Status Report

# Geo-scientific Investigations of Gas-hydrates in India

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The best solution to meet India's overwhelming energy requirement is to tap the nuclear and solar power to the maximum extent possible. Another feasible major energy resource is gas-hydrates (crystalline substances of methane and water) that have been identified by various geo-scientific methods along the Indian continental margin and later discovered by drilling and coring. The bathymetry, seafloor temperature, total organic carbon (TOC), sediment thickness, rate of sedimentation, geothermal gradient, and geological, geophysical and microbiological studies indicate that shallow sediments in deep water regions are good hosts for gas-hydrates (Sain and Gupta, 2008, 2012). First, we have prepared the gas-hydrates stability thickness map along the Indian margin, which provides the spatial and depth windows for the identification of gas-hydrates, and developed several geo-scientific methods for the qualification and quantification of gas-hydrates. We have delineated the most prospective zones of gas-hydrates in the Krishna-Godavari, Mahanadi and Andaman basins. The proxies for gas-hydrates have been recognized in the Kerala-Konkan and Saurashtra basins. The Kerala-Laccadive and Cauvery basins have also been found prospective for gas-hydrates by studying into various physical parameters. We have evaluated the resource potential of gas-hydrates to boost the development of viable production technology. Approximately, 1900 trillion cubic meter of methane has been prognosticated (Collett *et al.*, 2008) within the vast exclusive economic zone (EEZ) of India. This volume of gas is more than 1500 times of India's present natural gas reserve, and only 10% can meet India's burgeoning energy requirement for about a century. A brief description of all these is made in this article.

Key Words: Indian offshore; Gas-hydrates; Resource Potential; Geo-scientific Methods

### Introduction

The growing demand of carbon emission-free energy and depletion of fossil fuels necessitate looking for an alternate source of energy for sustainable development of energystarving countries like India. Besides nuclear and solar energy, gas-hydrates have attracted the global attention due to their wide-spread occurrences in outer continental margins and permafrost regions, and their huge energy potential. Gas-hydrates are crystalline substances (Fig. 1) consisting of 99.9% methane and water, and one volume of gas-hydrates release 164 volumes of methane gas and 0.8 volume of fresh water (Fig. 1 b) at standard temperature and pressure (STP). Unlike natural gas, oil and minerals, gas-hydrates are not stable at STP. They exist only at high pressure and moderately low temperature. Since methane is the cleanest of all hydrocarbon fuels, use of gas-hydrates as fuels will cause less pollution. The huge volume (1-120 x 10<sup>15</sup> m<sup>3</sup>) of methane trapped within global gas-hydrates seems to be a viable major energy resource of future (Boswell and Collett, 2011). Even, 15% production from this reserve is envisaged to meet the global energy requirement for about two centuries (Makogon *et al.*, 2007).

Globally, gas-hydrates have been identified from geophysical, geochemical and geological surveys, and by drilling and coring (Boswell and Saeki, 2010; Ruppel, 2011). Geophysically, gas-hydrates can be found out by identifying an anomalous seismic reflector, known as the bottom simulating reflector or BSR, based on its characteristic features of (i) mimicking the shape of seafloor, (ii) cutting across inclined sedimentary strata, and (iii) exhibiting large amplitude opposite polarity with respect to the seafloor reflection (Fig. 2). Presence of gashydrates reduces the permeability and hence trap 'free-gas' below. Thus, the BSR is a physical boundary between hydrate-bearing sediments above and gas-saturated sediments below, and is often associated with the base of gas-hydrate stability field. So the theoretical map of gashydrates stability zone helps guide to identify the right reflector on seismic section as BSR.

