
Salt and Methane Generation Initiated by Membrane Polarisation

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Abstract: The existence of deep marine hypersaline anoxic basins (DHAB) has been well-documented starting with the MedRiff Project in the Eastern Mediterranean. We suppose that there is analogy between the recent and ancient DHABs. This premise allows us to hypothesize that some methane accumulations in geological reservoirs may have been generated by historical euryhaline bacteria. The extreme life conditions of the bacteria and the facieses, as found in currently existing supersaturated salt brines DHABs, may have also existed in the geological past. Since salt basins overlap some of the most productive gas provinces, this article aims to introduce a new approach to salt and methane generation. It highlights the need to reconsider the classical approach to salt and methane generation due to new observations. Hereby we describe a new mechanism for DHAB generation due to membrane polarization. These phenomena generate a surface on which seawater of normal salinity meets the underneath brine of high salinity, and there is no diffusion between them. Hence we presume that non-crystallized, over-pressured, salty brine is the appropriate material to trap and host methane. Following overburden by deposited basin sediments, this viscous, gas-saturated brine can be an engine for diapir formation, which is prior to the crystalline phase. This new idea redefines our search for salt and methane deposits yet it requires further research and consideration, along with the new approach of salt diapir formation in specific salt basins.

Keywords: Salt and Methane Generation, DHAB, Membrane Polarization, Surface Tension, Flocculation, Coagulation, Reverse Osmotic Pressure, Salt Diapir Formation

1. Introduction

1.1. Inspiration and Research History

The first recorded firedamp explosion occurred on 9 September 1664 in Hallstatt (Austria), in a salt mine and not in a coal mine (Harris, 1908). Prior to the installation of a proper ventilation system in Wieliczka Salt Mine (Poland), skilled workers were responsible for burning off the methane that would accumulate in the ceilings of the mine chambers. In Solotvina Salt Mine (Aknaszlatina, Ukraine), the methane escaping from salt was used for illumination (Wanek, 2008) in the early 19th century. Nowadays salt mines are equipped with extensive ventilation systems to prevent similar firedamp explosions.

As for the classical view on salt formation, the name “evaporite” itself expresses that salt is generally seen a

product of evaporation by dry - out of sedimentary basins (Ochsenius&Van't Hoff theory in Arrhenius&Lachman, 2003). Further evaporitic minerals, gypsum, potash, etc. result from this phenomenon (Clarke, 1920). It is also well-known that numerous hydrocarbon accumulations are connected to salt basins. For successful exploration, it is crucial to understand the deposition and generation of evaporites, also how the subsequent deformation history can influence salt basin petroleum systems (Thomas, 2008).

The structural dynamics of salt systems is tackled in both theoretical and applied science literature (Jackson et al., 1994), yet describing when and how salt bodies may have been generated, has not been unambiguously completed until now. Arrhenius & Lachman (Arrhenius & Lachman, 2003) point out that no large-scale salt deposits are being formed under current geological conditions.

2. Evidences

2.1. Newly Discovered Hypersaline Anoxic Basins (DHAB)

During the 1980s, the MEDRIF (Mediterranean Ridge Fluid Flow) Project was carried out. The aim of the MEDRIF Project granted by the EU within the MASTIII Programme fulfilled bathymetric mapping of the Mediterranean Sea. The research cruises of MEDRIF discovered new hypersaline anoxic basins, namely: the Tyro Basin (1983), Bannock Basin (1984), Urania Basin, L'Atalante Basin and Discovery Basin (1993-94).

Later on, several similar brine accumulations were identified worldwide: Gulf of Mexico (Orca Basin, Brine Pool NR-1/GC233.), Red Sea (Conrad; Oceanographer; Shaban; Kebrit; Nereus; Wando; Albatross; Atlantis II; Chain; Discovery; Shagara; Valdivia; Erba; Port Sudan; Suakin Deep) (Antunes et al. 2011).

