

# Analysis of the Black Sea Gas Hydrates

Sukru Merrey, Caglar Sinayuc

**Abstract**—Gas hydrate deposits which are found in deep ocean sediments and in permafrost regions are supposed to be a fossil fuel reserve for the future. The Black Sea is also considered rich in terms of gas hydrates. It abundantly contains gas hydrates as methane ( $\text{CH}_4$ -80 to 99.9%) source. In this study, by using the literature, seismic and other data of the Black Sea such as salinity, porosity of the sediments, common gas type, temperature distribution and pressure gradient, the optimum gas production method for the Black Sea gas hydrates was selected as mainly depressurization method. Numerical simulations were run to analyze gas production from gas hydrate deposited in turbidites in the Black Sea by depressurization.

**Keywords**—Black Sea hydrates, depressurization, turbidites, HydrateResSim.

## I. INTRODUCTION

**G**AS hydrates are ice like crystalline structures formed by water and gas molecules at high pressure and low temperature values [1]. Hydrocarbon molecules such as methane ( $\text{CH}_4$ ), ethane ( $\text{C}_2\text{H}_6$ ), propane ( $\text{C}_3\text{H}_8$ ) and i-butane ( $\text{i-C}_4\text{H}_{10}$ ) form their own hydrate (simple or pure hydrate) at appropriate pressure and temperature conditions when there is enough water in the system [2]. Gas hydrate reservoirs are considered as future energy source because it is found abundantly in both permafrost regions and the sediments in oceans [3]. Johnson [4] estimated gas in place in hydrate-bearing sands, there is a huge range of GH resource between 133 and 8891 tcm. It can be concluded that even the most conservative estimates of the total quantity of gas in GH are much larger than the conventional gas resources (404 tcm) and shale gas (204–456 tcm) [5]. The magnitude of this resource can make hydrate reservoirs a substantial future energy resource.

As many places in the world, the Black Sea also has a huge gas hydrate potential and it is also considered as the world's most isolated sea, the largest anoxic water body on the planet and a unique energy-rich sea [6]. The Black Sea is an inland sedimentary basin, located between the latitudes of  $41^\circ$  to  $46^\circ\text{N}$  and longitudes of  $28^\circ$  to  $41.5^\circ\text{E}$  with an area of 423,000  $\text{km}^2$ , a volume of 547,000  $\text{km}^3$  and a maximum depth of 2200 m [7]. The salinity, temperature and isopycnal parameter values with sea level depth are shown in Fig. 1. Sea water salinity changes between 1.75–2.23% (17.5–22.3 ppt) [7], [8]. The salinity of the Black sea increases from 1.75% to 2.23% between sea surface and 200 m below sea level. Then, it is

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almost constant from 200 m below sea level to sea bottom [8].

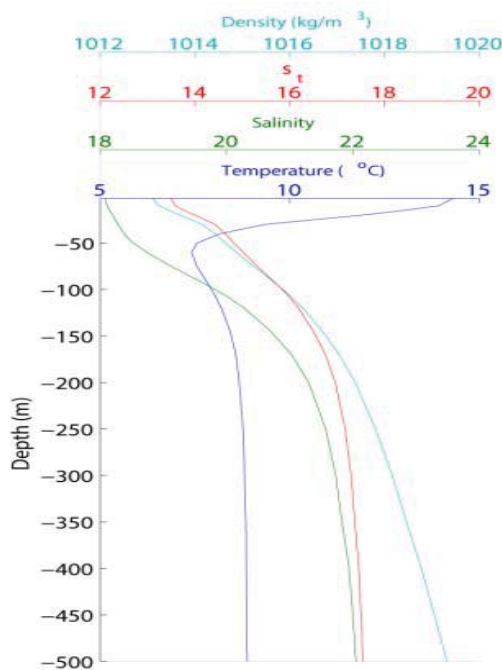


Fig. 1 Vertical profiles of temperature, salinity, density and  $\sigma_t$  (isopycnal parameter) in the Black Sea at the location with lat = 42.951, long = 39.114 [8]

In Fig. 2, the locations of the gas hydrate samples recovered as squares in ice blue color and the potential places in terms of gas hydrate inferred from other seismic studies (i.e. mud volcanoes) in the Black Sea are shown [9]. In Fig. 2, the gas seepage areas in the Black Sea are shown. These seepages are due the conditions in those places out of hydrate formation conditions. With the TTR-11 cruise of RV Professor Logachev, gas hydrate samples were recovered for the first time in the Northwestern part of the Black Sea in the area without mud volcanoes and at a water depth of 900 m as shown in [10]. As seen in Fig. 3, gas hydrates fill sediments in nodular filling type. According to Vassilev and Dimitrov [11], the area of the Black Sea suitable for gas hydrate formation is evaluated at 288,100  $\text{km}^2$ , representing about 68.5% of the total Black Sea or almost 91% of the deep-water basin.

Class 1  $\text{CH}_4$  hydrate reservoirs might be common in the Black Sea. For the determination of Class 1 hydrates, seismic studies have crucial importance [12]. Detection of bottom-simulating reflections (BSRs) during seismic studies can give clues about the potential of Class 1 hydrates. Bottom-simulating reflections (BSRs) are the typical seismic signature for most oceanic occurrences of gas hydrates. They consist of a reversed polarity reflection that approximately parallels the

sea floor and crosscuts the acoustic bedding structure of the sediments [13], [14]. The presence of a free gas zone beneath

the BSR is attested by high reflectivity and has been confirmed by drilling [13].

