

AAPG HEDBERG CONFERENCE
“NATURAL GAS GEOCHEMISTRY: RECENT DEVELOPMENT, APPLICATIONS, AND TECHNOLOGIES”
MAY 9-12, 2011-BEIJING, CHINA

Effect of Water Chemistry on Thermochemical Sulfate Reduction and Speciation In $MgSO_4$ (Aq)

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Thermochemical sulfate reduction (TSR), which commonly occurred in carbonate reservoir and is considered as a critical process leading to accumulation of sour gas, has been well observed and intensively studied by geochemists. Their works were mainly focused on the onset temperature, geochemical features and risk of TSR (Orr, 1977; Krouse, 1988; Worden et al., 1995; Heydari et al., 1997; Manzano et al., 1997; Machel, 2001; Cai et al., 2003; Dai, 2004; Zhang et al., 2005, 2008), and also on the effect of oil features and H_2S on TSR (Tang et al., 2005; Zhang et al., 2007, 2008). Little seems concerned with water chemistry, which may be a potential factor affecting TSR. Meanwhile, a former theoretical study has addressed that different sulfate species may present diverse reactivity with ethane (Ma et al., 2008), whereas no experimental work has been performed to discuss the relation of speciation of sulfate and TSR. In this paper, a series of isothermal gold-tube hydrolysis experiments were initially conducted to study the effect of water chemistry (including pH, salts type and concentration) on TSR involving *n*-alkane and $MgSO_4$. Furthermore, in situ Raman technology using fused silica capillary was employed to investigate species variations in aqueous $MgSO_4$ with temperature and solution salinity. Ultimately, we concluded that increase of temperature and certain salts ($MgCl_2$ and $AlCl_3$) concentration can avail the occurrence of $MgOSO_3$ contact ion pair (CIP), and consequently accelerate oxidation of hydrocarbon. It is notable that the presence of NaCl seems not to promote the relative content of CIP, but it can also accelerate the redox reaction.

1. Effect of water chemistry on TSR

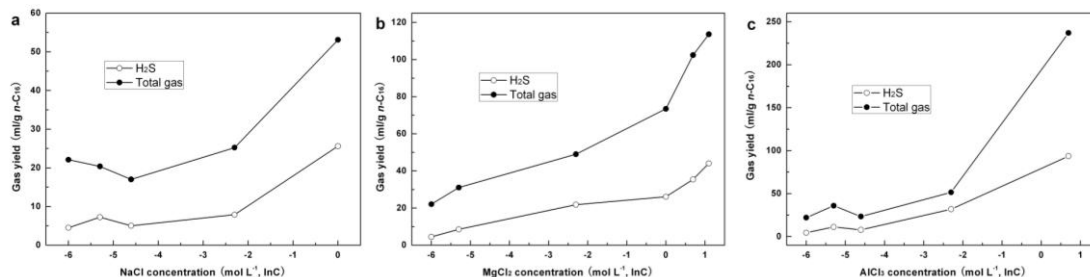


Fig. 1 Correlation between gas yield and additional chloride concentration in isothermal hydrolysis experiments involving *n*-C₁₆ and 1 M $MgSO_4$ (100 ul) at 360 °C for 240 h. The first plot (lnC = -6) of each profile refers to gas yield in 1 M $MgSO_4$ system without additional salts.

Prior to isothermal hydrolysis experiments, three chlorides with various concentrations were isometrically mixed with 2 M MgSO_4 (v:v = 1:1). Gas products were determined by a customized 6890 Series Gas Chromatograph (GC) interfaced with a Wasson ECE instrument. Fig. 1 shows the effect of additional salts on total gas and H_2S yields. Evidently, there is a positive correlation between gas yield and chloride concentration. Therein, the presence of AlCl_3 indicates a highest efficiency relative to NaCl and MgCl_2 . Moreover, results in control experiments with various pH demonstrate that TSR involving hydrocarbons and CaSO_4 or Na_2SO_4 is impossible to initiate in neutral to weak acid condition (pH=3.0~7.0), this may imply that sufficient HSO_4^- should not be formed in common aqueous environment, i.e., it is plausible that the actual oxidant of the organic-inorganic redox reaction is not free SO_4^{2-} or HSO_4^- .

2. Features of the Raman spectra of $\text{MgSO}_4(\text{aq})$

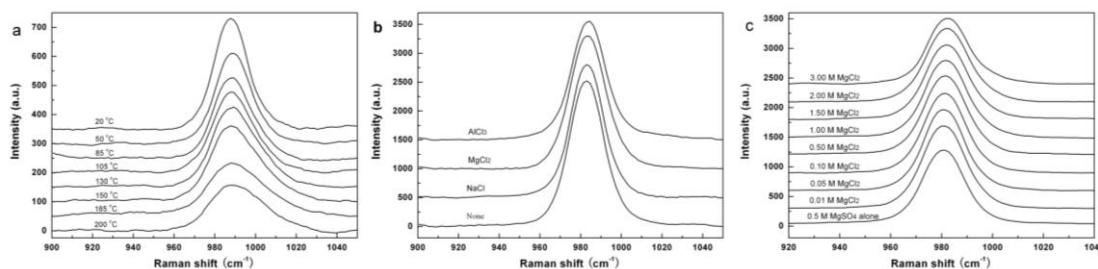


Fig. 2 Dependence of Raman spectrum in the $\nu_1\text{-SO}_4^{2-}$ region for MgSO_4 (1 M) on temperature (a), additional salts type (b) and additional MgCl_2 concentration (c).

Previous researches have proposed a following process for MgSO_4 aqueous solution:
 $\text{Mg}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$ [free hydrated ions] \leftrightarrow $\text{Mg}^{2+}(\text{OH}_2)_2\text{SO}_4^{2-}(\text{aq})$ [2SIP] \leftrightarrow $\text{Mg}^{2+}(\text{OH}_2)\text{SO}_4^{2-}(\text{aq})$ [SIP] \leftrightarrow $\text{Mg}^{2+}\text{SO}_4^{2-}(\text{aq})$ [CIP]

As shown in Fig. 2, the $\nu_1\text{-SO}_4^{2-}$ mode at *ca.* 980 cm^{-1} shifts to higher wavenumber and becomes more broad and asymmetric as temperature increases and additional salts are introduced. By fitting the $\nu_1\text{-SO}_4^{2-}$ mode into two components using the software PeakFit v4.12 with a linear baseline and Gaussian-Lorentzian area model, the relative content of CIP can be calculated by following formulation according to Rudolph et al. (2003): $[\text{CIP}]/C_T = I_{993}/(I_{980} + I_{993})$. It is revealed that the CIP content increased with the temperature and additional MgCl_2 concentration increasing.

Indeed, theoretical calculation has demonstrated that the species CIP is easier to react with hydrocarbons than free SO_4^{2-} . Therefore, we propose that the oxidant for TSR involving $\text{MgSO}_4(\text{aq})$ and hydrocarbons should be CIPs rather than free SO_4^{2-} or insufficient HSO_4^- . Meanwhile, the presence of additional chlorides, especially MgCl_2 and AlCl_3 , can avail the occurrence of MgOSO_3 CIP, and consequently accelerate the redox process.

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