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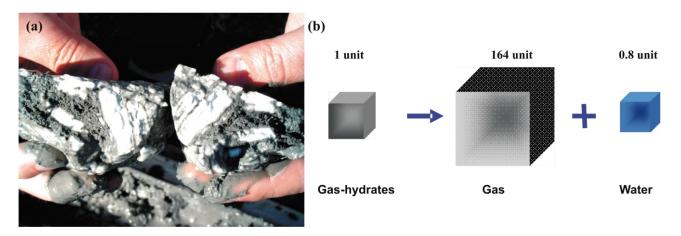


Fig.1: (a) Hydrate-bearing sediments, (b) One unit of gas-hydrates equals to 164 units of gas at STP

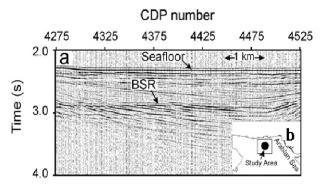


Fig. 2: (a) Seismic section showing a BSR in (b) the study area in the Arabian Sea (Sain *et al.*, 2000)

The Ministry of Petroleum and Natural Gas and the Ministry of Earth Sciences have formulated the national programs for the investigation of gas-hydrates along the Indian margin. The Directorate General of Hydrocarbons (DGH) at Noida, Oil and Natural Gas Corporation (ONGC) Limited at Delhi, Oil India Limited (OIL) at Delhi, Gas Authority of India Limited (GAIL) at Delhi, National Geophysical Research Institute (NGRI) at Hyderabad, National Institute of Oceanography (NIO) at Goa, National Institute of Ocean Technology (NIOT) at Chennai, Indian Institute of Technology (IIT) at Kharagpur and Kanpur, Indian School of Mines (ISM) at Dhanbad, Institute of Engineering and Ocean Technology (IEOT) at Navi Mumbai, are entrusted for delineating gas-hydrates followed by development of production technology. As a first step, the gas-hydrates stability thickness map was prepared using the-then available seafloor temperature, geothermal gradient and bathymetry data. Sain et al. (2011) have recently modified the map (Fig. 3) by incorporating new data generated later on. This map has been extensively used for the identification of wide-spread BSRs (main marker for gas-hydrates) on the recently acquired multichannel seismic (MCS) data in Krishna-Godavari (KG) and Mahanadi (Mn) basins (Sain and Gupta, 2012; Sain *et al.*, 2012).

Gas-hydrates were first recognized in India by an ONGC personnel (Chopra, 1985) in the Andaman (Am) region. By analyzing available MCS data, the BSRs had been identified in KG, Mn and Am regions in the eastern, and in Saurashtra (S) and Kerala-Konkan (KK) regions in the western Indian margin (Sain and Gupta, 2008, 2012; Sain and Ojha, 2008). The drilling and coring by Indian National Gas Hydrate Program (NGHP) during expedition-01 (Collett et al., 2008) have validated the ground truth in Miocene to Pleistocene/Recent sediments where gashydrates were predicted from surface seismic data in the eastern Indian margin. The main results are the delineation of (i) 120-m-thick massive gas-hydrates in 64% porous fractured shale in KG basin; (ii) the thickest (~340 m) disseminated gas-hydrates (4.4% saturation) in 62% volcanic ash in Am Sea; and (iii) coveted gas-hydrates deposits in sand reservoirs in Mn basins, respectively. This has boosted our efforts to further advance our research for the exploration followed by a strong initiative on production. In the Expedition-02, we aim for the identification of sites with sand dominated gas-hydrates reservoirs with free-gas underneath.

Though gas-hydrates have not been recovered from one hole in KK basin by the expedition-01, the geoscientific investigations indicate various proxies for gashydrates in the western Indian margin (Veerayya *et al.*, 1998; Rastogi *et al.*, 1999; Ramana *et al.*, 2006; Sain and Gupta, 2008). The specific characters of BSR near mud diapir, pockmarks, and gas-escape features (Shankar and Sain, 2007) and other geophysical proxies (Satyavani et al., 2003; Shankar *et al.*, 2008) have been used for the investigation of gas-hydrates in the western Indian margin.