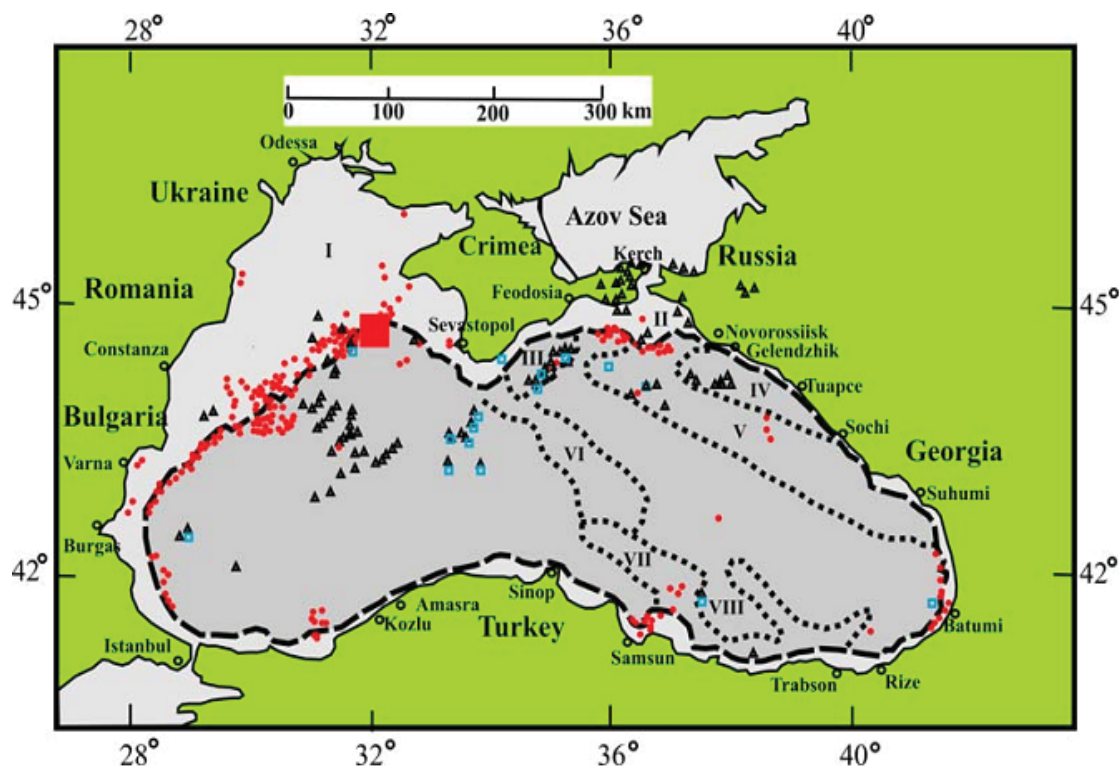


Fig. 2 Location of the mud volcanoes gas seeps and gas hydrates in the Black Sea: Triangles in black, mud volcanoes; circles in red, gas seeps; squares in ice blue, gas hydrate; bold dashed lines in black, shelf edge; bold squared lines, boundaries of tectonic units; filled rectangular in red [9]

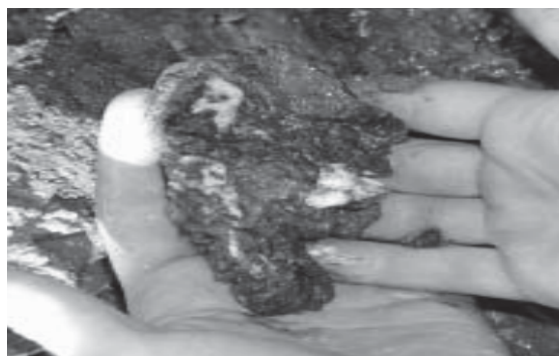


Fig. 3 Gas hydrates in the Core BS308K in the Northwestern part of the Black Sea [10]

There are lots of natural gas hydrate reservoir types in nature. However, not all of them are considered as a potential energy source. The most common gas hydrate reservoirs considered as an energy source are Class 1, Class 2 and Class 3 hydrate reservoirs [15], [16]. Class 1 hydrates are characterized with a hydrate layer above a zone with free gas and water. Class 2 deposits exist where the hydrate bearing layer, overlies a mobile water zone. Class 3 accumulations are characterized by a single zone of hydrate and the absence of an underlying zone of mobile fluids [16]. When all other conditions and properties being equal among these hydrate

reservoirs, Class 1 hydrates appear to be the most promising targets for gas production. It is because its pressure is close to hydrate equilibrium conditions and it is easy to produce (only small changes in pressure and temperature are necessitated for hydrate dissociation) and the existence of a free gas zone guarantees gas production even when the hydrate contribution is small [15], [16]. According to Haeckell et al. [17], high reservoir-quality in gas hydrate accumulations are expected in permeable sandy-silty deposits, such as turbidites and channel-levee-systems of the large paleo-river systems around the Black Sea. Similar observations in the Black Sea were obtained in the study of Xing [18]. Turbidites are the deposits of turbidity currents, which are gravity-driven turbid suspensions of fluid (usually water) and sediment. They form a class of subaqueous sediment gravity flow (see Gravity-Driven Mass Flows) in which the suspended sediment is supported during transport largely or wholly by fluid turbulence. Turbidites range in grain-size from mud to gravel, and may be of any composition—siliciclastic, carbonate, or even sulfide near deep-sea hydrothermal vents. Turbidite beds range in thickness from millimeters to tens of meters, and individual events can, in extreme cases, involve the resedimentation of hundreds of cubic kilometers of sediment. They are amongst the commonest of sedimentary deposits, and turbidite depositional systems such as submarine fans and

basin plains form the largest individual sedimentary accumulations on the Earth. Thick sequences of synorogenic turbidites (flysch) are common in the ancient record [19].

