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New Technique Detects Gas Hydrates

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CHAPEL HILL, N.C.–As exploration and development moves into deeper waters, the possibility of encountering gas hydrates within seafloor sediments becomes increasingly likely. The ability to accurately detect gas hydrates is key to producing deepwater fields, allowing operators to safely design and place offshore drilling and production platforms, subsea production equipment and flow lines, as well as pipelines.

To this end, a new geochemical technique has been developed that detects conditions conducive to gas hydrate formation using sediment pore water sulfate gradients as a potential indicator of gas hydrate presence in deepwater sediments.

To minimize engineering problems and risks to production infrastructure, operators attempt to avoid areas with significant occurrences of methane at the seafloor or in the shallow subsurface. Because seismic is very sensitive to gas bubbles, high-frequency seismic surveys are effective tools for seafloor hazard detection when methane is in the gaseous phase. For instance, amplitude anomalies or "bright spots" occur when free gas reaches a few percent of sediment pore space. Using seismic, the industry has been extremely successful in avoiding gas hazards on the Outer Continental Shelf and slope.

The deep Gulf of Mexico presents a new challenge, however. Because methane typically exists as dissolved methane and hydrates rather than free gas in the shallow subsurface of deeper waters, gas hydrates at or near the seafloor may not be detected by high-frequency seismic reflection surveys. The new geochemical technique detects methane in the hydrate phase, giving it specific application to deepwater environments.

Ice-Like Compounds

Gas hydrates are solid, ice-like compounds composed of methane and water. Water molecules, stabilized by hydrogen bonds, form a cage-like lattice structure enclosing a methane molecule. These "guest" molecules may also include carbon dioxide (CO_2), hydrogen sulfide (H_2S), noble gases, or higher hydrocarbons (ethane, propane, isobutane, n-butane and neopentane), but methane gas hydrates are most common, and higher hydrocarbon occurrences are almost always associated with methane.

Methane hydrates form at low temperature, high pressure, and adequate methane concentration–conditions common to the deepwater and the continental margins. Hydrates can form within sediments as shallow as 400 feet below the surface in arctic regions because of the low temperatures. Under more typical thermal conditions, however, methane hydrates are restricted to marine sediments beneath at least 1,500 feet of water. Deepwater activity already occurs in settings where gas hydrates are stable, and encountering substantial amounts of hydrates at the seafloor and within the upper sedimentary environment will become more common as the industry moves farther off the OCS.

Gas hydrates have the potential to cause a number of engineering and production problems, including:

- Sediment instability;
- Corrosion and dissolution of materials;
- Seabed erosion; and
- Formation of seafloor biological communities that subsist on methane.

These problems may not arise immediately, but take years to develop as fluid flow from the producing formation warms the surrounding sediments, heating ambient gas hydrates and causing their breakdown. The decomposition of gas hydrates affects physical, chemical and biological aspects of the production environment.

Shifting Sediment

Gas hydrates can yield significant amounts of methane and water (methane hydrates contain up to 164 times more methane than an equivalent volume of gaseous methane at standard temperature and pressure). By altering in situ temperature and pressure conditions on the seafloor or within sediments, production operations can cause hydrates to decompose, releasing methane and water into sediment pore spaces. This water and additional methane cause the sediment to become unstable and decreases its strength, resulting in problems analogous to those experienced in permafrost areas. Any seafloor structures located on the sediment may founder or shift.

Examples are shown in Figures 1 and 2. A pipeline is buried in deepwater sediments containing gas hydrates in Figure 1A. Over time, heat from hydrocarbons flowing in the pipeline warms the surrounding sediment, changing ambient temperature conditions (Figure 1B). The heating causes gas hydrates to dissociate, releasing methane and water into the pore spaces of the sediment and causing sediment instability and slumping on the seaof