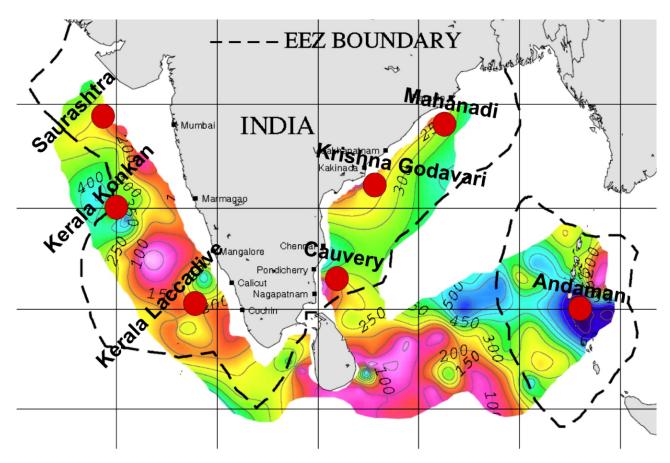


Fig. 3: Gas-hydrates stability thickness map along the Indian shelf with the EEZ boundary (modified after Sain *et al.*, 2011). The prospective zones (Krishna-Godavari, Mahanadi and Andaman) and less-explored but potential zones (Kerala-Konkan, Saurashtra, Kerala-Laccadive and Cauvery) of gas-hydrates are superimposed on the map

The study of sediment thickness, rate of sedimentation and TOC indicate probable prospects of gas-hydrates in Kerala-Laccadive (KL) and Cauvery (C) basins. Results of multidisciplinary geophysical surveys indicate that a large area in KG (Ramana et al., 2007, 2009; Dewangan et al., 2010; Sain and Gupta, 2012), Mahanadi (Sain and Gupta, 2012), and Andaman (Satyavani et al., 2008) basins are prospective for gas-hydrates. We have thus found out the most prospective zones of gas-hydrates in KG, Mn and Am regions, and less explored but prospective zones in KK, S, KL and C basins respectively. All these zones are superimposed on gas-hydrates stability thickness map of India in Fig. 3. Geochemical studies of sediment cores collected during the NGHP expedition-01 and on board Marion Dufresne were carried out to characterize the gashydrate deposits in KG, Mn and Am basins (Collett et al., 2008; Mazumdar et al., 2009; Ramana et al., 2009). The measurement of concentrations of various ions such as the SO<sub>4</sub><sup>2-</sup>, bicarbonate, HS<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>,  $C_4H_{10}$ ,  $CO_2$  in pore fluids, and the isotope ratio of dissolved inorganic carbon, gases, TOC, pore water and Cl-provided

vital information for the exploration of gas-hydrates. The activity of sulfate-reducing bacteria decreases the SO<sub>4</sub><sup>2-</sup> concentrations in pore fluid with depth producing the sulfate profile, which is a net result of sedimentation rate, lability of detrital organic load and flux of methane. We observed quasi-linear, sigmoid and kink-type sulfate profile in KG basin (Mazumdar et al., 2009), whereas a linear sulfate gradient was observed in Mn and Am basins. The sulfate methane transition zone (SMTZ) denotes a redox interface within the anoxic sediment column where pore water sulfate and methane concentration profiles intersect and are depleted to non-detectable concentrations. This depletion in sulfate and methane concentration is attributed to the anaerobic oxidation of methane (AOM) performed by a syntrophic consortium of CH<sub>4</sub>-oxidizing archaea and sulfate-reducing bacteria. The depth to SMTZ is a good indicator of high methane flux, and we found a close relationship with the kink-type sulfate profile and occurrence of high methane flux from deep sediment layers enriched in methane or gas-hydrates in KG basin (Mazumdar et al., 2009). The depth to SMTZ in KG basin

is  $\sim$ 6-15 m below sea floor (mbsf), whereas it is  $\sim$  20 mbsf in Mn and Am basins. The methane concentration increases sharply just below the SMTZ and shows a concave up pattern indicating methane consumption via AOM. Total alkalinity (primarily bicarbonate) and  $H_2S$  concentrations increase markedly at SMTZ. Episodic intensification of AOM and production of high alkalinity and  $H_2S$  have recently been reported (Joshi and Mazumdar, 2011; Peketi and Mazumdar, 2011). Expulsion of methane  $\sim$ 60-70 ky back in KG basin resulted in the proliferation of cold seep ecology (Mazumdar *et al.*, 2011a) characterized by the occurrences of chemosynthetic bivalves and unique carbonate trace fossils.