Depressurization, inhibitor injection, thermal stimulation and CO<sub>2</sub> injection methods are the main ways to produce gas from hydrate reservoirs. Depressurization is decreasing the reservoir pressure below hydrate equilibrium pressure but production rate is low due to slow hydrate dissociation. Inhibitor injection method is injecting chemical additives such as methanol or glycol to shift the pressure-temperature equilibrium however there is a risk of polluting the environment and it may not be economical. Thermal stimulation method is done by increasing the reservoir temperature above hydrate equilibrium temperature with hot water or steam injection but it may not be economical. Finally, CO<sub>2</sub> injection method is to replace the methane molecules trapped in the gas hydrate structure with CO<sub>2</sub> molecules and its disadvantage is slow replacing speed [20]. All of these production methods has some advantages and disadvantages. Therefore, it is important to choose the right one in terms of engineering and economy. However, especially for Class 1 reservoirs, depressurization appears to have a clear advantage in all three classes [21], [22].

In this study, it was aimed to show gas production differences between thin gas hydrate sections deposited in turbidites and Class 3 hydrate reservoir with one thick hydrate section in the Black Sea conditions numerically.

## II. SIMULATION OF THE GAS PRODUCTION FROM A HYPOTHETICAL METHANE HYDRATE RESERVOIR DEPOSITED IN TURBIDITES IN THE BLACK SEA CONDITIONS

Numerical simulation of gas production from gas hydrates in laboratory scale and reservoir scale is very important for gas hydrate studies because there are not many real gas production data from hydrate reservoirs. HydrateResSim is a code for the simulation of the behavior of hydrate bearing geologic systems. It is written in standard Fortran 95/2003 to take advantage of all the object-oriented capabilities and the enhanced computational features of that language. By solving the coupled equations of mass and heat balance, HydrateResSim can model the non-isothermal gas release, phase behavior and flow of fluids and heat under conditions typical of common natural CH<sub>4</sub>-hydrate deposits. The model equations are obtained by incorporating the multiphase Darcy's law for gas and liquid into both the mass component balances and the energy conservation equations. Two sub-models in HydrateResSim for hydrate dissociation are also considered: a kinetic model and a pure thermodynamic (equilibrium) model. It can be used from laboratory to reservoir (i.e., in the permafrost and in deep ocean sediments) at which Darcy's law is valid. It can be used for depressurization, thermal injection, chemical injection or their combination. The pressure  $P < 100$  MPa (6800 psi) [23].

## III. RESULTS AND DISCUSSION

In this study, in order to understand the differences between gas hydrate reservoirs deposited in different layers of turbidites and Class 3 reservoirs in the Black Sea conditions, their gas production simulations were compared. As discussed earlier, Class 1 hydrate reservoirs might be common in the Black Sea because many BSRs were detected in seismic studies. However, these seismic studies do not describe the formations below and above this BSR lines well. If there are fine silty, clay or shaly formation just above BSR lines and hydrate zone is above fine silty, clay or shaly formation, classical gas production method from Class 1 hydrate reservoirs cannot be applied. In Class 1 hydrates, perforations are opened in the free gas zone below hydrate zone and this way, hydrate zone dissociates but silty, clay or shaly zone at or just above BSR line in turbidites might avoid this production method. However, compared to Class 3 hydrate reservoirs with thick hydrate section, turbidites might be advantageous because turbidites have generally thin hydrate section so heat transfer is very effective from silty, clay and shaly layers of turbidites. It is known that heat conductivity of gas hydrates is low so when hydrate is thicker, heat conductivity is lower.

TABLE I  
PROPERTIES OF THE HYPOTHETICAL CH<sub>4</sub> HYDRATE DEPOSITED IN TURBIDITES AND CLASS 3 CH<sub>4</sub> HYDRATE IN THE BLACK SEA CONDITIONS

Parameters	Hydrate Deposited in Turbidites	Class 3
Radius	500 m	500 m
Thickness of Hydrate Zone	20 m (Separated 4 layers with 5 m thickness each)	20 m
Thickness of Each Shale Layer	50 m (Separated 5 layers with 10 m thickness each)	50 m (Top and bottom boundary with 25 m thickness)
Porosity	0.50	0.50
Permeability of Hydrate Zone	$9.869 \times 10^{-13}$ m <sup>2</sup> (1 D)	$9.869 \times 10^{-13}$ m <sup>2</sup> (1 D)
Rock Grain Density	2700 kg/m <sup>3</sup>	2700 kg/m <sup>3</sup>
Wet Thermal Conductivity	2.4 W/(m.K)	2.4 W/(m.K)
Average Pressure	24 MPa	24 MPa
Temperature Gradient	0.034 °C/m	0.034 °C/m
Temperature Interval	16.514-18.724 °C	16.514-18.724 °C
Hydrate Zone Saturations	S <sub>h</sub> :0.50; S <sub>aq</sub> :0.50	S <sub>h</sub> :0.50; S <sub>aq</sub> :0.50
Total CH <sub>4</sub> Amount, m <sup>3</sup>	$6.7959113 \times 10^8$	$6.7969273 \times 10^8$
Total Water Amount, kg	$7.11004176 \times 10^9$	$7.10990760 \times 10^9$
Relative Permeability Parameters- Modified of Stone Equation	S <sub>ar</sub> :0.25 S <sub>gr</sub> :0.02 n: 3.0	S <sub>ar</sub> :0.25 S <sub>gr</sub> :0.02 n: 3.0
Capillary Pressure Parameters- Van Genuchten function	S <sub>ar</sub> : 0.24 n: 1.84 a:10.0	S <sub>ar</sub> : 0.24 n: 1.84 a:10.0

Turbidites are commonly found in the Black Sea and it was considered that they might include gas hydrates. In order to investigate gas production difference between Class 3 and hydrate deposited in turbidites, hypothetical hydrate reservoirs were formed. In the study of Küçük et al. [14], BSR lines were observed at 305 mbsf when sea depth is around 2010 m in Amasra, Bartın, Zonguldak-Kozlu in the central Black Sea. Therefore, just above this BSR line, two hypothetical hydrate reservoirs were formed in the Black Sea conditions by using

the necessary data for simulation studies. These data are listed in Table I by using thermal gradient, pressure gradient, porosity etc. gained from [14] and [11].

