Review

Mechanisms for Overpressure Development in Marine Sediments

Chong Li 1, Linsen Zhan 1,2 and Hailong Lu 1,*

1 Beijing International Center for Gas Hydrate, School of Earth and Space Sciences, Peking University, Beijing 100871, China; lichong189@pku.edu.cn (C.L.); zhanlinsen@pku.edu.cn (L.Z.)
2 College of Engineering, Peking University, Beijing 100871, China
* Correspondence: hlu@pku.edu.cn

Abstract: Overpressure is widely developed in marine sediments; it is not only a critical factor related to hydrocarbon accumulation, but also a serious safety issue for oil/gas exploration and exploitation. Although the mechanisms for overpressure development in sedimentary basins have been intensively studied, some new mechanisms are proposed for overpressure development with the advancements in marine geological investigation, e.g., natural gas hydrate formation and microbial activity. In this study, the mechanisms for overpressure development are reviewed and further classified as being related to associated physical, chemical, and biological processes. The physical overpressure mechanisms include disequilibrium compaction, hydrate formation sealing, degasification, buoyancy, hydrothermal pressuring, tectonic movement, overpressure transfer, etc. The chemical overpressure mechanisms are ascribed to hydrate decomposition, diagenesis, hydrocarbon generation, etc. The biological overpressure mechanisms are mainly induced by microbial gas production and microbial plugging. In gas hydrate-bearing sediments, overpressure is a critical factor affecting the formation and distribution of gas hydrate. The mechanisms for overpressure development in marine gas hydrate systems are associated with permeability deterioration due to hydrate formation and free gas accumulation below bottom-simulating reflectors (BSR). In marine sediments, overpressure developments are generally related to a sediment layer of low permeability above and natural gas accumulation below, and overpressure is mainly developed below a sulphate–methane interface (SMI), because methane will be consumed by anaerobic oxidation above SMI.

Keywords: overpressure; disequilibrium compaction; hydrocarbon generation; natural gas hydrate; microbial activity

1. Background

Marine sediments refer to the deposits of insoluble materials from various sources that accumulate on the seafloor [1]. Based on their origins, the components of marine sediments are classified as lithogenous, biogenous, hydrogenous, and cosmogenous [2]. The lithogenous sediments originate from the weathering of land materials, volcanic eruptions and blown dusts, and their major components are quartz sands, muds and clays. Silica and calcium carbonate are the most common chemical compounds in biogenous sediments, which are formed by marine organisms such as corals, mollusks, foraminifera, etc. The hydrogenous sediments are produced by the chemical reactions and precipitation in supersaturated seawater. The cosmogenous sediments refer specifically to micrometeorites from outside the earth, and form a rare component of marine sediments [1]. Roughly 90 percent by volume of marine sediments are deposited near continents, covering approximately 25 percent of the seafloor, and the remaining 75 percent of the deep seafloor is covered by slowly accumulated pelagic sediments [1].

Diagenesis refers to all processes, chiefly chemical, by which changes in a sediment are brought about after its deposition, but before its final lithification (conversion to rock) [3].
Considering the alterations of both inorganic and organic materials, the process of diagenesis can be divided into three main phases: the pre-burial stage, shallow-burial stage and deep-burial stage [4]. During the pre-burial stage, the physicochemical processes take place in the surficial layer of sediments in the presence of oxygen [4]. However, this is negligible for the development of overpressure in sediments. In the shallow-burial stage, after deposition, the sediments are subjected to the influence of physical, chemical and biological processes. Above the sulfate–methane interface (SMI), chemical reactions play a dominant role. Oxidants such as $O_2$, $NO_3^-$, $SO_4^{2-}$ and certain amounts of $Fe^{3+}$ and $Mn^{4+}$ are reduced by hydrocarbons in the sediments and methane migrating from the deep. At the same time, authigenic minerals such as carbonate and iron sulfide are formed. When the pore water is saturated with methane and other natural gases under the thermobaric conditions of the gas hydrate stability zone (GHSZ), gas hydrate will be formed. With the formation of natural gas hydrate, the porosity of hydrate-bearing sediments decreases [5]. In the deep-burial stage, the pore space of the sediments is further compressed. However, there is not much room for porosity reduction, because most of the pore space is compressed in the shallow burial stage. With the increases in burial depth and temperature, the organic matter in the sediments gradually matures and generates oil and gas. Gypsum, montmorillonite and other minerals will dehydrate in a certain temperature range, increasing the water content in sediments. On the other side, the cementation of authigenic carbonate and silica will reduce permeability. These processes have the potential to result in overpressure development in marine sediments. When the temperature exceeds 200 °C, it is considered to be in the metamorphic stage.

Pressure is an important physical property in sedimentary layers and mainly involves overburden pressure, pore pressure, and effective stress (Figure 1).

The overburden pressure (lithostatic pressure), $S$, is generated by the total weight of sediment matrix and pore fluid overlying a certain portion in sediments. Generally, the overburden pressure increases with depth.

$$S = g \int_0^z \rho_b(z) dz$$

(1)

where $g$, $\rho_b$, and $z$ are the acceleration of gravity, bulk density, and depth, respectively.

Pore pressure (formation pressure), $P$, refers to the pressure exerted on the fluid at certain points in sediment pores. The difference between overburden pressure and pore pressure is known as the differential pressure, represented by $\Delta P$, i.e., $\Delta P = S - P$.

The effective stress, $\sigma$, refers to the pressure acting on the solid sediment frame skeleton. The effective stress is equal to the difference between the overburden pressure and pore pressure, based on Terzaghi and Biot’s effective stress principle [6,7]. The modified effective stress principle is that the effective stress is equal to the difference between the overburden pressure and equivalent pore pressure [7]. The equivalent pore pressure equals the product of pore pressure and effective stress coefficient. Therefore, the effective stress can be expressed as:

$$\sigma = S - \alpha P$$

(2)

where $P$ is the pore pressure; $S$ the overburden pressure; $\sigma$ the vertical effective stress; and $\alpha$ the Biot effective stress coefficient, ranging from 0 to 1.

Hydrostatic pressure (normal pressure), $P_h$, is generated by the weight of the fluid in the sediment.

$$P_h = \rho_f gh$$

(3)

where $\rho_f$, $g$ and $h$ are fluid density, acceleration of gravity, and the height of the fluid column, respectively.

