mineral phases. Other mineral phases may have precipitated directly from the solution due to the change in its chemistry. Subsurface growth of minerals may also take place by the effect of the pore brine as indicated by the presence of crystals of some evaporite minerals embedded in the sediments (Jassim, 1997; Jassim et al., 1999).

Gypsum would be the first evaporite phase to precipitate from the Shari Lake brine until the buildup of sodium ion concentration reaches to the extent of being able to alter gypsum to glauberite partially (gypsum + glauberite) then totally (glauberite) according to equation (1) (Hardie, 1968):

\[
2\text{CaSO}_4\cdot2\text{H}_2\text{O} + 2\text{Na} \rightarrow \text{CaSO}_4\cdot\text{Na}_2\text{SO}_4 + \text{Ca}^{2+} + 4\text{H}_2\text{O}
\]

305
This reaction is only initiated when the activity of Na is high enough and/or the activity of H$_2$O is low enough, in the existence of gypsum in contact with the brine.

Further increase of Na$^+$ concentration yields glauberite directly from the solution (in the presence of Ca$^{2+}$ and SO$_4^{2-}$) as in equation (2) (Hardie, 1968);

\[
\text{Ca}^{2+} 2\text{Na} + 2\text{SO}_4^{2-} \rightarrow \text{CaSO}_4 \cdot \text{Na}_2\text{SO}_4 \quad (2)
\]

Precipitation of thenardite (glauberite + thenardite assemblage) and halite (glauberite + thenardite + halite assemblage) may follow as evaporation continues. These minerals may show spatial distribution related to the volume decrease and concentration increase of the brine.
mother brine. Thus, gypsum was precipitated in the Shari Saltern from high volume of brine with relatively low concentration. Decrease of the brine volume by evaporation left gypsum at the outer peripheries of the saltern, not in contact with the concentrated brine and, therefore, it was not altered to glauberite. In contrast, gypsum in the central part of the lake remained in contact with the brine and thus it was partially or totally altered to glauberite. Therefore, zonation of these minerals may take place in the sequence mentioned above (Jassim, 1997; Jassim et al., 1999).

RESERVE ESTIMATION OF SODIUM SULFATE

Based on chemical analyses of the sediments and calculation of sodium sulfate minerals with relation to bed thickness and extensions, Jassim (1992) calculated its reserve in the Shari Saltern to be 19.5 million tons of $\text{Na}_2\text{SO}_4$ including the amount present in the Shari lake brine which is 169176 tons. Jassim (1999a) recalculated the sodium sulfate reserve in the Shari Saltern depending on the results of his extensive work in 1997. The sodium sulfate reserve was recalculated on the basis of concentration, thickness and coverage area and found to be about 22 million tons.

EXPLOITATION AND EXTRACTION OF SODIUM SULFATE

The State Organization of Minerals (S.O.M., 1978) made an in situ large scale experiment to separate sodium sulfate from the surface brines of the saltern, which accumulate at the catchment area in winter (after rainy season). The lake water is condensed by evaporation as the water supply stops and the water volume decreases. In this experiment, four precipitation basins were constructed on the western peripheries of the saltern, each about 100 m long and 80 m wide. The first and fourth basins were for brine collection, the second for the precipitation of hydrated sodium sulfate and the third for sodium chloride precipitation. The experiment failed due to the precipitation of all salts in one basin and shortage of brines at the required density as the evaporation was very fast.

The second experiment was carried out by Jassim (1992) by constructing 20 basins (only 11 were used) each of them was (20 x 5 x 0.8) m in dimensions. The brine pumped to the basins was the sediment’s pore brine seeped from the walls of a ditch (120 x 5 x 20) m constructed in one of the basins excavated by S.O.M. (1978). This experiment aimed to precipitate mirabilite ($\text{Na}_2\text{SO}_4\cdot10\text{H}_2\text{O}$) at low atmospheric temperatures in winter. The brine was pumped during the day hours and mirabilite was precipitated during the night and harvested in the morning. The ditch brine contained 3.67% $\text{Na}_2\text{SO}_4$ and 10.28% $\text{NaCl}$. About 6 m$^3$ of the brine was pumped to the basins and about 450 kg of $\text{Na}_2\text{SO}_4\cdot10\text{H}_2\text{O}$, which contained 56% water of crystallization and 44% other constituents, were collected and sent to the State Company of Vegetable Oils for detergent manufacturing. The dried (dehydrated) sample was found to contain 96.6% $\text{Na}_2\text{SO}_4$, 2.1% $\text{NaCl}$ and 0.9% insoluble residue. Jassim (1993) excavated some amount of the saltern sediments and separated glauberite by mixing with water and sieving. Sodium sulfate was dissolved by mixing the glauberite with water then mirabilite was crystallized (which tends to precipitate almost pure) by cooling to low temperature. Mirabilite was dried up forming thenardite which is the anhydrous form of sodium sulfate.