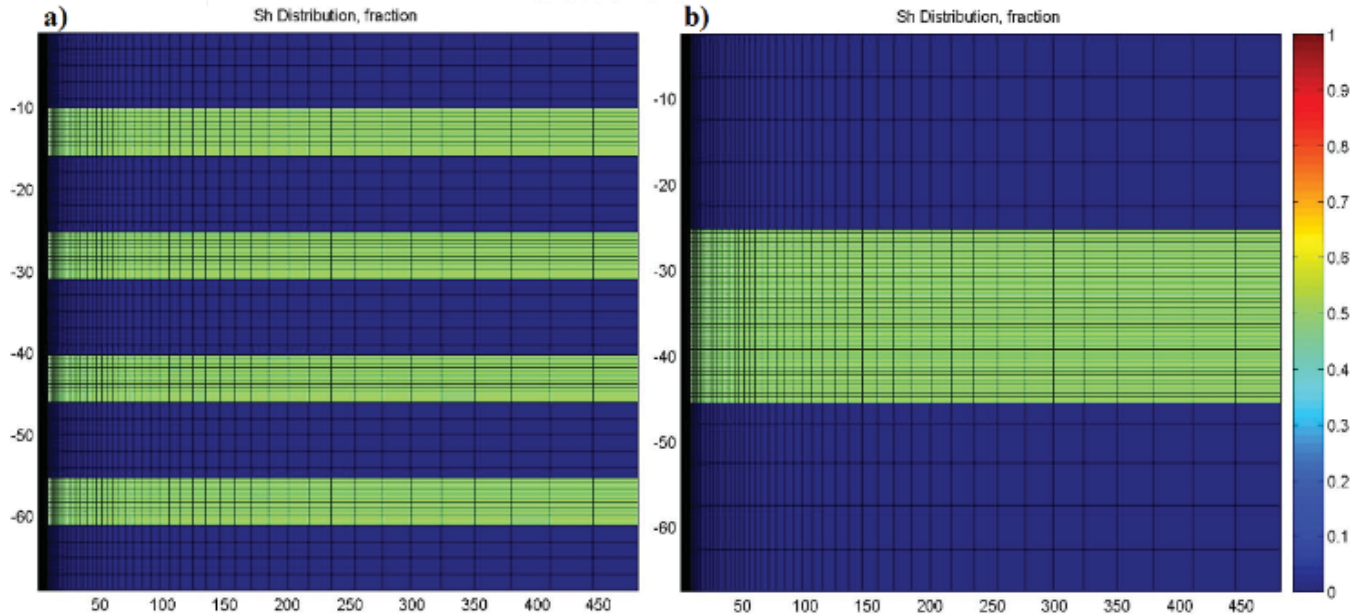


Fig. 4 Hydrate saturations and gridding in (a) turbidites, (b) Class 3 reservoir

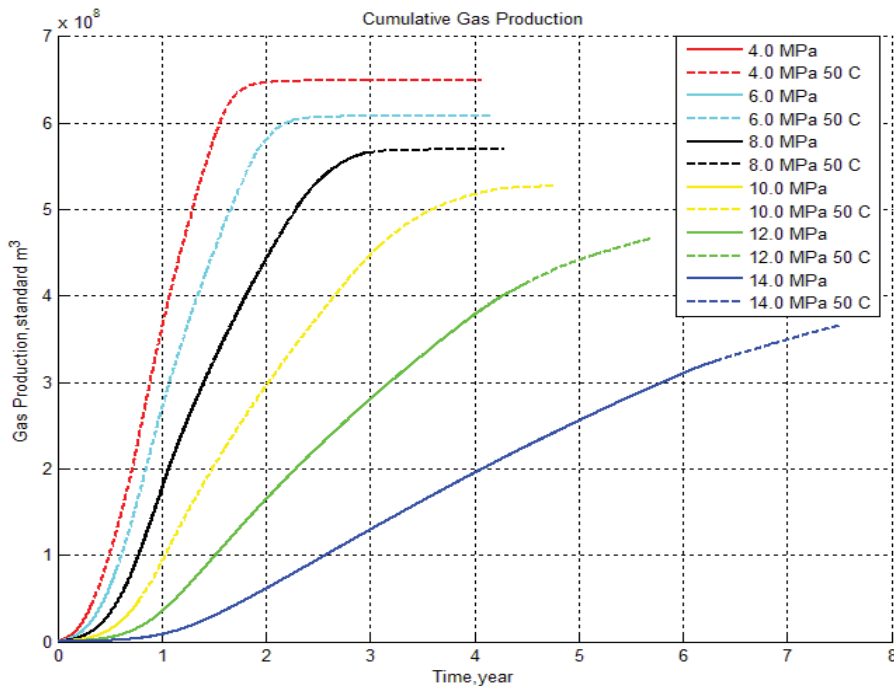


Fig. 5 Cumulative Gas Production by depressurization in the hypothetical hydrate deposited in turbidites