2.2. Unusual Physical Properties

The means to spot these brines was the sonic response while surveying the Mediterranean. In several deep zones (3,000-4,000 m), the bottom presented a "flat" reflection when the sonic signal had encountered a DHAB layer. An important feature of the DHAB is its high viscosity inasmuch as the "flat" reflection surface can and does support deposited fine grain sediments (Corselli et al., 1995).

DHABs seem to have high viscosity, bearing properties of a non-Newtonian fluid, as if solid. Anomalous superficial tension was found between normal salinity seawater and salt brine layers supporting the deposited sediments.

Researchers found abruptly increasing conductivity at the brine surface (Corselli et al., 1995). For example, conductivity in the Discovery Basin varies from 45 to 125 mS/cm (Figure 1). In the same basin, salinity abruptly increases at the same depth from 40 ppt to 120 ppt (Figure 1).

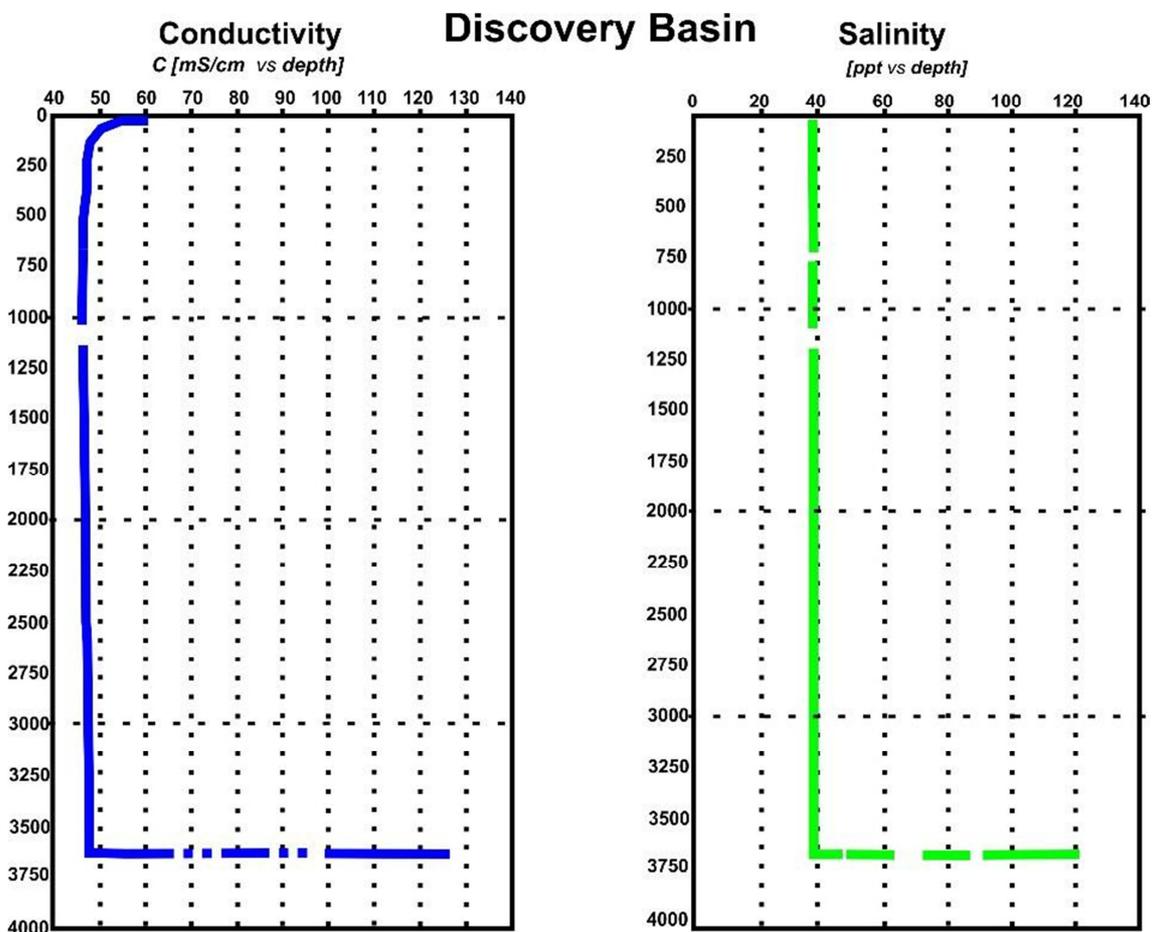


Figure 1. Increased conductivity and salinity of seawater versus depth (courtesy to Medriff Consortium 1995.).