FIGURE 1

Gas Hydrate Dissociation Causing Sediment Instability

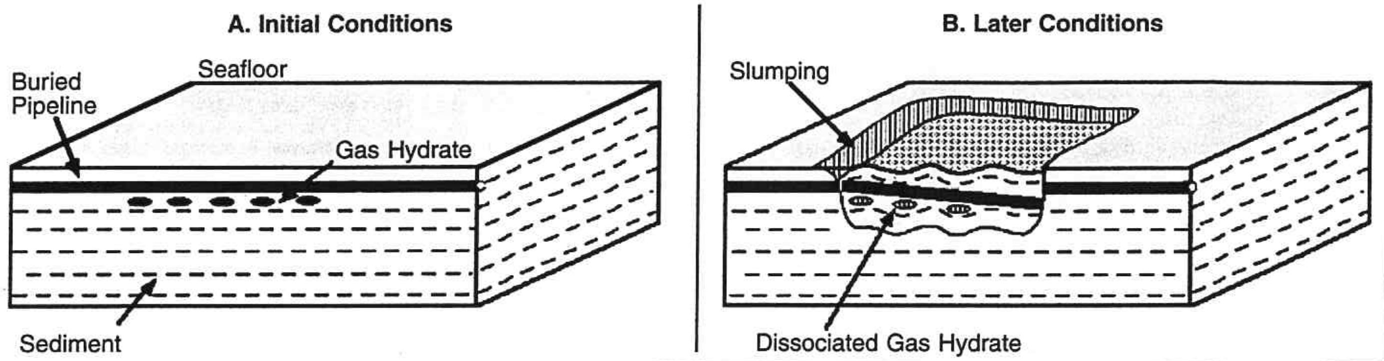

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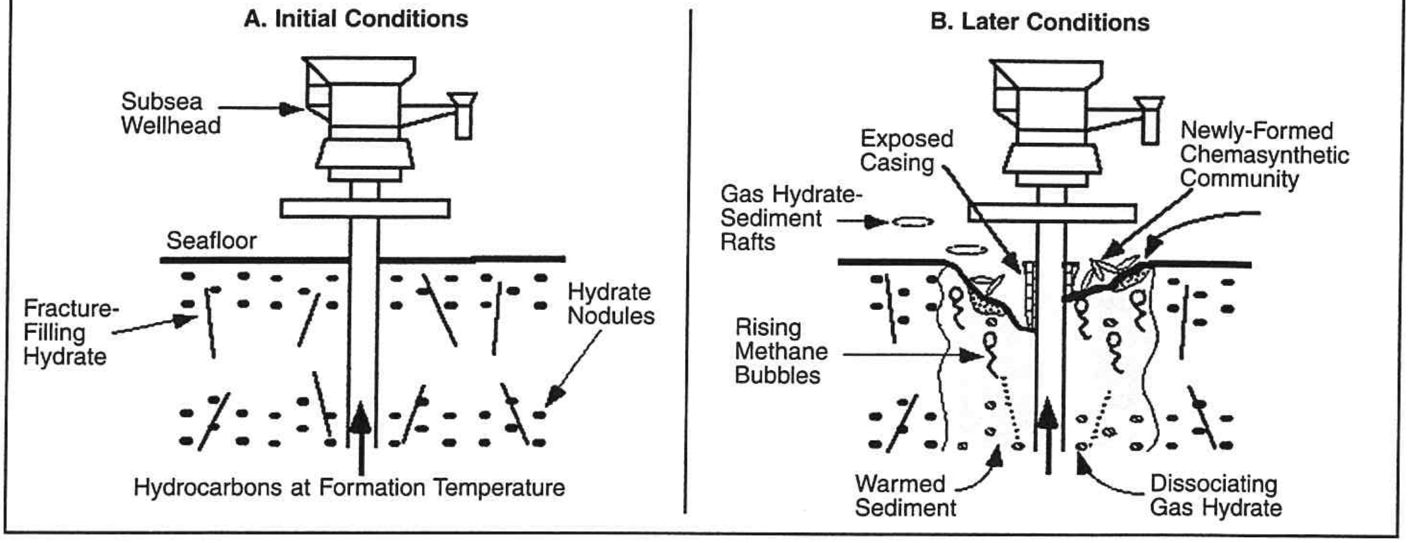
FIGURE 2

Effects of Decomposing Gas Hydrate on Subsea Production



floor. The line ruptures when the sediment founders and shifts.

In Figure 2A, a subsea wellhead produces hydrocarbons from a subsurface reservoir. Produced hydrocarbons (Figure 2B) from warmer formations below cause the slow heating of sediments surrounding the well bore. Any gas hydrates within the sediment break down and release methane and water. Methane then moves up toward the seafloor, creating a new methane source and reforming as gas hydrates.

