

Carboniferous shales – A probable source of nitrogen in gas accumulations of the North German Basin

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Nitrogen is one of the most abundant non-hydrocarbon gas components in Permian gas reservoirs of the North German Basin (NGB). The eastern part of the NGB, therefore, represents a key study area for the assessment of the behaviour of nitrogen in the sedimentary cycle: i.e. sedimentation, fixation, burial and release of nitrogen. Terrestrial or marine organic matter is the parental source of nitrogen in sedimentary basins. Although most of the organic nitrogen can get lost by de-nitrification, considerable amounts of the remaining nitrogen are incorporated into sediments. Biodegradation of fixed organic nitrogen is the principal process during early diagenesis followed by thermal decomposition during sediment burial. The NH_4^+ released during this process may substitute for K^+ in clay minerals.

In the NGB the natural gas is mainly sourced from coal-bearing strata and organic-rich shales of Carboniferous ages. Open-system, non-isothermal pyrolysis in combination with elemental analysis has been applied to study the thermal liberation of molecular nitrogen from Palaeozoic sedimentary rocks and kerogen concentrates. Heating rates ranged from 0.5 to 2 K/min with final temperatures between 1100 and 1200°C. The N/C_{org} (atomic) ratios of the Palaeozoic shales ranged between 0.035 – 0.108 and were substantially higher than those of the corresponding kerogen concentrates (0.005 to 0.014), the latter representing the range commonly observed for coals. This indicates the presence of significant amounts of inorganic nitrogen in the shales.

Studies of clay mineralogy, vitrinite reflectance, determination of organic and inorganic fixed nitrogen, stable isotopes of nitrogen and carbon yielded indications for potential nitrogen storage in the form of ammonium during diagenesis and deep burial. Calculation of nitrogen loss and isotopic fractionation suggest a release of nitrogen from Upper Carboniferous shales of up to 50 % mainly as ammonia during enhanced thermal conditions and/or fluid-rock interaction. Formation waters and fluid inclusions of this sequence are especially enriched in NH_4^+ . Most of this NH_4^+ can be oxidized to N_2 during upwards migration through the red beds of the Rotliegend section.

TSR and sour gas accumulation: A case study in the Sichuan Basin, SW China

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The enormous sour gas accumulations have recently been discovered in the Lower Triassic oolitic reservoirs from the northeastern Sichuan Basin, SW China. The H_2S contents are generally over 10% and the maximum reaches 17%. Results from 1-D basin modeling indicate that the sour gas accumulations have involved much higher temperature (100–200 °C), and represent the products of both thermal maturation and thermochemical sulfate reduction of early accumulated light oils that had migrated considerable vertical distances. The origins of the gases are supported by their chemical and stable carbon isotope compositions, as well as the occurrence of pyrobitumens in the reservoir. The sour gas is dominated by CH_4 , amounting to about 77% in volume besides 10–17% of H_2S , 6–14% of CO_2 , and less than 0.1% of C_2H_6 . There are almost no heavier hydrocarbons than C_3H_8 . The carbon isotopic composition of methane and ethane shows that the higher the H_2S content is, the heavier the carbon isotopic composition of methane and ethane is. The measured $\delta^{13}\text{C}$ value of methane increases by 1.0–2.5‰ while that of ethane increases more greatly by 4.0–5.0‰. That indicates the preferential participation of C^{12} in TSR. The carbon isotopic compositions of carbonate also indicate an obvious interaction between organic and inorganic carbons in the area studied. The $\delta^{13}\text{C}$ values of the oolitic carbonate rock in the Lower Triassic reservoirs vary from 0.9‰ to 3.7‰ with an average of 2.0‰. However, those of blocky and drusy authigenic calcite crystals are remarkably negative while the minimum is -18.2‰ with average of -14.5‰. This indicates the transfer of organic carbon from hydrocarbons to the secondary calcite (CaCO_3), i.e. $n\text{CaSO}_4 \cdot m\text{H}_2\text{O} + n\text{C}_n\text{H}_{2n+2} \rightarrow n\text{CaCO}_3 + \text{H}_2\text{S} + (n-1)\text{S} + n\text{H}_2\text{O}$, which results in the lighter carbon isotope of the secondary calcite derived from degypsification. The distribution of the gas accumulations is controlled dominantly by the combination of lithologic and structural factors, and the regional variation in the concentrations of H_2S in the gases is closely related to the presence and thickness of anhydrite-bearing evaporitic rocks interbedded/intercalated with oolitic reservoirs.