Overpressure means that the pore pressure is greater than the hydrostatic pressure in sediments. The overpressure represents the difference between the pore pressure and
hydrostatic pressure. In the overpressure system, the effective stress coefficient, $\alpha$, is usually set to 1. Therefore, effective stress is equal to differential pressure:

$$\sigma = S - P$$  \hspace{1cm} (4)$$

Figure 1. Pressure–depth profile in marine sediments (modified from Dutta [8]).

Sediment overpressure is found to significantly affect hydrocarbon accumulation and well drilling. Knowledge of the mechanism for overpressure development is required for pressure prediction and is critical for the understanding of hydrocarbon accumulation. It is generally believed that disequilibrium compaction (also known as under compaction) is the main cause of sediment overpressure. However, more studies suggest that the development of sediment overpressure is often the result of the interaction of several factors [9–11]. Regarding the mechanism of overpressure development in sediments, quite some studies have been carried out [8,12–15]. However, previous studies are mainly on terrestrial sedimentary basins. Marine sediments are deposited and compacted under water-saturated conditions, thus sediment pores are always hydraulically connected. The authigenic minerals (including natural gas hydrate) formed in the marine sediments are different from those in a terrestrial sedimentary basin. As a result, the mechanisms for overpressure development should be different between marine and terrestrial sedimentary basins.

Overpressure is widely developed in marine sedimentary basins [16,17]; it is not only closely related to the formation and distribution of marine oil and gas reservoirs, but is also considered to be an impetus of submarine geological hazards [18,19]. Evidence indicates that it has caused many risks and challenges to offshore drilling safety [20–23]. As an important type of marine resource [24–26], the formation and decomposition of natural gas hydrate have a significant impact on pore pressure [27,28]. For instance, in a gas hydrate occurrence area, when the temperature increases or the pressure decreases, natural gas hydrate will dissociate [29], resulting in fluid volume expansion and generation of overpressure in sediment pores [28]. In gas hydrate exploitation, the overpressure caused by hydrate decomposition will increase the risk and difficulty of drilling in hydrate reservoirs. Although natural gas hydrate is attracting more interest, the effect of gas hydrate on overpressure development has not been well discussed. Recently microbial activities have also been recognized as a possible factor for overpressure in marine sedimentary layers, but such a mechanism has not been investigated in the context of overpressure.

In this review, the mechanisms of overpressure development in marine sediments are systematically summarized, including those associated with natural gas hydrate and microbes.
2. Classification of the Mechanisms for Overpressure Development in Marine Sediments

The mechanisms for overpressure developed in sedimentary basins are commonly classified into disequilibrium compaction, tectonic movement, buoyancy, overpressure transfer, hydrothermal pressuring, hydraulic head, hydrocarbon generation, and diagene-
sis [9,12,30]. However, marine sediments are water-saturated, and the sediment pores are

generally hydraulically connected in the longitudinal direction. As a result, overpressure
caused by the difference in the height of hydraulic heads between the datum plane (ground
surface or water level) and the recharge area of a sealed caprock, which is common in
terrestrial basins, will not be found in marine sediments. Although osmosis is proven
to be able to induce overpressure development in shales, it is not yet reported in marine
sediments. In addition, the existence of gas hydrate and microbes are the mechanisms for
overpressure in marine sediments, which are not found in terrestrial sedimentary basins.

In this review, the mechanisms for overpressure development in marine sediments
are divided into physical, chemical, and biological overpressure (Table 1), each of which is
briefly discussed in the following sections.

Table 1. The mechanisms for overpressure development in marine sediments.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Mechanism</th>
<th>Intrinsic Driving Force</th>
<th>Cases Reported</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overpressure development</td>
<td>Disequilibrium compaction</td>
<td>Deposition rate greater than drainage rate in compaction</td>
<td>Gulf of Mexico; Baram province, Brunei; South China Sea; Nile Delta; Offshore Mumbai, Western India</td>
<td>[8,9,13,16,31,32]</td>
</tr>
<tr>
<td>Overpressure development</td>
<td>Hydrate formation sealing</td>
<td>Permeability reduction</td>
<td>Mahanadi basin, India; Krishna-Godavari basin, India</td>
<td>[5,27,33,34]</td>
</tr>
<tr>
<td>Overpressure development</td>
<td>Degasification</td>
<td>Gas solubility change</td>
<td>Central diapir zone of the Yinggehai basin</td>
<td>[35,36]</td>
</tr>
<tr>
<td>Overpressure development</td>
<td>Buoyancy</td>
<td>Density difference between fluids</td>
<td>Dabis oilfield in the Malay basin</td>
<td>[37–39]</td>
</tr>
<tr>
<td>Overpressure development</td>
<td>Hydrothermal pressuring</td>
<td>Difference in thermal expansion coefficients of fluids</td>
<td>Gulf Coast</td>
<td>[40–42]</td>
</tr>
<tr>
<td>Overpressure development</td>
<td>Tectonic movement</td>
<td>Stress related permeability reduction</td>
<td>Barbados accretionary prism</td>
<td>[43–45]</td>
</tr>
<tr>
<td>Overpressure development</td>
<td>Overpressure transfer</td>
<td>Overpressured fluid migration due to permeability difference</td>
<td>New Jersey continental slope; Yinggehai basin; Baram province, Brunei</td>
<td>[9,19,46,47]</td>
</tr>
<tr>
<td>Overpressure development</td>
<td>Hydrate decomposition</td>
<td>Fluid volume expansion by gas released from hydrate dissociation</td>
<td>Nankai Trough; Hikurangi margin; Shenhui in the northern South China Sea</td>
<td>[28,29,48–50]</td>
</tr>
<tr>
<td>Overpressure development</td>
<td>Diagenesis</td>
<td>Fluid volume expansion or permeability reduction by authigenic mineral formation</td>
<td>Gulf Coast; Halten Terrace offshore mid-Norway and the Gulf of Mexico</td>
<td>[13,51–53]</td>
</tr>
<tr>
<td>Overpressure development</td>
<td>Hydrocarbon generation</td>
<td>Fluid volume expansion by oil/gas generation</td>
<td>Gulf Coast; Amazon Fan; Krishna-Godavari basin, India</td>
<td>[13,54–57]</td>
</tr>
<tr>
<td>Overpressure development</td>
<td>Microbial gas production</td>
<td>Generation of biogenic gas</td>
<td>Offshore Nile Delta, Egypt; Shenhui area in the northern South China Sea</td>
<td>[58–61]</td>
</tr>
<tr>
<td>Overpressure development</td>
<td>Microbial plugging</td>
<td>Permeability reduction</td>
<td>Shenhui area in the northern South China Sea Nankai Trough</td>
<td>[62,63]</td>
</tr>
</tbody>
</table>