If the sediment pore waters contain sulfate, hydrogen sulfide will form as methane is released into the sediment and oxidized. The H_2S, of course, can corrode metal infrastructure, and perhaps dissolve casing cement within the sediments.

Once released from the shallow subsurface, methane percolates upward to reform as hydrates at the seafloor. Be cause they have lower density than seawater, gas hydrates have the potential to lift sediment off the bottom and eventually create seafloor excavations or pockmarks near subsea production equipment, exposing additional infrastructure (and casing) to the corrosive action of H_2S-charged waters.

Finally, methane from dissociating hydrates may move upward to the seafloor to stimulate the formation of chemosynthetic communities where there was no prior seepage or biologic activity. These organisms can foul subsea equipment or cause litigious actions because they are protected faunas.

Pore Water Sulfate

Seawater is effectively an infinite reservoir for sulfate, a dissolved ion that is also present in marine pore waters. Within sediment, pore water sulfate is involved in two chemical reactions induced by microbial activity. These biochemical processes deplete sulfate within the pore water, so that sulfate concentration generally decreases with increasing sediment depth.

In the first process, sulfate is used as an oxidant by interstitial microbes to break down sedimentary organic matter (termed sulfate reduction). The second reaction involving sulfate occurs at the interface where significant concentrations of sulfate and methane co-exist (called the sulfate-methane interface). Here, sulfate and methane are linked to one another in a process called anaerobic methane oxidation (AMO), where both sulfate and methane are consumed. This relationship between sulfate and methane increases in importance as the amount of methane moving up from below the sulfate-methane interface increases and alters the overlying sulfate gradients.

If the inventory of methane below (and its upward movement to the interface) is sufficient, sulfate depletion within sediment pore waters will become increasingly dependent on the consumption of sulfate at the sulfate-methane interface. Movement of methane toward the interface can occur by molecular diffusion, movement of fluids that carry methane, buoyant migration of methane in the gaseous phase, or any combination thereof.

True methane gradients have almost never been measured in deepwater marine sediments. Methane is relatively insoluble in water compared to other geologically common gases such as H_2S or CO_2. Because of its relatively low solubility and the large pressure differential between sea level and in situ sediment conditions of deepwater environments, methane tends to bubble out of solution from pore fluids during core recovery. Therefore, most of the original interstitial methane in deepwater sediments is lost (as much as 95 percent). Unless pressure vessels are used to preserve in situ pressure (which is costly and prone to failure), measured methane concentrations and resulting gradients are incorrect and grossly underestimated using conventional approaches.

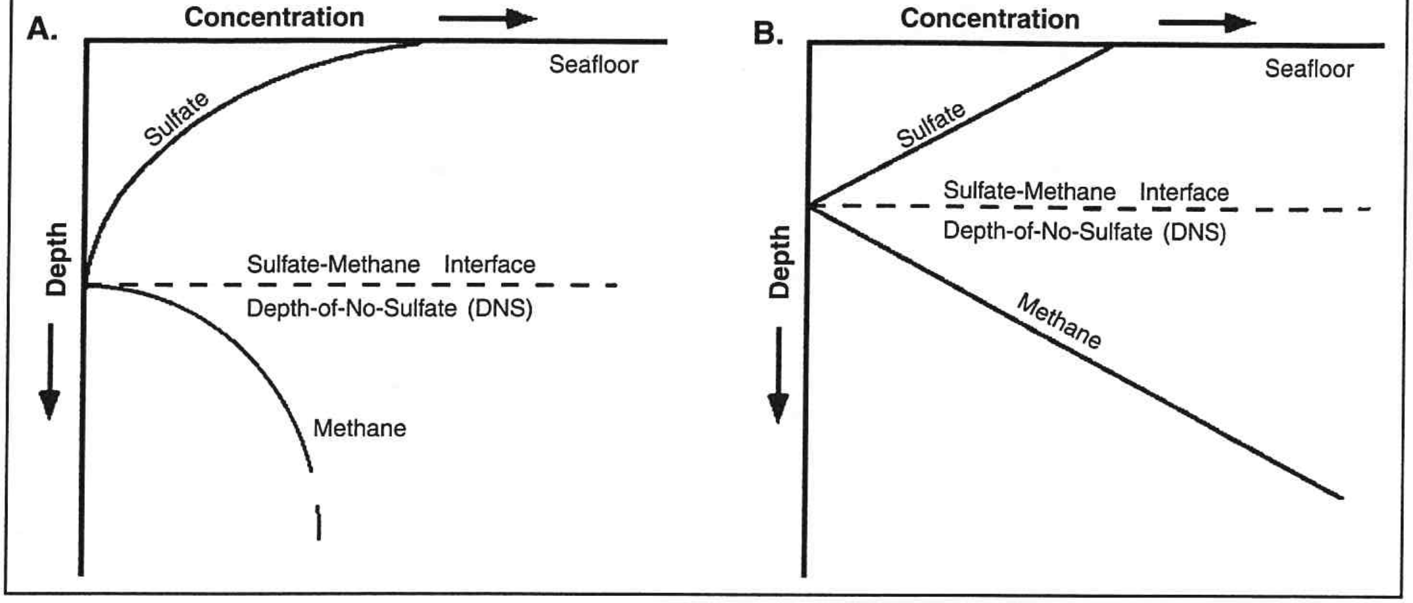
Conditions prone to gas hydrate formation could be recognized by high interstitial methane concentrations, although any direct methane measurements reflect the gas saturation concentration of methane at surface conditions where sediment samples are processed and methane amounts are measured, rather than the actual methane concentration at in situ temperature and pressure.