2.3. Biological and Chemical Characteristics

Along with physical properties, biological characteristics were also investigated by MEDRIF.

Methanogenesis in brines has been described in several articles. Borin et al. (2008) mention that methanogenesis greatly exceeds sulphate reduction in most of the saline

layers in Urania DHAB where extremely high bacterial abundance varies from layer to layer. The researchers labelled these as "hot-spots" of microbial activity, which can occur in geological time scale, too.

For the DHABs studied in the Mediterranean Sea, Karisiddaiah (2000) published data on methane concentration between $128-2692 \times 10^3 \text{ nM}$ (2.048-43.072 mg/L). In Lake Madee DHAB (Eastern Mediterranean), an intensive and

stratified bacterial ecosystem was identified (Yakimov et al., 2013). Besides the bacterial phylogeny, a detailed chemical composition of the brine was documented layer by layer.

Yakimov (2013) also recorded daily biogenic methane production rate and acetate content (Table. 1).

Table 1. [after Yakimov, M. M. et al. (2013).].

| Parameters | Brine L1 2 940m | Brine L2 2 975m | Brine L3 3 010m | Brine L4 3 102m |
|-------------------------------|-----------------|-----------------|-----------------|-----------------|
| Density [kg/dm ³] | 1,19 | 1,21 | 1,22 | 1,22 |
| Salinity [mmol/kg] | 304 | 314 | 325 | 345 |
| CH ₄ [μmol/L] | 18.0 ± 3.1 | 70.3 ± 2.3 | 24.1 ± 3.3 | 13.9 ± 1.4 |
| Acetate [μmol/L] | 132 ± 21 | 532 ± 42 | 508 ± 37 | n.d. |
| MPR [μmol/L/day] | 2.1 ± 0.2 | 3.1 ± 0.4 | 1.5 ± 0.6 | 0.5 ± 0.4 |
| Glycerine Betaine [nmol/kg] | 170 ± 9 | n.d. | 44 ± 7 | n.d. |

3. Discussion

There is sufficient evidence that DHABs exist. The follow-up questions are:

1. Why does diffusion not work across the “flat” reflection?
2. How is that surface formed and maintained?
3. What sediment load can it support?
4. Can this phenomenon occur over geological timescale?

3.1. Dhab Generation

3.1.1. Membrane Polarisation; Surface Tension; Reverse Osmosis

From M. L. Wells (2013) we have learned that seawater is a marine colloid, a dimension long neglected when describing sea water phenomena.

At a certain depth in deep sea, argillaceous particles from the colloid suspension may reach the critical micelle concentration (CMC), changing abruptly the physical properties of the system (Cao, Fangyu et al 2015) (Figure 2.).

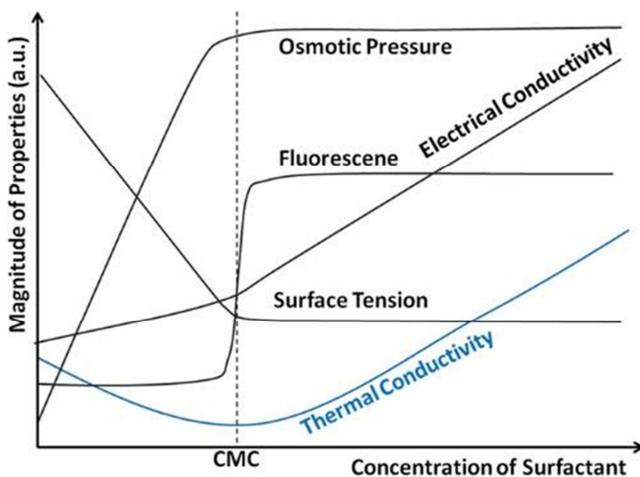


Figure 2. A schematic representation of the dependence of common physical properties of surfactant solutions on the surfactant concentration.

