

## Acid gases speciation in H<sub>2</sub>S-CO<sub>2</sub>-Portland Cement-H<sub>2</sub>O system

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This study presents the interactions of H<sub>2</sub>S and CO<sub>2</sub> with the cementitious material used in the oil wells construction to determine the speciation of these chemicals in a closed system conditions at high temperatures and pressures. Using a charge balance was possible to determine the mass of each of the species involved in the chemical balance of the system and make the corresponding mass balance. H<sub>2</sub>S and CO<sub>2</sub> are aggressive agents and their action against the cementitious material is influenced by the characteristics of cement, porosity, permeability, type of hydration products, partial pressure of CO<sub>2</sub> and H<sub>2</sub>S, temperature and composition of formation water, in particular is important to consider the salinity. The CO<sub>2</sub> attack is preferential on portlandite [Ca (OH)<sub>2</sub>] present in cement and its initial impact is minimal on calcium silicates; deteriorates the outer surface of cement and migrates through the matrix affecting its internal structure. Chemical attack of samples was performed in a closed system under high temperature and pressure (ATAP), with known concentrations of CO<sub>2</sub> and H<sub>2</sub>S, establishing conditions under which is progressively increased aggressiveness of the attack (approximately up to 38 atm CO<sub>2</sub> 16 atm H<sub>2</sub>S). Each test series includes the following time intervals: 20, 40, 80 days. The mass balance allowed calculating the concentrations of sulfide (HS<sup>-</sup>) and bicarbonate (HCO<sub>3</sub><sup>-</sup>), according to the following expressions:

$$[HS^-] = pH_2S \cdot 10^{-7} (2[Ca^{2+}] + [Na^+] + [K^+] - 2[SO_4^{2-}])$$

$$[HCO_3^-] = 2[Ca^{2+}] + [Na^+] + [K^+] - [HS^-] - 2[SO_4^{2-}]$$

The main conclusion suggests an inhibitory effect of CO<sub>2</sub> on the solubility of H<sub>2</sub>S.

## Lignin decomposition in paddy soils as affected by redox conditions

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In submerged soils, lignin constitutes a major portion of the total organic matter (OM) because of hampered degradation under anoxic conditions. Paddy soils management involves alternating redox cycles with periodic changes in soil solution chemistry and microbial metabolism. Such an environment might promote both degradation and preservation of lignin, affecting the overall composition and reactivity of total and dissolved OM.

We sampled two soils either subjected to cycles of anoxic (rice growing period) and oxic (harvest and growth of other crops) conditions since 700 and 2000 years. We incubated suspended Ap material, sampled from the two paddy plus two corresponding non-paddy control soils under oxic and anoxic condition, for 3 months, interrupted by a short period of three weeks (from day 21 to day 43) with reversed redox conditions. At each sampling time (day 2, 21, 42, 63, 84), we determined lignin-derived phenols (by CuO oxidation) as well as phospholipids fatty acids contents and composition. We aimed to highlight changes in lignin decomposition as related to changes in microbial community composition.

In well-established paddy soils relative short (3 weeks) changes in redox conditions had no effect on lignin decomposition or oxidation state. Also, lignin was not altered during oxic incubation. Since fungi represented only small portion of the microbial biomass in the studied soils, they were obviously not capable to cause much degradation, even under favourable conditions. On the contrary, 3 months of anoxic conditions resulted in a decrease in lignin-derived phenols. This decrease was likely not a result of degradation but of (partial) dissolution and/or pH-induced changes of the surface properties of Fe and Mn hydrous oxides causing the release of mineral-associated lignin-derived phenols. Thus, we speculate, that oxidised lignin fragments produced during the (oxic) dry period do not remain in the soils but leach with water drainage during the flooding period.