As seen in Table I, hydrate saturation in the hydrate zone was chosen as 0.50 and gas saturation in the free gas zone was chosen as 0.50. Equilibrium model option of HydrateResSim was selected because at the reservoir conditions, kinetic model and equilibrium models give similar results [12]. For 2D gridding for the cylindrical reservoir in turbidites, 65 grids (Cartesian) along z direction and 75 grids (logarithmic) along r

direction are placed. 10 grids (Cartesian) along z direction and 5 grids (Cartesian) along z direction are placed for each hydrate and impermeable boundary, respectively. For 2D gridding for the Class 3 cylindrical reservoir, 50 grids (Cartesian) along z direction and 75 grids (logarithmic) along r direction are placed. 40 grids (Cartesian) along z direction and 10 grids (Cartesian) along z direction are placed for hydrate

and impermeable boundaries, respectively. Grids for both hydrate deposited in turbidites and Class 3 reservoir is shown in Fig. 4. Therefore, 14,625 equations were solved for 11,250 elements at each time step for hydrate deposited in turbidites and Class 3 reservoir.

For both hypothetical hydrate reservoirs, perforations are opened in hydrate sections and gas production simulations were held by using depressurization with and without wellbore heating methods. HydrateResSim numerical simulator was

used in the simulations. When cumulative gas production, cumulative water production and gas production rates of two reservoirs are compared in Figs. 5-10, it is obvious that gas production in the hypothetical gas hydrate reservoirs deposited in turbidites are quite higher than gas production in the hypothetical gas hydrate reservoirs deposited in turbidites because heat flow boundaries are high in thin hydrate zones in turbidites. Therefore, this can be advantageous for the Black Sea.

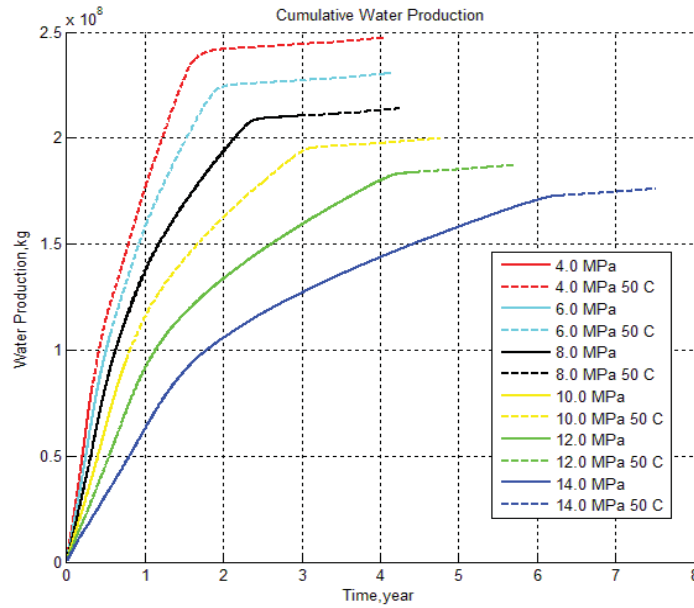


Fig. 6 Cumulative Water Production by depressurization in the hypothetical hydrate deposited in turbidites

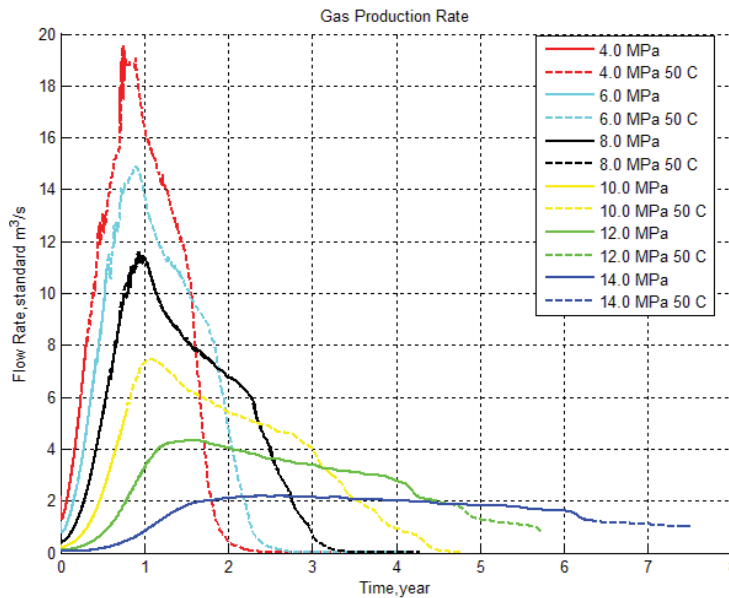


Fig. 7 Gas production rate by depressurization in the hypothetical hydrate deposited in turbidites

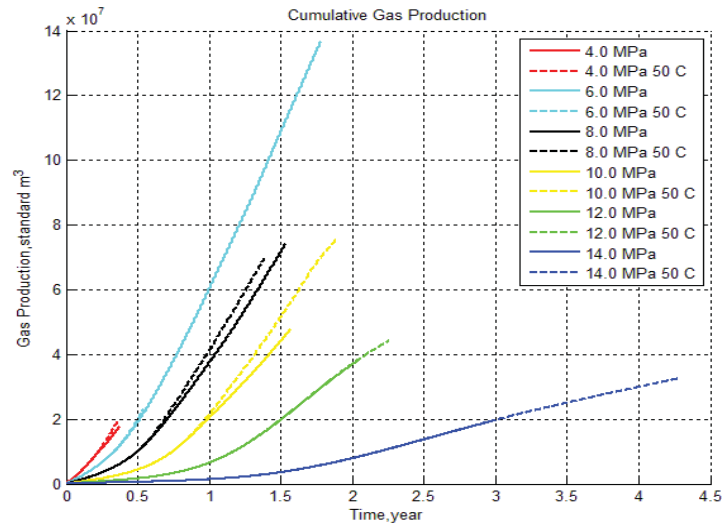


Fig. 8 Cumulative Gas Production by depressurization in the hypothetical Class 3 reservoir