The source of methane is identified by measuring the concentrations and carbon-hydrogen isotope ratios in  $CH_4$ ,  $C_2H_6$ ,  $C_3H_8$ ,  $C_4H_{10}$  in headspace gas. <sup>13</sup> $C_{CH4}$  is the commonly reported number owing to low concentrations of other lighter hydrocarbon gases. The ratio of C1/ (C2+C3) is a good indicator of thermogenic, biogenic or mixed methane source. Highly depleted carbon isotope ratios (~-80 % vPDB) of methane (Mazumdar et al., 2009) below the SMTZ coupled with high C1/(C2+C3) ratio proved the biogenic origin of methane in KG basin. The enrichment observed in carbon isotope ratio of methane above SMTZ is attributed to preferential consumption of <sup>12</sup>CH<sub>4</sub> via AOM. The increase in C1/(C2+C3) ratio above SMTZ is due to preferential consumption of methane relative to heavier hydrocarbon gases. The nature of organic load in KG basin and isotope ratios have recently been reported by Mazumdar et al. (2011b). The methane in recovered gas-hydrates from NGHP Expedition-01 is predominantly microbial in nature. There is an evidence of thermal origin for a portion of gas-hydrates in Mn and Am regions. Mostly, structure-I gas-hydrates has been found. There may be structure-II or structure-H gashydrates depending on the size of guest gas molecules.

The hydrate crystallization involves increase in Cl<sup>-</sup> concentrations in pore water since the hydrate structure involves pure H<sub>2</sub>O molecules forming the clathrate (cage) around methane host, resulting in increase in residual salt concentrations. High salt concentrations (~550 mM) in pore water exceeding sea water value is an indicator of gashydrates formation in sediments. This effect is typically seen above the hydrate layers and termed as 'roof top effect'. In contrast, hydrate thawing while coring and transportation results in release of large volume of fresh water causing drastic drop in Cl<sup>-</sup> concentrations. Remarkable depletion in pore water Cl concentrations relative to sea water has been recorded within the hydratebearing zones at many sites in KG, Mn and Am basins (Collett et al., 2008). Fluids with high iodine and low chlorine concentrations indicate a deep-seated organic-rich formations which probably acted as the source for methane in gas-hydrates. I<sup>-</sup>/Cl<sup>-</sup> indicate mixing between deep-seated, iodine-rich fluids and shallow fluids, dominated by seawater. <sup>129</sup>I/I ratio may be used to calculate the age of organic matter from which the methane is derived. Measurement of iodine concentration and <sup>129</sup>I/I ratio has been planned in future explorations.

The geological exploration is closely coupled to the acquisition of geophysical data like the swath bathymetry, high-resolution sparker, and heat flow data. The bathymetric mounds and linear features have been linked to shale diapirs and faults in KG basin (Dewangan et al., 2010), which are commonly associated with fluid/gas migration features and show numerous fault/fracture systems facilitating the accumulation of gas-hydrates and formation of cold seeps. Both surface and buried mass transport deposits have been recognized in KG basin indicating sediment slides (Ramprasad et al., 2011). The BSRs have been observed on the high-resolution seismic data. Integrated analysis of seismic and drilling data shows that the deposition of gas-hydrates is localized in KG basin in spite of regional occurrence of BSRs and is primarily controlled by the fault/fracture system formed by shale tectonism/neotectonism. A remotely operated vehicle (ROV) rated for 6000 m water depth has been developed at NIOT (Ramadass et al., 2010), and the first scientific expedition has brought out chemosynthetic habitats at 1017 m depth implying the surface expression of gas-hydrates in KG basin. Presence of authigenic carbonate in shallow sediments indicates methane for gas-hydrates (Kocherla et al., 2006), which was further corroborated by a paleocold seep activity with sharp increase in carbonate content (10-55% by volume) within 16-20 m below mbsf in KG basin (Mazumdar et al., 2009; 2011a).