Wherever critical micella concentration (CMC) of normal salinity sea water (as a neglected colloid system) is reached, polar particles will aggregate and generate coagulation and flocculation. This process creates a potential field in which positive ions (Ca²⁺ and Mg²⁺) will be forced to migrate. This causes the increased conductivity detected (Figure 1.), which

is a phenomenon called membrane polarization (Ward 1990). The flocculation of argillaceous particles in the presence of the Ca²⁺ and Mg²⁺ ions is a process described in the article “Relative factors influencing membrane filtration effects in geologic environments” by Frederick A. F. Berry (1969).

The membrane generated by this polarisation will function as an osmotic, semipermeable membrane, allowing only certain ions to pass through. Considering the above mentioned depth (~3000m) and pressure (>300atm ~4,500psi), the phenomenon will be one of a reverse osmotic process. This facilitates the solvent, i.e. water to pass upward through this membrane into a region of normal seawater concentration.

Meanwhile, ions remain behind, thus increasing their concentration beneath the membrane. By this process, hypersaline brine DHAB is generated, reaching very high salinity and viscosity. Diffusion between normal seawater and brine is blocked by the surface tension created via membrane polarisation.

If the phenomenon described above is repeated pending on CMC, membrane polarisation cycles are formed. This yields a layered brine separated by thin argillaceous films.

3.1.2. DHABs in Geological Frame

According to the MedRiff Consortium (1995), this viscous brine is able to support deposited sediments. Over geological time, a large number of DHABs might be buried and isolated within a sedimentary basin. These hidden, over-pressured and layered brine pools of high viscosity bear non-Newtonian fluid properties. They behave as solid bodies between the sedimentary deposits. They have been able to preserve their internal properties, and support large, basin-fill sedimentary sequences.

3.1.3. Buried DHABs Hosting Methane

If the methane content of current DHABs continues to be confirmed (Karisiddaiah, 2000 and Yakimov et al., 2013), then substantial volumes of biogenic methane are likely to be trapped in the buried brines (~40mg/L).

Since acetate decomposes into methane and carbon dioxide (CH₃-COOH = CH₄ + CO₂), an additional source is available for yielding methane in the brine (~500μmol/L = ~30mg/L).

Thus, primary bacterial generation ~40 mg/L and secondary acetate decomposition ~30 mg/L will increase the aggregated methane concentration to ~70mg/L in buried

brine. As a consequence, these brines can serve as hydrocarbon resources.

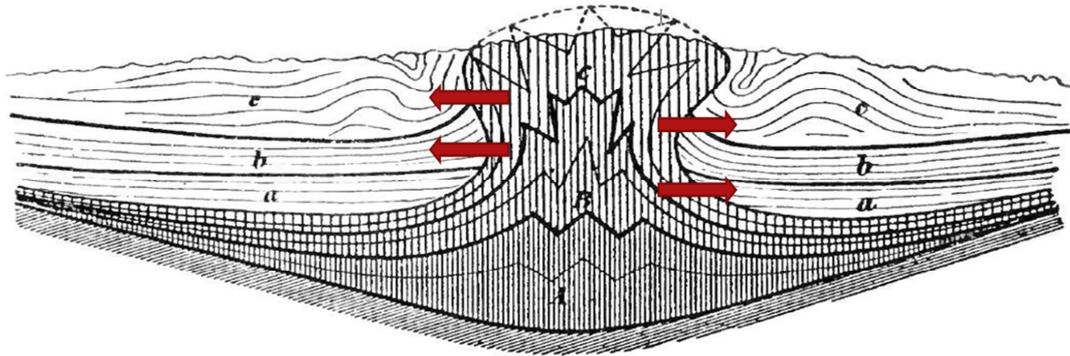
In case of the buried DHABs, the volume of these brines as non-Newtonian fluids will determine the trapped methane quantity in the ancient DHABs. In geological timescale the thickness of such buried DHABs may be higher than the actual brines, because it depends on the basin filling rate.