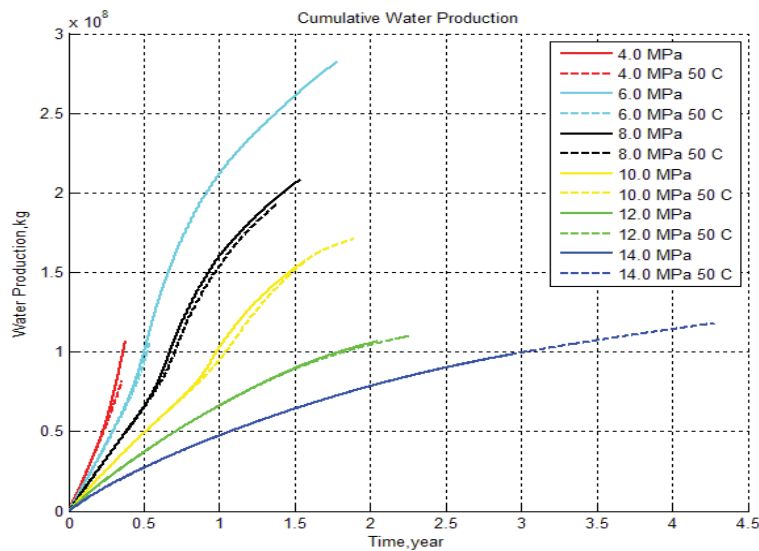


Fig. 9 Cumulative Water Production by depressurization in the hypothetical Class 3 reservoir

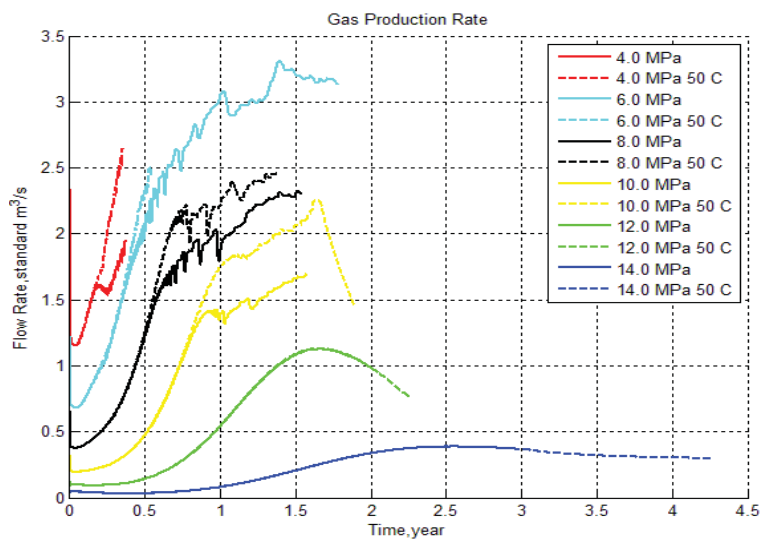


Fig. 10 Gas production rate by depressurization in the hypothetical Class 3 reservoir