3. Overpressure Development Associated with Physical Processes

Overpressure development associated with physical processes refers to that caused by
mechanical processes and/or differences in physical properties between sediments and
pore fluids, while no new chemical product will be formed. Several physical processes can result in overpressure in marine sedimentary environments, such as disequilibrium compaction, tectonic movement, buoyancy, overpressure transfer, hydrothermal pressuring, etc. In addition, degasification from water can also cause abnormal pressure and form overpressured gas reservoirs. The formation of gas hydrate will cause the permeability to be reduced due to the occupation of gas hydrate in sediment pores, leading overpressure from gas accumulation below the hydrate layer.

3.1. Disequilibrium Compaction

Disequilibrium compaction, also known as under compaction, is generally developed in low-permeability sediment, where the deposition rate is greater than the gravity dehydration. Due to the low permeability of sediment and lower compaction rate than the overlying sediment, the pore fluid will be trapped in the sediment. Disequilibrium compaction also occurs when sediments with different particle sizes are interbedded, for example in turbidites. In such cases, the pore fluid will sustain the partial weight of overlying sediments and fluids, and the pore pressure is then greater than hydrostatic pressure, resulting in overpressure [8] (Figure 2). Overpressure caused by disequilibrium compaction mainly occurs in the shallow-burial diagenetic stage.

![Figure 2. Schematic diagram for overpressure development associated with disequilibrium compaction.](image)

The development of overpressure in many sedimentary basins is related to disequilibrium compaction [64]. For example, about 75% of the overpressure in the Pleistocene basin along the Gulf of Mexico originates from disequilibrium compaction [16]. The overpressures of 54 areas in the Brunei Baram basin are mainly caused by the disequilibrium compaction in the prodelta shales, and for the rest the overpressure is transferred by fluid expansion which is developed in the delta sequence on the continental shelf [9]. The gradient of the pore overpressure up to 12 MPa/km is caused by disequilibrium compaction in the sediments of about 240–370 mbsf (meters below the seafloor) at Site 1144 in the north of the South China Sea [31]. Based on the one-dimensional mathematical model of Mann and Mackenzie [65], the fitting results of the actual pressure data show that the pressure due to under compaction is with a similar gradient to the overburden pressure observed in the Nile Delta [14]. Likewise, the prevalent disequilibrium compaction directly led to overpressure with a near-lithostatic gradient (22 MPa/km) in the underlying Paleocene shales in western India [32].

Before the mid-1990s, disequilibrium compaction had been considered the dominant factor for overpressure in many sedimentary basins. However, other mechanisms for overpressure development have attracted more attention in recent years [13].

3.2. Hydrate Formation Sealing

The gas trapped in gas hydrate is usually of biogenic or thermogenic origin [66–69]. Water and gas molecules can form gas hydrate in a certain range of temperatures and pressures after the gas migrates upward through sediment pores or fractures to the gas
hydrate stability zone (GHSZ) [70]. Pore pressure should be increased because the density of methane hydrate (~0.93 g/cm$^3$) is less than water. However, generally, hydrate formation does not increase pore pressure significantly, because the formation rate of natural gas hydrate is very low due to limited CH$_4$ availability. With the growth of gas hydrate, sediment permeability will be decreased by hydrate occupation of pore space. Experimental and numerical studies on methane or carbon dioxide hydrate [5,27,71–74] suggest that the permeability of the sediment decreases with increasing hydrate saturation. Konno et al. [75] found that the absolute permeability of clay-rich sediments and silty sediments without gas hydrate are in the tens mD, and the absolute permeability of sandy sediments in the methane hydrate reservoir can reach 1.5 D in the eastern Nankai Trough, Japan. Further study shows that in the gas hydrate-bearing layer of sandy sediments, the effective permeability of water is only 47 mD when the hydrate saturation is 70%, while the absolute permeability is about 840 mD after hydrate decomposition [75]. As a result, the formation of gas hydrate will significantly decrease permeability and hinder the upward migration of fluid [76]. When the permeability of the gas hydrate-bearing layer is too low for free gas to pass through, the gas from deep strata will be sealed by the less permeable hydrate-containing sediments, below which gas accumulates to develop overpressure.

The large difference in wave impedance between the gas hydrate-bearing layer and the underlying gas-bearing layer often generates a strong reflection called BSR (bottom-simulating reflector) on the seismic profile. BSR is approximately parallel to the seafloor reflection and has opposite polarity [77–79]. As the result, BSR is usually regarded as the bottom of the gas hydrate stability zone. The deepest BSR found to date is about 500 mbsf in Black Ridge. In the sediments with hydrate occurrence, overpressure usually develops below BSR, associated with free gas accumulation. However, when a layer of mixed hydrate and free gas appears beneath a gas hydrate-bearing layer, overpressure can also develop. Overpressure under BSR is caused by hydrate formations [33,34].

3.3. Degasification

Gas solubility refers to the volume of gas dissolved in one volume of water at a certain temperature and standard atmospheric pressure (101 kPa). In sediments, CH$_4$, H$_2$S, CO$_2$, and other gases are more or less dissolved in water. The gas solubility is affected by the combined effects of temperature, pressure, and salinity. Methane solubility generally decreases first and then increases with the temperature, increases at higher pressure, and decreases at higher salinity [35,80]. Wang et al. [81] found that methane solubility actually increases first and then decreases with increases in salinity. However, methane solubility at liquid–hydrate equilibrium in the gas hydrate occurrence area shows a monotonically increasing trend with temperature and pressure [68,82–85]. Assuming that the seawater depth is 2 km, the seafloor temperature is 3 °C and the geothermal gradient is 30 °C/km, Figure 3 depicts the changing trend of methane solubility in marine sediments [35,83]. The pressure in the liquid phase is equal to the hydrostatic pressure (10 MPa/km). The black dashed lines represent the base of the methane hydrate layer in marine sediments. The purple, red and blue lines represent methane solubility in pure water, seawater with 3.5 wt% NaCl and seawater with 7.0 wt% NaCl respectively. In marine sediments, when the temperature is above 20 °C, methane solubility changes insignificantly with pressure, and even decreases slightly with pressure/depth increases (Figure 3). When the temperature is below 20 °C, methane solubility decreases significantly with the decrease in temperature and burial depth. As a result, the methane dissolved in the fluid migrating upward will be partly exsolved, and overpressure will be developed when it encounters a low permeability cap, such as a hydrate-containing sediment layer.
Figure 3. Trend of methane solubility in seawater with temperature and water depth (modified from Duan et al. [35] and Rui and Duan [83]).