The distribution pattern of benthic foraminifera, relation with the bacterial population, the morphological variation and carbon isotopic excursion in hydrate-rich KG basin are being worked out at ISM to determine the gashydrates/methane-rich environment. Certain genera of benthic foraminifera (Bolivina, Bulimina, Cassidulina, Chilostomella, Fursenkoina, Uvigerina etc.) prefer to live in methane-rich environment, and thus their count act as proxy for gas-hydrates. Also few species (Chilostomella oolina, Melonis barleeanum, Uvigerina peregrina etc.) prefer to feed on the bacteria and/or on bacterial mat available in the seep zone. Till now, debates are there about the effect of methane on the negative carbon isotopic values of benthic foraminifera. Some people believe that there are no effect of methane on carbon isotope present in faunal test, whereas most of the scientists believe the foraminiferal carbon isotope are too depleted in methane-rich environment. However, carbon isotopic study of epifaunal benthic foraminifera from Blake-Ridge reveals an intermediate depletion pattern which mostly reflects the bottom water productivity rather than the emission/presence of methane (Bhaumik *et al.*, 2011).

# Qualification of Gas-hydrates

Since seismic velocity of pure gas-hydrates is much higher than that of host sediments, presence of gas-hydrates increases the P- and S-wave velocities, and underlying freegas decreases the P-wave velocity respectively with almost negligible change in S-wave velocity. Thus, the velocity anomaly across the BSR can be used for qualifying gashydrates and free-gas-bearing sediments. We have shown that study of seismic attributes like blanking, reflection strength, and instantaneous frequencies (Ojha and Sain, 2009) provides useful inputs to characterize hydrate- and gas-bearing sediments, and to identify BSR without any crosscutting phenomena. By computing these attributes, the deep BSR in Am offshore has been inferred as due to gas-hydrates (Satyavani et al., 2008). As gas-hydrates stiffen the sediment matrix, the hydrate-bearing sediments are associated with low attenuation or high quality factor (Q), whereas underlying gas-bearing sediments exhibit high attenuation or low Q (Fig. 4). This shows that the attenuation (Q<sup>-1</sup>) attribute can be used for the detection of gas-hydrates if BSR is not convincingly observed or for ascertaining whether an identified reflector is a hydrate-BSR or a diagenetic BSR (Berndt et al., 2004). The gashydrate stability thickness map also helps to distinguish between the diagenetic and hydrate-related BSR.

#### Assessment of Gas-Hydrates

Seismic method is the best tool for the assessment of gashydrates. We have estimated 15.5% gas-hydrates and 4.5% free-gas across a BSR near CDP 4405 in the Arabian Sea based on traveltime inversion and AVO modeling, coupled with rock physics (Ojha and Sain, 2008). Application of sophisticated effective medium modeling to the same data has provided 20% gas-hydrates and 2.8% free-gas (Ghosh and Sain, 2008). Using the AVO A-B crossplot together with rock-physics modeling, Ojha et al. (2010) have quantified lateral variation of gas-hydrates from 4.5% to 15% above the BSR (Fig. 5). The free-gas below the BSR varies laterally from 2.0% to 3.5%. The gas-hydrates and free-gas estimated as 13.5% and 3.5% respectively at the same location (CDP 4405) using this third approach, and comparable results obtained by different methods to the same data show the reliability of estimation.

The challenge of quantifying gas-hydrates in fractured shale in KG basin has been overcome by using the effective medium modeling (Ghosh *et al.*, 2010a). The average saturation of gas-hydrates, which varies vertically between 60 to 140 mbsf, has been estimated as 38% (Fig. 6) of total porosity. The results for anisotropic background (due to fractures) match quite well with the pressure core data available at 78 mbsf. To demonstrate the usefulness of this method elsewhere, we have estimated the average

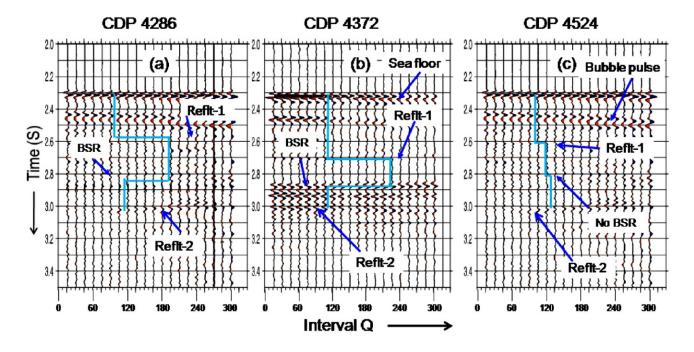


Fig. 4: Seismic gathers at CDPs 4286, 4372 and 4524 respectively along the line shown in Fig.2, each superimposed with interval-Q (Sain and Singh, 2011)