3.2. A Hypothesis

3.2.1. New Hypotheses on Diapir Formation

As methane-hosting buried brine is generated (DHAB) and covered by a significant volume of sediments, the substantial

weight of the deposits will create overpressure in the brine layers throughout geological time. It is likely that the initial equilibrium of this almost solid, non-Newtonian fluid can reverse as a fluid caused by the impact of an earthquake. As a consequence, the energy transferred to this liquid will breach the covering deposits, penetrating into them. This uplift of the brine from the buried DHABs will incorporate rock fragments of the covering deposits. The over-pressured, methane saturated brine on the bubble point will release the gas and the remaining water into the reservoir packages of the covering sediments (Figure 3. Posepny, 1871).



after Posepny, 1871

Figure 3. Breach of the trap, allowing methane to escape from the over-pressured brine.

The de-gasification and dehydration of the hypersaline ascending brine suffer volume collapse when the surrounding- and covering breccia is formed. This loss of material initiates salt crystallization, meanwhile preserving the folds generated during the penetration and plastic ascent. The incorporated foreign bodies and rock fragments from the covering deposits can be found in the crystalline salt diapir Figure 4.

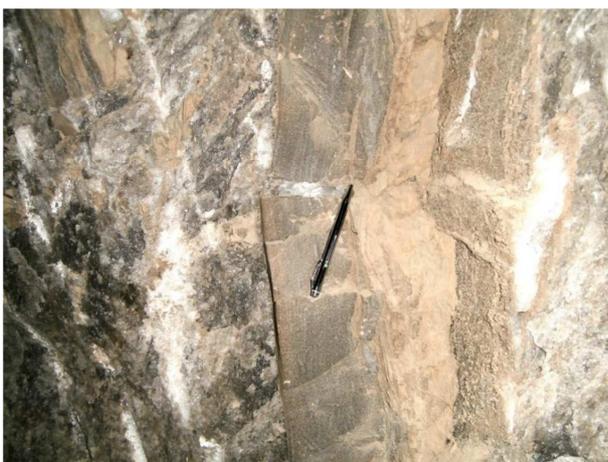


Figure 4. The foreign, broken rock fragments in a salt diapir body (photo shot by the authors).

4. Conclusions

1. Recent scientific knowledge about deep marine

processes and phenomena, especially the evidence of Deep Hypersaline Anoxic Basins/Lakes led us to a new hypothesis on salt and biogenic methane generation.

2. Sea water of normal salinity is not merely a solution but also a colloid system. At a particular depth, micella reach critical concentration. Duly, physical properties: conductivity, salinity concentration and osmotic pressure will change abruptly. We presume that the phenomenon of membrane polarisation is responsible for the increase of conductivity due to the presence of argillaceous ions of negative charge and the positive Ca^{2+} and Mg^{2+} ions.
3. Membrane polarisation creates a semipermeable membrane and generates a reverse osmotic process due to hydrostatic pressure. This is the phenomenon responsible for the increase of the salinity beneath the membrane layer; this is how DHABs are generated. This semipermeable membrane is responsible for the surface tension between normal sea water and brine, serving as a physical barrier against diffusion.
4. The oversaturated, viscous brine is an ideal environment both for the halophile bacteria, i.e. methane generating bacteria and for acetate decomposition. Throughout these processes, methane generation reaches 70 mg/l ($\text{CH}_4 \sim 40$ mg/l bacterial + ~ 30 mg/l acetate decomposition).
5. As found by MedRIFF, the viscous brine surface can

support deposited sediments. This allows the brines to be trapped and buried over geological time, generating an over-pressured, non-crystallized body of high methane and acetate concentration (~70mg/l).

6. As non-Newtonian fluids, DHABs could grow in volume along geological time to dimensions vaster than those of the currently known ones;
7. Once the buried, over-pressured brine hosting methane is exposed to tectonic events, the over-pressured brine will breach the seal and expel the trapped methane into the sandy sedimentary layers above it. As a result, crystalline salt diapirs are formed.

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