“Aqueous phase exsolution type” in the isolated overpressure system is a gas accumulation model in the central diapir zone in the Yinggehai Basin [36]. Degasification may release a great amount of gas. However, the relationship between gas dissolution and overpressure generation seems to be two-way, rather than just promotion. Degasification will increase the amount of free gas, expand the fluid volume, increase the pore pressure, and result in overpressure in reservoir pores. In turn, overpressure will enhance gas solubility and reduce the rate of degasification. Although their relationship is complex, degasification can cause local overpressure. The contribution of degasification to basin overpressure needs to be further studied and understood.

3.4. Buoyancy

Buoyancy, due to the difference in the density of fluids in sediment pores, has the potential to cause overpressure. The buoyancy phenomenon is common in oil–water, gas–water, or oil–gas–water reservoirs. Buoyancy will occur when the water is replaced by hydrocarbons in sediment pores, because the density of oil or gas is less than that of water, leading to the development of pore pressure. The main factors associated with overpressure are the density difference between pore water and oil (or gas), and the positions of oil and gas in sediment column [14,37,38]. In gas hydrate-bearing sediment, buoyancy can also cause overpressure in the free gas layer below the low-permeability hydrate layer, as the gas density is much less than the density of pore water in sediment layers (Figure 4).

Sahagian and Proussevitch [86] suggested that the buoyancy effect of gas bubbles will transport the hydrostatic pressure upward from the lower portion to the top in a reservoir via incompressible fluid (e.g., water), resulting in the increase in pressure. However, the effect of the compressibility of the actual fluid, gas content, sediment permeability, gas solubility, and the changing properties of gas with temperature and pressure on sediment pressure need further quantitative studies [14]. Buoyancy occurs in oil and gas reservoirs; however, the overpressure originating from buoyancy varies greatly in different oil and gas reservoirs. This mechanism plays an obvious role in the pressure field in Dabis oilfield in the southeast of the Malay Basin, whereas only insignificant overpressure is generated in some hydrocarbon traps in the North Sea Basin [39]. Overall, overpressure related to buoyancy mainly arises from the difference in density between different fluids (oil, gas, water, etc.), generally occurring in oil/gas reservoirs or under BSR [87].
Figure 4. Schematic diagram to show buoyancy related overpressure development in gas hydrate occurrence area (modified from Zhang [38]).

3.5. Hydrothermal Pressuring

Hydrothermal pressuring was first proposed by Barker [40], based on the overpressure isolations observed on the northern coast of the Gulf of Mexico. The fluid in the sediment will expand when it is heated. Hydrothermal pressuring is produced because the thermal expansion coefficient of pore fluid is greater than that of the sediment matrix. The increasing temperature will lead to the volume expansion of pore fluid when it is buried and isolated, thereby creating overpressure (Figure 5) [8]. The pressure generated by hydrothermal pressuring depends on the burial depth and geothermal gradient [40, 88, 89]. There is no transition zone on the pressure curve since hydrothermal pressuring can only occur in isolation [89].

Figure 5. Schematic diagram for overpressure development by hydrothermal pressuring.

The hydrothermal pressuring mechanism is still a controversial issue. Some scholars believe that it can play an important role for effective closure [88, 90], however, other scholars pointed out that unless it is completely closed, the fluid volume expansion due to hydrothermal expansion is too small to produce significant overpressure [14]. Numerical simulations reveal that the overpressure generated by hydrothermal mechanisms is very small, even in a completely closed system [91]. In addition, this overpressure development requires a rapid temperature rise [89]. In marine sediments, these two conditions are difficult to meet simultaneously. The pore water cannot be completely isolated because of the actual non-zero permeability in the sediment. Hydrothermal pressuring is supposed to play a role in overpressure generation, but it might not be the main mechanism. Overpressure of this type may occur in some special geological conditions, such as upon magma intrusion and thermal fluid arching [39]. Magara [41]’s study on the overpressure along the coast of
Gulf of Mexico shows that, in the overpressure zone, the average increasing rate of pore pressure is about 1.4 psi/ft after isolation, which is apparently higher than the overburden pressure gradient (usually less than 1 psi/ft). Because relative isolation and temperature rises in a system are the prerequisite for the overpressure development on this mechanism, hydrothermal pressurization mainly occurs in the deep-burial stage.

3.6. Tectonic Movement

Tectonic movement will change the transverse and/or longitudinal stress of sediments. For instance, tectonic uplift and subsidence will change the overburden pressure, meanwhile, compression and shear deformation will destroy the structure of original strata, resulting in the rearrangement of rock skeleton stress and abnormal pressure [43,92]. Nevertheless, tectonic stress directly acts on sediment particles rather than the pore fluid. Luo [44] suggested that the tectonic effect on pore pressure can be significant through sediment compaction by reducing sediment pore volume and causing permeability and porosity decreases. When sediments are consolidated to some extent, tectonic movement might create overpressure. In such a condition, tectonic overpressure mainly occurs in deep-burial stage.

Tectonic compression and shear stress can produce strong tectonic overpressure. The pressure peak usually appears at the position deformed most intensely and gradually attenuates away from it (Figure 6). In provinces such as the Orinoco Delta, Venezuela, Trinidad, Sumatra, and California, significant overpressure can be induced by tectonic compression and wrench faults [8]. The quantitative study of tectonic overpressure also reveals that the additional pressure generated by tectonic movement in the lithosphere may have the same order of magnitude as the lithostatic pressure. The abnormally high fluid pressure (>90% of lithostatic pressure), which is calculated from the logging data collected during ODP Leg 156 below the thrusts in the Barbados accretionary prism, is presumably due to the increase in overburden and lateral tectonic loading [45].