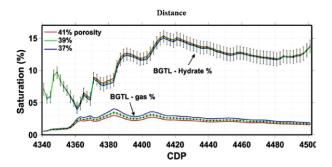


Fig. 5: Gas-hydrates and free-gas (modified after Ojha *et al.*, 2010) at BSR along the line shown in Fig. 2

gas' (Fig. 7). The lateral extension of gas-hydrates has been delineated in KK basin using the traveltime inversion of identifiable reflected phases from MCS data (Singh and Sain, 2012). Likewise, if we derive velocity tomogram from 3-D seismic data, we can delineate the areal and vertical extension of hydrate- and gas-bearing sediments. The accurate velocity and fine-structure (in which gas-hydrates often occur) across a BSR can be derived using the full waveform inversion (Sain *et al.*, 2000) of surface seismic data. This velocity (without any log data) can be used for quantifying gas-hydrates, if coupled with the rock physics modeling.

As seismic Q varies with gas-hydrates and free-gas,

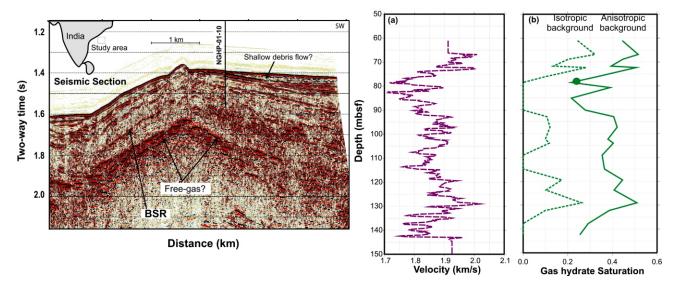


Fig. 6: BSR on seismic section in fractured shale in KG basin. (a) Sonic velocity used for the estimation of gas-hydrates by effective medium modeling; (b) saturation of gas-hydrates with subsurface depths (mbsf) in isotropic and anisotropic (with fractured porosity of 5%) background respectively (modified after Ghosh et al., 2010a). Solid circle shows the estimation from pressure core data

saturations of gas-hydrates as 10.5 %, 11.5 % and 12.5 % of pore spaces respectively at drilling sites 994, 995 and 997 in the clay-dominated Blake ridge area using VSP data (Ghosh *et al.*, 2010b). We have shown that the estimation of gas-hydrates and free-gas using various rock physics model depends on the mineralogy, porosity, and choice of background etc (Sain *et al.*, 2010). Using the constrained AVA and rock physics modeling, Ojha and Sain (2007) have explained the origin of BSR in KK basin as mainly due to gas-hydrates.

Since gas-hydrates and free-gas-bearing sediments exhibit higher and lower velocities across a BSR, the traveltime tomography of large-offset 2-D MCS data or ocean bottom seismic (OBS) data can be used for delineating sediments containing gas-hydrates and 'free-

we can estimate gas-hydrates and free-gas by translating the Q anomaly against the background Q in a similar manner that has been done from seismic velocity anomaly.

# **Exploitation Status**

The research for exploitation of gas-hydrates is in nascent stage. The experiments on thermodynamics and kinetics of gas-hydrates in marine sediments, and on technology development for production of gas from gas-hydrates reservoirs are being pursued mainly at NIOT, IEOT, NGRI, and ISM. The gas-hydrates core repository has been established at IEOT for the preservation of hydrate-bearing core samples under cryogenic conditions. Since the amount of gas contained within gas-hydrates depends on structure, the crystal structure of gas-hydrates is to be investigated.