In 1994, on the basis of Jassim (1992) work on the Shari Saltern, decision was made to construct a sodium sulfate pilot plant at a capacity of 30000 tons/year to be located beside the Shari Saltern. The plant was designed and constructed by Iraqi hands only and from the available materials in the local market and production started in 1996. The sediments were
excavated by a backhoe excavator and transported by trucks to the plant where glauberite crystals were separated from the mud by washing with water and screening. Glauberite was partially dissolved and calcium sulfate remains in the solid form. Another amount was dissolved by the same brine to elevate its concentration. Cooling of the resultant brine to low temperature (about 5 °C) induced mirabilite crystallization which was separated by screening and moved to a rotating kiln for dissolution and subsequent thenardite crystallization by heating. In this process mirabilite was dissolved in its water of crystallization and the water was gradually evaporated to turn into a paste then to thenardite. The plant succeeded in producing industrial grade sodium sulfate which was supplied to the State Company of Vegetable Oils and the State Company for Glass Industry. Production of the plant was halted shortly after the American invasion of Iraq in (2003) and unfortunately the facilities were looted afterwards.

OTHER POTENTIAL RESOURCES OF SODIUM SULFATE IN IRAQ

Although the main reserve of sodium sulfate is present in the Shari Saltern, other salterns are said to have some concentrations of sodium sulfate minerals. Sodium sulfate was reported in the Jazera salt pans (Jassim, 1999b). These salt occurrences show minor concentrations of sodium sulfate, such as the Snaisla Saltern which contains about 19% glauberite in some samples, Ashgar Saltern, contains about 28% glauberite, Kbaisha, contains about 24% glauberite and Qattar Saltern contains about 19% glauberite (Jassim, 1999b). Al-Hawiya Saltern, which is located near the Hemrin Mountain, was found to contain sodium sulfate in some samples recorded up to 12.34% (Al-Mhaidi, 1968). These salt deposits can be added to the Iraqi resources after assessment for Na-sulfate potential.

CONCLUSIONS

• Sodium sulfate is present in Iraq, as an economic deposit, in the Shari Saltern only. The reserves were estimated by about 22 million tons. Other resources of sodium sulfate may be present in some salterns of the Jazera area, but these require detailed exploration work to assess their economic and industrial potential.
• The Shari Saltern, originated about 6500 years from the present day, was formed by a series of subsiding faults forming a graben. The faults are of almost N – S direction which intersects two other sets resulting in the formation of seepages.
• The origin of sodium sulfate in the Shari Saltern is from the water supplied from the surroundings including the Hemrin Mountain through ephemeral streams and also from the ground water of the Mukdadiya Formation aquifer through faults which come to the surface as seepages.
• The mineral content in the saltern sediments reveal that the precipitation of evaporate minerals started with gypsum, followed by gypsum + glauberite, then glauberite, followed by glauberite + thenardite, glauberite + thenardite + sodium chloride, then thenardite + sodium chloride forming the salt crust. In winter, minerals present in the black mud slurry are gypsum and hydrated sodium sulfates (mirabilite), while in summer they are gypsum + unhydrated sodium sulfate (thenardite).
• Laboratory experiments and later pilot plant installation to produce sodium sulfate proved the possibility of Na-sulfate production from the saltern deposits. Sodium sulfate can also be separated from the saltern brine by cooling and the rest of the brine can be used for sodium chloride production.
ACKNOWLEDGMENTS

This article is prepared on the basis of information related to sodium sulfate deposits and occurrences in Iraq, reported in the archives of the Iraq Geological Survey and the postgraduate research work of the author and his scientific publications in association with other colleagues.

REFERENCES


Jassim, R.Z., 1989. Field experiments to extract sodium sulfate salts from Shari Lake brines, Samarra. GEOSURV, int. rep. no. 1841 (in Arabic).


Shakir, S., 1989. Preliminary study about the groundwater quality and the possibility of extraction of sodium sulfate salts in Shari Lake. GEOSURV, int. rep. no. 1881.