![Figure 6. Schematic diagram of tectonic-related overpressure development: (a) compression, (b) shear.](image)

3.7. Overpressure Transfer

The distribution of overpressure is dynamic in sediment sections. The overpressure developed in deep sediments can be transferred to a shallow portion through fluid flow, and it will be redistributed in an isolated and closed reservoir to maintain hydrostatic balance [9]. Overpressure transfer usually involves fluid expansion. Faults and/or inclined sand bodies which are inter-beded with clay-rich sediment may behave as fluid migration channels. Driven by abnormally high pressure, deep overpressure fluid migrates from the lower sediment section and releases at the top of the faults or sand layer due to permeability differences. These activities cause the pore pressure around the channel bottom to be lower than that in the sediments of the overpressure interval at about the same depth. At the top of the fluid migration channel, the opposite is the case [8,12,19]. This process is referred to as the lateral migration of overpressure by Yardley and Swarbrick [93]. Overpressure may also
be transferred vertically through the fractures or faults in the cap layer if one overpressure isolation keeps hydraulic connection with another isolation with lower pressure [10,94,95].

Based on the actual seismic and logging data on the continental slope of New Jersey, Dugan and Flemings [46] created a deposition–compaction model. In the model, the flat and permeable silt strata with permeability of $3 \times 10^{-16} \text{ m}^2$ is overloaded by low-permeability ($1 \times 10^{-18} \text{ m}^2$) silt and clay. The distribution of pressure and fluid fields on the slope profile is simulated after the lateral differential deposition and compaction for 1 Ma. In this process, the excess fluid in the low-permeability formation transfers to the permeable silt layers. The flow model successfully predicts the overpressure observed at Site 1073 at the downdip part of the slope. If the covering layer is thin at the lower part of the slope, the pore pressure will be close to the overburden pressure, and the transfer of pressure may trigger slope failure [19]. The activities of the strong lateral and vertical overpressure fluid in the Yinggehai basin reveal the interaction between the fault system and overpressure transfer. Tensile faults first induce the episodic breakthrough of overpressure fluid, then overpressured fluid flows through the main faults or fractures, and finally the overpressured fluid is released along the transport corridor. In parallel, the overpressure fluid event will open new faults or activate old faults, which will become an incentive for further overpressure fluid breakthroughs [47]. Overpressure in the inner-shelf deltaic sequences in Baram basin in Brunei is transferred from the prodelta shales through faults as well [9]. Diapir/mud volcanoes and gas chimneys are also the main migration channels for the deep overpressured fluid in both Shenhua area in China and offshore Nile Delta in Egypt [49,60,61]. Therefore, the fault system, inclined sandstone, mud diapir, and gas chimneys are all important channels for overpressure transfer [96].

It should be noted that engineering accidents in the drilling process may cause the quality of well cementation to deteriorate, and it will artificially establish hydrodynamic communication between the upper and lower formations that were originally isolated from each other. As a result, such wells can become a special channel for overpressure transfer as well [15]. As long as the condition of isolation is present and the connection between them is established, the transfer of overpressure could occur.

4. Overpressure Development Associated with Chemical Process

Overpressure development associated with chemical processes refers to overpressure that is related to chemical reactions, by which fluid volume expansion and large-scale or local overpressure will result due to the formation of new material in sediment pores. In marine sedimentary basins, chemical reactions including kerogen maturation, oil cracking, smectite dehydration, gypsum dehydration, hydrate decomposition, etc. can lead to fluid expansion. In addition, chemical cementation in diagenetic processes can induce over-pressure because the cementation may reduce sediment permeability. Based on the direct mechanism that results in the development of overpressure, chemical reaction-related overpressures are divided into hydrate decomposition, diageneis and hydrocarbon generation.

4.1. Hydrate Decomposition

Natural gas hydrate usually occurs in the sediments within a certain range of temperatures and pressures. When temperature or pressure changes exceed the stability regime of gas hydrate, the hydrate will decompose to free gas and water. As the released gas and water from hydrate decomposition is sealed by the overlying hydrate-bearing sediment layer with low permeability, overpressure will develop [33].

The water and gas from hydrate decomposition will lead to fluid volume expansion and overpressure [25,97]. Xu [28] found that the overpressure caused by hydrate decomposition in marine sediments can be up to tens of megapascals (MPas) in confined pore spaces. It is estimated that about 164 units volume of methane can be released from the decomposition of one unit volume of gas hydrate under standard conditions [26]. According to the ideal gas equation of state, the decomposition of gas hydrate per unit volume will generate about 2.36, 1.95, 1.52 units volume of gas respectively around the BSRs at the
sites of ODP 204, NGHP expedition 01, and IODP expedition 311. The shallower the burial depth, the larger the volume of released gas and the greater the overpressure development. As a result, hydrate decomposition is an important factor for overpressure development.

Due to the thermodynamic and kinetic principles of natural gas hydrate, hydrate decomposition is most likely to occur in the three-phase zone in which gas hydrate, water and free gas coexist under equilibrium conditions, and the place with such conditions is around BSR \([85,98]\). Tectonic uplift or sea level fall, continuous fast sedimentation, and hydrothermal fluid rise have the potential to induce hydrate decomposition \([28,99]\).

Tectonic uplift or sea level fall will decrease the pressure of the gas hydrate stability zone, and consequently the gas hydrate near BSR will be outside its stable regime and begin to decompose, releasing free gas into the sediment pores. As the less permeable upper hydrate-bearing layer is still in the regime ofhydrate stability, the free gas released will be sealed and overpressure will develop (Figure 7a). The formation and decomposition of gas hydrate are dynamic processes controlled by temperature and pressure. To maintain the dynamic balance, the bottom of the hydrate stability zone will move upward. The three-phase medium, consisting of gas hydrate, free gas, and water, will eventually reach equilibrium in the rebuilt stability zone \([85]\). After reaching the new balance, a new BSR (BSR2) above the original BSR (BSR1) will appear when only part of the hydrate above the old BSR is decomposed, and double BSRs will be observed on the seismic profile \([29,100]\). The magnitude of overpressure generated by tectonic uplift or sea level fall is related to the rate and duration of the movement. However, it should be noted that the overpressure developed by hydrate decomposition is with remarkable impact only in the relatively shallow hydrate stability zone \([28]\).