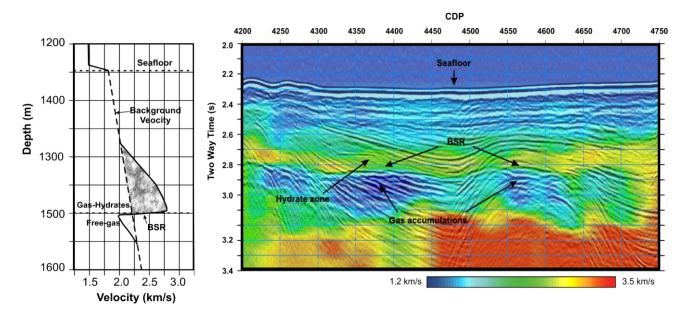


Fig. 7: (left) Typical 'velocity increase' due to gas-hydrates and 'velocity drop' by free-gas across the BSR against the background (without gas-hydrates and free gas) trend. (right) Higher velocity anomaly above the BSR shows the zone of gas-hydrates, and underlying low-velocity anomaly indicates free-gas bearing sediments (Ojha and Sain, 2009) along the line shown in Fig.2

The study involving the X-ray diffraction (XRD), nuclear magnetic resonance (NMR) and Raman Spectroscopy is being carried out at NGRI (Prasad *et al.*, 2008). The laboratory facilities for synthesizing gas-hydrates with different composition and crystal structures, and measuring the physical properties are being carried out to study on how to enhance the gas-hydrates stability to a manageable limit and to recover gas from gas-hydrates without disturbing the natural balance. Recently, Chari *et al.* (2011) at NGRI have shown that the usage of promoter molecules such as the Tetrahydrofuran or THF or tert-butylamine can be used to shift the methane hydrate stability to higher temperatures.

# **Discussion and Conclusions**

A suite of geophysical approaches have been developed for the identification and quantification of gas-hydrates (Sain and Gupta, 2012 and references therein). We have identified the most prospective zones of gas-hydrates in KG, Mn and Am basins, and potential zones in KL, C, KK and S basins. By employing the indigenously developed approaches to the MCS data in various offshore basins of India, we have been pursuing research for (i) ascertaining whether the identified regions are related to gas-hydrates, (ii) understanding the petroleum system of gas-hydrates, (iii) delineating sediments containing gas-hydrates and freegas, and (iv) quantifying the amount of gas-hydrates in these regions. The information derived from the geological, geochemical, and microbiological data sets have been and/

or are being assimilated at the prospective zones for evaluating the resource potential of gas-hydrates. A total volume of ~1900 trillion cubic meter of methane gas has been predicted (Collett et al., 2008) within the Indian EEZ, which is more than 1500 times of current natural gas reserve of India. We anticipate that 10% recovery from this huge cache can meet our overwhelming energy requirement for about 100 years. Though, at this moment, the production technology is not available anywhere in the world. The recent success in production tests at the Mackenzie delta (Canada) and Nankai Trough (Japan) provides great hopes for commercial production of gas bron gas-hydrates in near future. We have mapped the prospective zones of gashydrates along the Indian margin searching for new zones using various geo-scientific methods before the technology is made available for commercial production. It is expected that gas trapped below gas-hydrates can be exploited first, followed by production of gas from gas-hydrates.

Since the depth of BSR is a function of pressure and temperature, the BSR and seismic velocity have been used in deriving the geothermal gradient and heat flow in Makran, KG and KK basins (Vohat *et al.*, 2003; Ghosh *et al.*, 2006; Shankar and Sain, 2009; Shankar *et al.*, 2012). This provides important inputs to understand the thermal structure and evolution of basins with much less expenditure without any heat-flow probes.

Being a greenhouse gas, release of methane due to dissociation of gas-hydrates might impact the climate

significantly. Again, destabilization of gas-hydrates may reduce the sediment strength leading to the slope failure or sub-marine landslides (Maslin *et al.*, 2010; Ramprasad *et al.*, 2011; Gupta and Sain, 2012). Gas-hydrates may inhibit normal sedimentation and compaction, and underlying freegas may produce excess pore pressure causing drilling hazards. This overpressure in free-gas zone below the hydrate-bearing sediment can be detected by analyzing the P-P and P-S AVO responses (Dash *et al.*, 2004). This study is pre-requisite to avoid any drilling hazard.

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