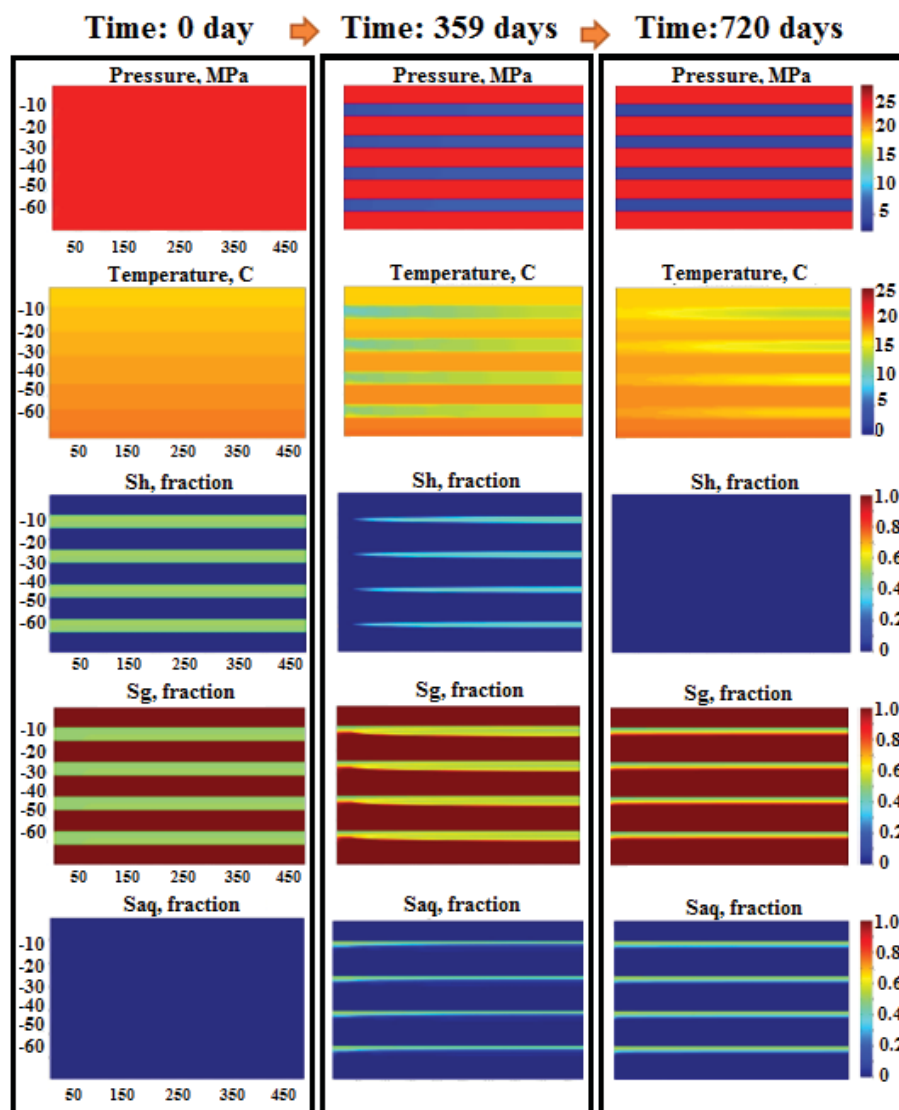


Fig. 11 Changes in pressure, temperature, Sh, Sg and Saq with depressurization at 4.0 MPa with wellbore heating at 50 °C

As depressurization pressure increases, gas production increases and much more water is produced. However, in some cases, there might be hydrate formation along wellbore and in this case, wellbore heating might be necessary. Because of faster thermal flux from impermeable boundaries to thin hydrate section in turbidites, much more gas might be produced compared to thick hydrate sections in the same conditions.

In Figs. 11 and 12, gas production behavior during depressurization for hydrate deposited in turbidites and Class 3 reservoirs are shown. As seen in these figures, temperature in hydrate sections decrease while production. The reason of this is mainly endothermic nature of hydrate dissociation. However, as an average, temperature decreases from 17.5 °C to 10 °C. Therefore, it is obvious that in the Black Sea conditions, ice formation in hydrate reservoirs is not possible. For hydrate deposited in turbidites, it was assumed that hydrate sections have uniform hydrate saturation as 50%.

However, in really cases, their saturations might be difference. Hence, well completion strategies should be developed for these cases. In this study, it was only aimed to show that gas hydrate deposited in turbidites as thin sections can be advantageous compared to Class 3 hydrate reservoirs in the Black Sea conditions.

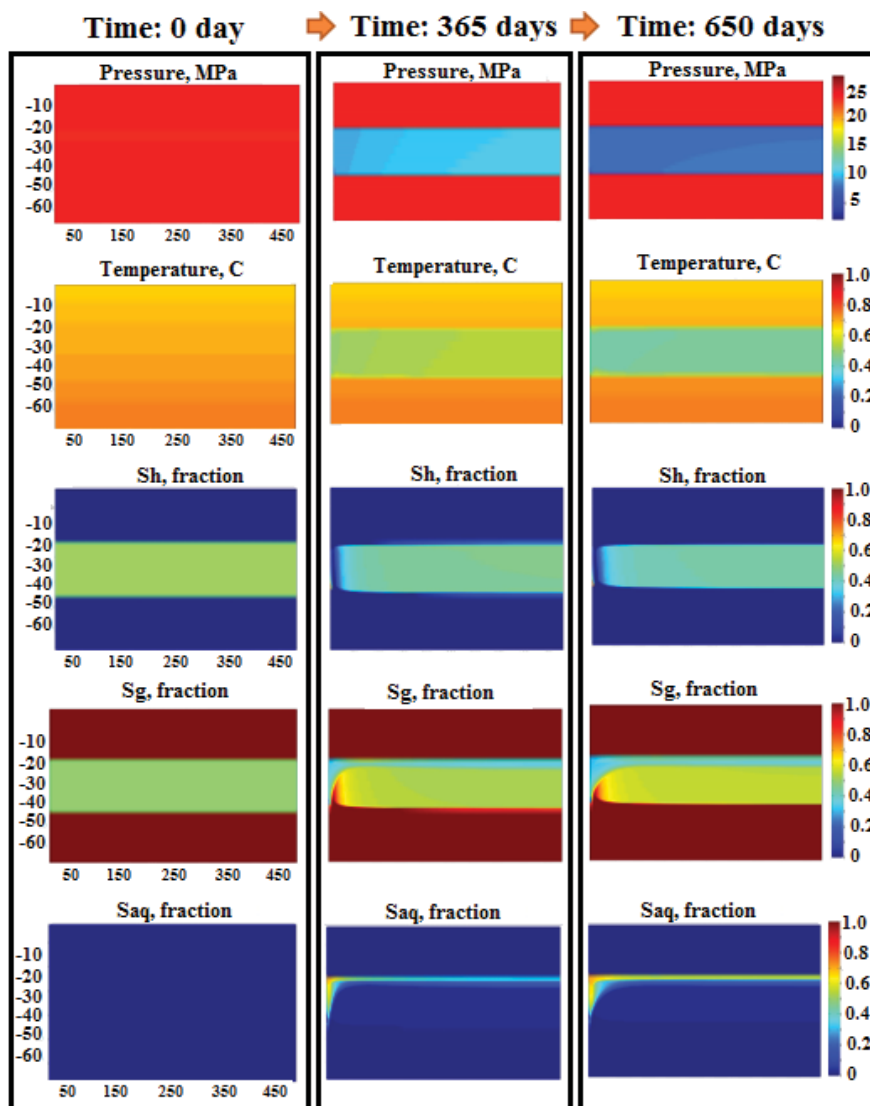


Fig. 12 Changes in pressure, temperature, Sh, Sg and Saq with depressurization at 6.0 MPa without wellbore heating