![Figure 7. Overpressure development associated with hydrate decomposition due to tectonic uplift/Sea level fall, continuous sedimentation, hydrothermal fluid rise (modified from Foucher et al. \([29]\)). T, temperature; P, pressure; SF, seafloor; BSR, bottom-simulating reflector.](image)

The continuous sedimentation will constantly thicken the sediment section and increase the temperature of the hydrate stability zone. With the thickening of the sedimentary layer, the gas hydrate near the BSR moves downward relative to the seafloor. When it reaches the phase equilibrium boundary, the gas hydrate begins to decompose (Figure 7b), so the continuous sedimentation will lead to the upward migration of the bottom of the hydrate zone. The magnitude of the resultant overpressure is related to the sedimentation rate \([28]\). However, if the sedimentation rate is so fast that the gas produced by hydrate decomposition has no time to migrate, a new BSR will not form, and the original BSR may become weakened or even disappear \([99]\).
The thermal effect of the hydrothermal fluid, which is migrated from deep in the basin through faults, mud diapirs, and mud volcanoes, etc., could also cause hydrate decomposition. Site SH5 in the northern South China Sea is a typical case. Although the BSR is clear at site SH5, the drilling results confirm that there is no gas hydrate. That is because the deep hydrothermal fluid invades along the mud diapir and fault channel, increasing the temperature of the hydrate stability zone and leading to the decomposition of the gas hydrate \([49,50]\). However, if the mud diapir does not penetrate the hydrate stability zone and the thermal effect of mud diapir is not strong enough to break the gas hydrate-bearing layer, the thermal effect may only result in the decomposition of gas hydrate near the BSR. Then, a large amount of gas will be released and accumulate at the top of the mud diapir, and overpressure will develop. Meanwhile, the interface between the gas hydrate-bearing layer and the gas-bearing layer will change due to the local decomposition of gas hydrate. When a new equilibrium state is reached, the BSR above the mud diapir may subsequently bend toward the seafloor (Figure 7c).

As discussed above, hydrate decomposition mainly occurs in a mixed layer of mixed hydrate and natural gas and in hydrate-bearing sediments above the BSR.

4.2. Diagenesis

After the deposition and burial of sediments, dissolved oxidants such as \(O_2, NO_3^-, SO_4^{2-}, Fe^{3+}\) and \(Mn^{4+}\) may be present in surficial marine sediments. With the involvement of microbes, these oxidants react with the organic matter and migrating hydrocarbons from the deep [101]. As a result, overpressure does not easily develop in sediments above SMI due to the consumption of methane and other hydrocarbons. Below SMI, dehydration of gypsum or montmorillonite and cementation of calcite or quartz can lead to overpressure development.

The reduction in the porosity of clay-rich sediments during diagenesis may be accompanied by slow chemical changes, such as the transformation of smectite into illite [102]. Smectite or swelling clay has been commonly identified. At 65–120 °C, smectite begins to dehydrate and is transformed to illite by the catalysis of potassium feldspar. The bound water in the interlayer of smectite is released into the pore space, resulting in the increase of pore pressure and the decrease of effective stress [8], so smectite dehydration can cause pore fluid expansion and weaken the sediment skeleton. This process causes the pressure originally borne by the rock skeleton to partially transfer to the pore fluid, and such load transfer induced by illitization will also lead to an increase in pore pressure [103].

Because the transformation of gypsum to anhydrite will decrease its volume by about 39%, it is considered to be a crucial factor for overpressure development in evaporite layers. The reaction is mainly controlled by the temperature and pressure of pore fluid and fluid activities in pores. In the temperature range of 40–60 °C, great overpressure could be generated at depth of about 1.0 km [51]. Since this process usually occurs during shallow burial, it will not be a factor for overpressure in deep sediments [14].

It is suggested that the dissolution and cementation of quartz in sandstone and mudstone can also induce overpressure [52,104–106], because dissolution and cementation can significantly reduce the porosity and permeability of sediments. When the fluid is trapped in sediments due to extremely low permeability, overpressure will be generated. As indicated by carbonate concretions, calcite cementation may take place at the beginning of shallow-burial stage, however, generally during a later period in deep-burial stage [4]. Zhao et al. [13] suggested that quartz cementation could locally affect overpressure generation; however, Wangen [107] pointed out that pore space cementation is the most likely mechanism of overpressure development in deep reservoirs.

Shaw and Primmer [52] took illitization and calcite cementation as having the same importance as disequilibrium compaction for the overpressure development in the Tertiary strata off the coast of Texas. The models on fluid flow and pressure development reveal that diagenesis contributes about 25–80% to the overpressure in the Halten Terrace, offshore mid-Norway, and the Gulf of Mexico [53].
Diagenesis can generate overpressure, and in turn overpressure also affects diagenesis. Overpressure may inhibit pressolution and quartz generation in the late diagenesis process [108], restraining the transformation of clay minerals and carbonate cement [109].

4.3. Hydrocarbon Generation

With increasing burial depth and temperature, hydrocarbons can be generated from organic matter in sediments by either biological or chemical processes. Hydrocarbon generation can be divided into four stages. In the first stage, biochemical gas is generated, being part of the shallow-burial diagenetic stage. In this stage, generally the temperature is 0–80 °C, the depth less than 1500–2000 mbsf, and the Ro (vitrinite reflectance) ≤0.5%. It will be discussed in detail in the section concerning microbial gas production. The second is the thermo-catalytic oil/gas generation stage, in which the temperature is 80–150 °C, the depth greater than 1500–2000 mbsf, and Ro 0.5–1.3%. The third is the thermo-cracking condensate gas generation stage, with a temperature of 150–200 °C, a depth of more than 3500–4000 mbsf and Ro 1.3–2.0%. The fourth is the deep pyrometric gas generation stage, with a temperature of 200–300 °C, a depth of more than 5000–6000 mbsf and Ro > 2.0%, which belongs to the scope of metamorphism [110].

Within the hydrocarbon generation threshold, either maturated kerogen decomposition or hydrocarbon cracking will generate certain amounts of oil and gas, and such extra fluid in sediment pores will cause the expansion of fluid volume and result in overpressure in a closed system [54]. Although overpressure generation related to oil/gas generation is primarily dependent on kerogen type, organic matter abundance, temperature history, and rock permeability [14], thermal effect is the controlling factor. It should be noted that only when the thick sediments contain a large amount of organic matter and the evolution of kerogen has reached the massive oil and gas generation stage will hydrocarbon generation play a role. It means that the overpressure may only occur in mature enough or overmature, organic, rich source rocks [39]. Hydrocarbon generation can continuously generate pressure in the course of sedimentation and burial, mainly in the deep-burial stage. As a result, overpressure can be sustained over a long period, except that the source rocks are greatly lifted to a much shallower location where the condition is not favorable for oil/gas generation [13].