Geochemical Technique

With the new geochemical technique, methane amounts and the gas hydrate

FIGURE 3

Shapes of Sulfate Profiles under Diffusive Conditions



potential of sediments is monitored by measuring interstitial sulfate concentrations of sediments collected by piston coring. The measurement of interstitial sulfate and the construction of sulfate gradients are not affected by methane loss or sediment retrieval to surface temperature and pressure. Therefore, sulfate concentration gradients are indicators of the amount of methane under formation conditions.

Fresh sediment samples containing pore waters are collected from a surface ship using piston coring as an independent operation or during geotechnical drilling. Core sediments must be sampled and geochemically analyzed immediately after collection. The cores are sectioned at regular intervals, and sediment is placed within "squeezers" to extract pore waters. The concentration of pertinent chemical species within the pore waters is measured at sea using various techniques (ion chromatography, gas chromatography, and spectrophotometry). These data are used to construct pore water concentration gradients.

The shape of the sulfate profiles indicates the relative importance of sulfate and methane co-consumption (Figure 3). Under dominantly diffusive conditions where the supply of methane is low, sulfate profiles will exhibit concave-down curvature (Figure 3A), because the reaction between sulfate and methane is a relatively unimportant process in depleting sulfate. Conversely, when methane supplies are higher, sulfate gradients become linear (Figure 3B), because sulfate depletion is primarily driven by methane consumption at the sulfate-methane interface. Under the conditions that exist in many continental rises, lateral variations in sulfate gradients are direct indicators of differing amounts of methane below the sulfate-methane interface (Figure 4).

Figure 3 shows differences in the shapes of sulfate profiles under diffusive conditions when sulfate and methane co-consumption is relatively unimportant (A), and when sulfate and methane co-consumption at the sulfate-methane interface controls sulfate depletion(B). Note the concave-down curvature of the sulfate profile in (A) and the linear profile in (B).