#### REFERENCES

- [1] J.J. Carroll, *Natural Gas Hydrates, 2<sup>nd</sup> Edition A Guide for Engineers*. Gulf Professional Publishing, 2009.
- [2] E.D. Sloan, E.D. and Koh, C.A., *Clathrate Hydrates of Natural Gases*, 3<sup>rd</sup> Edition, Taylor & Francis/CRC Press, 2008.
- [3] K. Abid, G. Spagnoli, C. Teodoriu, G. Falcone, "Review of pressure coring systems for offshore gas hydrates research" *Underwater Technology*, Vol. 33, No. 1, pp. 19–30, 2015.
- [4] A.H. Johnson, "Global Resource Potential of Gas Hydrate—A New Calculation" in *Proceedings of the 7<sup>th</sup> International Conference on Gas Hydrates (ICGH 2011)*, Edinburgh, Scotland, United Kingdom, July 17–21, 2011.
- [5] Z.R. Chong, S.H.B. Yang, P. Babu, P. Linga, X.S. Li, "Review of natural gas hydrates as an energy resource: Prospects and challenges" *Applied Energy* 2016, 162, 1633–1652.
- [6] J. Overmann, A.K. Manske, *Past and Present Water Column Anoxia*. Leiden, the Netherlands: Springer, 2006.
- [7] J.W. Murray, "Black Sea oceanography. Results from the 1988 Black Sea expedition". *Deep Sea Res.* 38:S655–S126, 1991.
- [8] E.V. Stanev, Y. He, J. Staneva, E. Yakushev, "Mixing in the black sea detected from the temporal and spatial variability of oxygen and sulfide and ash; Argo float observations and numerical modelling" *Biogeosciences*, 11(20), 5707–5732, 2014.
- [9] V.I. Starostenko, O.M. Rusakov, F.F., Shnyukov, V.P. Kobolev, R.I. Kutas, R.I. "Methane in the northern Black Sea: characterization of its geomorphological and geological environments". Geological Society, London, Special Publications-2010-Starostenko-57-75, 2010.
- [10] N.H. Kenyon, M.K. Ivanov, A.M. Akhmetzhanov, G.G. Akhmanov, "Geological Processes in the Mediterranean and Black Seas and North East Atlantic- Preliminary results of investigations during the TTR-11 cruise of RV Professor Logachev" *Intergovernmental Oceanographic Commission technical series 62*. SC-2002/WS/62, July–September, 2001.
- [11] A. Vassilev, L. Dimitrov, "Model Evaluation of the Black Sea Gas Hydrates". Tome 56, No.3, 2003.
- [12] S. Mery, C. Sinayuc, C. "Investigation of gas hydrate potential of the Black Sea and modelling of gas production from a hypothetical Class 1 methane hydrate reservoir in the Black Sea conditions" *Journal of Natural Gas Science and Engineering*, 29, 66–79, 2016.
- [13] I. Popescu, M. De Batist, G. Lericolais, H. Nouzé, J. Poort, N. Panin, W. Versteeg, H. Gillet, "Multiple bottom-simulating reflections in the Black Sea: Potential proxies of past climate conditions" *Marine Geology*, 227(3–4), 163–176, 2006.
- [14] H.M. Küçük, D. Dondurur, Ö. Özel, Ç. Sınayuc, Ş. Mery, M. Parlaktuna, G. Çifçi, G. "Acoustic Investigations of Gas and Gas Hydrate Formations, offshore southwestern Black Sea." in *American Geophysical Union-Fall Meeting*, December 14–18, 2015, San Francisco, USA.
- [15] G.J. Moridis, T.S. Collett, R. Boswell, S. Hancock, J. Rutqvist, C. Santamarina, T. Kneafsey, M.T. Reagan, M.P. Darvish, M. Kowalsky, E.D. Sloan, C. Koh, Chapter 37: Gas Hydrates as a Potential Energy



Source: State of Knowledge and Challenges-Lee, W.J. (ed.) Advanced Biofuels and Bioproducts, Springer Science+Business Media New York, 2013.

- [16] C.G. Xu, X. Li, "Research Progress on Methane Production from Gas Hydrates" RSC Adv.,5, 54672-54699, 2015.
- [17] M. Haeckel1, J. Bialas, L. Klaucke, K. Wallmann, G. Bohrmann, K. Schwalenberg, "Gas Hydrate Occurrences in the Black Sea – New Observations from the German Sugar Project" Fire in the Ice. Methane Hydrate Newsletter. 015 Vol. 15, Issue 2, 2015.
- [18] J. Xing, Seismoacoustic Study of the Shallow Gas Transport and Reservoirs in the Vicinity of Seabed Fluid Seepage of the Black Sea" PhD Thesis, Im Fachbereich der Geowissenschaften der Universität Bremen, Germany, 2013.
- [19] B.C. Kneller, *Sedimentology*. Part of the series Encyclopedia of Earth Science pp 1250-1256, 2003.
- [20] Y. Ye, C. Liu, *Natural Gas Hydrates, Experimental Techniques*, Springer Geophysics, 2013.
- [21] M. Kurihara, "Gas Production from Methane Hydrate Reservoirs" in Proceedings of the 7th International Conference on Gas Hydrates (ICGH 2011), Edinburgh, Scotland, United Kingdom, July 17-21, 2011.
- [22] A. Demirbas, "Methane from Gas Hydrates in the Black Sea" Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 32(2), 165–171, 2009.
- [23] G.J. Moridis, M.B. Kowalsky, "Gas Production from Unconfined Class2 Hydrate Accumulations in the Oceanic Subsurface" Report LBNL-57299, Lawrence Berkeley Natl. Laboratory, Berkeley, California, 2005.