Hydrocarbon generation is considered to be the main mechanism for overpressure development in many basins and has attracted more and more attention. It has been found that, to a certain degree, hydrocarbon generation contributed to overpressure development in the Beihai basin, Gulf of Mexico basin, Mahakam Delta, Niger Delta, Malay basin, and Carnarvon basin in Western Australia [13], and Hunt et al. [55] suggested that gas generation is the main cause of overpressure in the Gulf of Mexico. It was overpressure, induced by hydrocarbon generation, that induced the detachment of Cretaceous rocks in the Amazon sedimentary fan [57]. Logging data in the east of the Krishna-Godavari basin off India reveals that the abnormally high pore pressure might be caused by gas generation [56].

5. Overpressure Development Associated with Biological Activity

Biological overpressure development mainly refers to the involvement of microbiological activities in overpressure generation, including microbial gas production and microbial plugging.

Microbial gas production is essentially similar to hydrocarbon generation in the chemical development of overpressure, which can result in the volume expansion of pore fluid as well. Different from thermogenic gas, the gas produced by biological processes is usually called biogenic gas or biogas. Biogenic gas and thermogenic gas are different in molecular and isotopic composition, the former being predominantly composed of methane with carbon isotope ($\delta^{13}C$) lighter than −60‰ [58] and hydrogen isotope between −158‰ and −368‰ [59]. The heavy hydrocarbons in biogenic gas are generally less than 2%, or else the gas must be mixed with thermogenic gas [58].
The high levels of molecular biopolymer produced or CaCO₃ precipitation induced
by microbes have the potential to block sediment pore space or cement the sediments,
leading to a reduction in sediment permeability and deterioration of pore fluid migra-
tion. These processes will cause microbial plugging and are with the potential to induce
local overpressure.

5.1. Microbial Gas Production

Microbial gas production generally occurs in the shallow-burial stage. Except for
the participation of microbes during gas production, microbial gas production has the
same effect as hydrocarbon generation. In a reductive environment, the organic matter in
the shallow sediments can generate methane-rich gas by microbial activity, and the gas
generated can accumulate to form a biogas reservoir [59]. In rapidly accumulated marine
sediments, microbes commonly employ aerobic respiration in the beginning, and then
sulfate reduction becomes the main form of respiration after the oxygen is consumed. The
generation and accumulation of methane will play a dominant role when the sulfate in
the pore water is exhausted [58,101]. Microbial activities are restricted by the surrounding
conditions, such as the temperature, nutrients, pressure, salinity, and acidity of the water.
Temperature will be the most important factor if sufficient nutrients are given to the
microbes. The suitable temperature is 0–80 °C; outside this range, the microbial activity
decreases sharply or even disappears [59]. Therefore, most biogenic gases occur in shallow
immature sediments with organic matter.

Biogas reservoirs are widely distributed and generally under-pressurized. That is be-
cause biogas reservoirs are usually shallowly buried and the cap sediment layers are poorly
consolidated. Therefore, the gas can easily break through the sediments [59,111]. However,
a few studies reveal that biogas can also contribute to overpressure. Helal et al. [60] sug-
gest that the origin of the gas chimney in the Baltim area is related to the overpressure in
deeper areas. The overpressure was generated by fast burial during the mega deposition
of Post-Messinian succession. The hydrocarbon source of the Post-Messinian succession
is only biogas, although Pre-Messinian oil and gas are thermogenic. Similarly, most of
the methane gases in hydrate-bearing sediments are biogenic in the Shenhu area in the
northern South China Sea [112], while gas chimneys and a large number of small-scale
fault systems provide vertical and lateral migration channels for gas-bearing fluids [61].

In marine sediments, pore spaces are always water-saturated due to the existence
of overlying seawater. The cracks do not develop easily in soft sediments [113], which
are conducive to biogas accumulation. At certain pressures and temperatures, biogenic
methane and water can combine to form natural gas hydrate when pore water is over
saturated by methane [58]. With hydrate formation sealing, microbial gas production could
also result in overpressure in the hydrate stability zone.

5.2. Microbial Plugging

The basis of microbial oil recovery technology is that microbial metabolism can pro-
duce acid (formic acid, propionic acid, sulfuric acid), organic solvent (alcohol, ester, etc.),
biosurfactant (alkanoic acid, lipopeptide, glycolipid, etc.), biopolymers (polymer polysac-
charide), and gas (carbon dioxide, hydrogen, methane, etc.), and such products can dissolve
and emulsify crude oil, reduce oil viscosity, increase pore pressure, and improve crude
oil fluidity [62,114]. The plugging effect of the microbes can be achieved in two ways, by
occupying the pore space of sediments via the growth and reproduction of the microbes on
the surface of the sediment particles, and by producing biopolymers by metabolism to block
the fluid channels. Among them, the biopolymers have a stronger plugging effect [114].

Experimental studies found that microbial plugging can remarkably decrease the
permeability of sediments. The biofilm formed during microbial growth can reduce the
average permeability of the porous media to 12% [115]. Cheng et al. [116] also reported
that microbial growth can reduce permeability by more than 80%, although it may form
a relatively stable plugging only when the sediment is with low permeability (less than
Microbial plugging technology can also help consolidate the soft sediments at the seafloor. Microbes are applied to induce CaCO$_3$ precipitation to cement porous media at high pH and to reduce geological disasters such as submarine landslide and sand production during oil and gas exploitation. Currently, the primary flora studied in the field of biogeotechnics are *Sporosarcina pasteurii* and *Sporosarcina aquimarina* [117,118]. *Sporosarcina pasteurii* is an alkalophilic bacterium with high urease activity isolated from the surface soil, while *Sporosarcina aquimarina* from the estuaries of South Korea is a urease-producing bacterium with high salt tolerance that can survive in seawater. Both of them have the characteristics of producing urease to hydrolyze urea into ammonia and carbon dioxide. Ammonia increases the pH value of the environment, and then induces CaCO$_3$ precipitation [63,119]. Recently, Hata et al. [63] obtained a new urease-producing microbe, *Sporosarcina newyorkensis*, from the pressure cores of the methane hydrate-bearing layer in the Nankai Trough, Japan. The triaxial experimental results demonstrate that this native microorganism can promote CaCO$_3$ precipitation through urea hydrolysis, improving the strength of the seabed sediments, and then benefit the safe production of natural gas hydrate.