Figure 4 shows how upward methane flux controls sulfate profiles and the

FIGURE 4

Sulfate Profiles and DNS

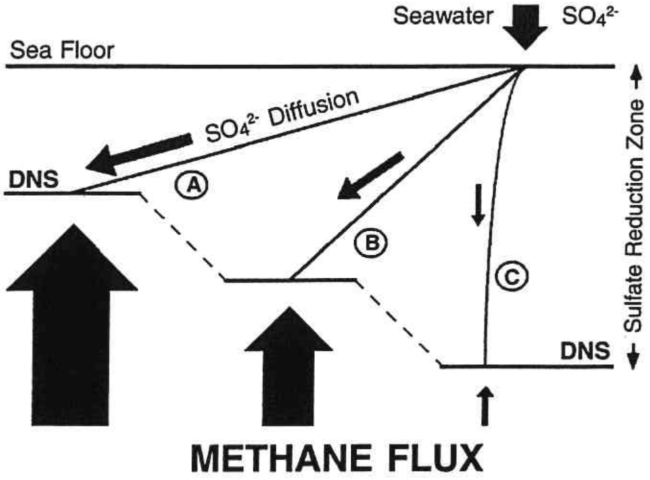
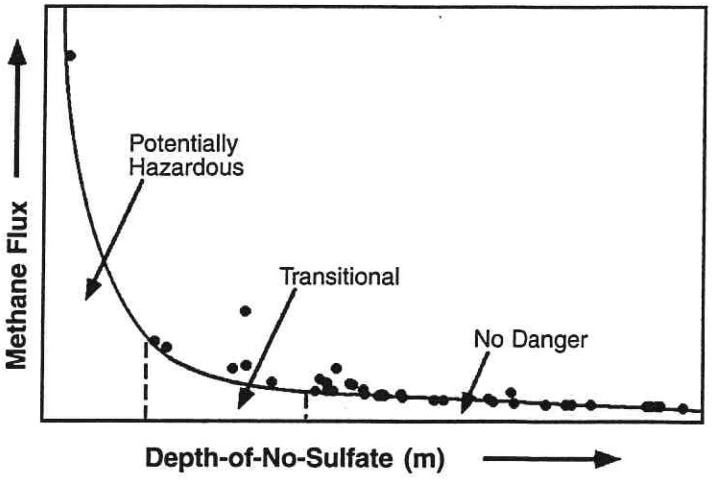


FIGURE 5

Upward Methane Flux and DNS



depth-of-no-sulfate (DNS). Arrow size is proportional to upward methane flux. Typical sulfate profiles display convex-up curvature (A), reflecting sulfate reduction of in situ organic sedimentary matter. Linear sulfate profiles (B and C) result when focused sulfate consumption, driven by methane flux from below, occurs at the DNS at rates substantially greater than those for sulfate reduction of in situ sedimentary organic matter.

In these cases, sulfate diffuses into the sediments from overlying seawater and is consumed by reaction with methane at the base of the sulfate reduction zone. The rate of sulfate consumption and the steepness of the sulfate gradients are controlled by the flux of methane from below.

Potentially Hazardous

The DNS occurs where sulfate concentration approaches zero and marks the boundary between microbial reactions involving sulfate above, and microbial reactions producing methane below. The DNS becomes shallower as the upward methane flux, and concomitant sulfate and methane consumption increases at the sulfate-methane boundary. Therefore, a relatively shallow DNS reveals enhanced vertical methane flux (movement of a substance quantified in the units of amount per unit area per unit time) and indicates more methane at depth. Increased methane flux and a shoaling DNS indicate potentially hazardous conditions due either to the presence of methane gas or gas hydrates.

Figure 5 shows the relationship between upward methane flux and the DNS. Methane flux is estimated from the sulfate flux, which is calculated from measured sulfate gradients and from pertinent sediment properties (porosity and tortuosity). Sites with a shallow DNS are indicative of high methane fluxes and an environment prone to substantial gas hydrate formation–those sites that are potentially hazardous to deepwater production operations. Conversely, sites with a deep DNS are indicative of low methane flux and predict less danger.

Enhanced methane flux and a shoaling DNS over methane-charged sediments indicate the potential occurrence of gas hydrates, and an environment potentially hazardous for deployment of seafloor structures and anchor points. Potential gas hydrate hazards can be ranked according to sediment gas content as estimated by DNS in two ways:

- By estimating the amount of pore-water methane from linear sulfate gradients; and
- By identifying or computing the depth-of-no-sulfate (DNS) from interstitial sulfate concentration profiles.

The first approach permits quantitative comparisons of methane amounts if diffusive conditions dominate. The second approach is applicable under conditions of both diffusion and upward flow, and provides a relative comparison of underlying methane amounts predicted by sulfate gradients. Put simply, the shallower the DNS, the larger the relative upward movement of methane, the larger the underlying methane reservoir, and the more likely that gas hydrates are present.

By identifying the potential for gas hydrate deposits within shallow sub-bottom sediments, this geochemical technique has the potential to reduce risk to drilling and production facilities in the deep water. ❐

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