According to the experimental results and field application of microbial plugging technology, microbial plugging has great potential in overpressure development in marine environments. The growth and metabolism of some flora in marine sediments may effectively reduce permeability and prevent the migration of pore fluid under certain conditions. Because microbial activity is affected by temperature, salinity, pH, pressure, permeability, and crude oil properties [62,120], the overpressure caused by microbial plugging might only have local impact and probably occurs in the shallow-burial stage. The development conditions, scope, and magnitude of such kinds of overpressure need to be further studied.

After the introduction of the mechanisms of overpressure development in marine sediments, each overpressure mechanism, which is associated with either physical, chemical, or biological processes, is located in certain stage after deposition, as shown in Figure 8. Overpressure development is often associated with not only a single factor, but several factors can be involved. For example, overpressure in many sediments has been proven to be caused by hydrocarbon generation and clay mineral diagenesis because they occur in close temperature and depth conditions [13]. For another instance, tectonic movement can generate physical overpressure by changing the overburden pressure; meanwhile, it may produce chemical overpressure from hydrate decomposition by changing the temperature and pressure in the gas hydrate occurrence area. Previous studies suggest that, except for disequilibrium compaction and hydrocarbon generation, other mechanisms can only cause insignificant and local overpressure [107,121]. The overpressure developments associated with chemical and biological processes are closely related with temperature, sedimentary history and rate. Therefore, these factors should also be taken into account [30].

To determine the factors of overpressure development, geophysical and geochemical results, regional geological history, structural evolution, and pressure and temperature conditions should be comprehensively considered.
According to the experimental results and field application of microbial plugging technology, microbial plugging has great potential in overpressure development in marine environments. The growth and metabolism of some flora in marine sediments may effectively reduce permeability and prevent the migration of pore fluid under certain conditions. Because microbial activity is affected by temperature, salinity, pH, pressure, permeability, and crude oil properties [62,120], the overpressure caused by microbial plugging might only have local impact and probably occurs in the shallow-burial stage. The development conditions, scope, and magnitude of such kinds of overpressure need to be further studied.

After the introduction of the mechanisms of overpressure development in marine sediments, each overpressure mechanism, which is associated with either physical, chemical, or biological processes, is located in certain stage after deposition, as shown in Figure 8.

Figure 8. The appearance of each overpressure mechanism in the process after deposition of marine sediments. The solid lines indicate the most likely stage where overpressure appears, and the dotted lines indicate the stage where overpressure is likely to appear. SMI, sulphate methane interface; BSR, bottom-simulating reflector. Not to Scale.

6. Conclusions

As discussed in the previous sections, overpressure development can occur in a certain stage in the marine sediments below SMI. Overpressure developments in marine sediments are classified into physical, chemical, and biological mechanisms. The factors related to physical overpressure development include disequilibrium compaction, hydrate formation sealing, degasification, buoyancy, hydrothermal pressuring, tectonic movement and overpressure transfer; the chemical overpressure mechanisms are generally associated with hydrate decomposition, diagenesis and hydrocarbon generation; and biological overpressure mechanisms are induced mainly by microbial gas production and microbial plugging.

Regarding the physical overpressure mechanisms, (1) disequilibrium compaction is an important factor for overpressure development in most cases because the deposition rate is greater than the drainage rate, which greatly reduces the permeability of the overlying sediments; (2) the overpressure developed below the hydrate layer is caused by gas accumulation below the hydrate-bearing sediment, which has low permeability due to hydrate formation; (3) degasification may yield a great quantity of free gas with the gas solubility decreasing; (4) buoyancy-associated overpressure usually occurs in oil and gas reservoirs due to the different densities of oil, gas, and water. It can also be developed below gas hydrate-bearing layers in marine environments; (5) hydrothermal pressuring is generated due to the difference in the thermal expansion coefficient between the pore fluid and sediment matrix; (6) tectonic movement-related overpressure is mainly caused by the stress change resulting from tectonic compression and shear activities, resulting in strong local overpressure depending on the degree of compaction; (7) overpressure transfer
occurs through overpressured fluid activity, which is closely related to fluid channels such as permeable sandstone, fault systems, mud diapirs, and gas chimneys.

About the chemical overpressure mechanisms, (1) a large amount of free gas produced by hydrate decomposition may be sealed by a low-permeability gas hydrate-bearing layer, and they will accumulate to generate overpressure near the BSR. Tectonic uplift or sea-level fall, continuous sedimentation, and hydrothermal fluid rise will induce hydrate decomposition. (2) During the process of diagenesis, illitization and gypsum dehydration will generate a lot of excess pore fluid, whereas cementation will reduce the porosity and permeability of the sediments. Therefore, diagenesis may cause fluid volume expansion and restrain the migration of fluid, forming overpressure. (3) Overpressure associated with hydrocarbon generation mainly occurs in sufficiently mature or overmatured source rocks. Hydrocarbon generation can produce strong and large-scale overpressure, and its effect on overpressure has been widely recognized.

In marine sediments, (1) microbial gas production, accompanied by hydrate formation sealing, can induce overpressure; (2) under certain conditions the growth, reproduction, and metabolism of microbes can cause biological plugging, significantly reducing permeability and leading to overpressure development.

Author Contributions: H.L. conceptualized the study; C.L. wrote the original draft; L.Z. refined the draft text and all authors contributed to the editing and final reviews of the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This research received funding from the China Geological Survey (Grant No. DD20221703).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: We highly appreciate the two anonymous reviewers for their comments and suggestions, which benefited us greatly in revising this manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References
7. Biot, M.A. General Theory of Three-Dimensional Consolidation. J. Appl. Phys. 1941, 12, 155–164. [CrossRef]


71. Kumar, A.; Maini, B.; Bishnoi, P.R.; Clarke, M.; Zatsepina, O.; Srinivasan, S. Experimental determination of permeability in the presence of hydrates and its effect on the dissociation characteristics of gas hydrates in porous media. *J. Pet. Sci. Eng.* 2010, 70, 114–122. [CrossRef]


