

Experimental determination of the kinetics and mechanisms of Thermochemical Sulphate Reduction (TSR) reactions at reservoir conditions of pressure and temperature

M. M. Cross
D. A. C. Manning
P. E. Champness

Department of Earth Sciences, University of Manchester,
Manchester M13 9PL, UK

R. H. Worden

School of Geosciences, The Queen's University of Belfast, Belfast
BT7 1NN, UK

S. H. Bottrell

Department of Earth Sciences, University of Leeds, Leeds LS2
9JT, UK

The distribution of H₂S and petrographically altered anhydrite within the gas reservoirs of the Permian Khuff Formation (Abu Dhabi) depends on temperature. Very low H₂S contents and unaltered anhydrite are present at depths and temperatures less than 4300 m and 140°C respectively. At greater depths and temperatures, anhydrite shows replacement by calcite, and gas H₂S contents rise rapidly, reaching almost 40 vol. % (Worden *et al.*, 1995). These phenomena, and similar observations elsewhere, have been interpreted as indications that reaction kinetics play an important part in Thermochemical Sulphate Reduction (TSR), with the following overall reaction:



Previous experimental work has been limited in its ability to accurately simulate the temperature and pressure conditions present in oil and gas reservoirs, and to allow the inert containment of reaction fluids. Autoclave experiments (e.g. Goldhaber and Orr 1995), are necessarily performed at temperatures far in excess of those present in hydrocarbon reservoirs in order to obtain an observable rate of reaction. However the pressures obtained in such reactions are low compared to those present in natural reservoirs, and corrosion of the steel autoclaves occurred. This would be responsible for introducing iron, a very important variable, into the system.

Our study involves the experimental determination of the rates of TSR reaction and anhydrite dissolution, and an investigation into the mechanisms by which the reaction occurs. The initial aim is to determine the rate-limiting step of the reaction. Further work is being undertaken to elucidate the reaction mechanisms at reservoir pressure and temperature. This work involves using different sulphur species and different organic reducing

agents in repeat TSR experiments. An investigation into whether TSR results in any characteristic textural features visible by optical, scanning or transmission electron microscopy (SEM/TEM) is in progress. Sulphur, carbon and oxygen isotope analyses have been performed on reactants and reaction products drawn from the experimental apparatus during experimental runs. The isotope data are targeted to resolve some of the details of the reaction mechanism.

Methods. Fluid-sampling hydrothermal pressure-vessels (Seyfried *et al.* 1987), which have critical advantages over autoclave experiments, have been utilised in the execution of this project. Independent pressure and temperature control up to 50 Mpa (500 bars; 7500 psi) and 350°C are possible. These values correspond to a burial depth of

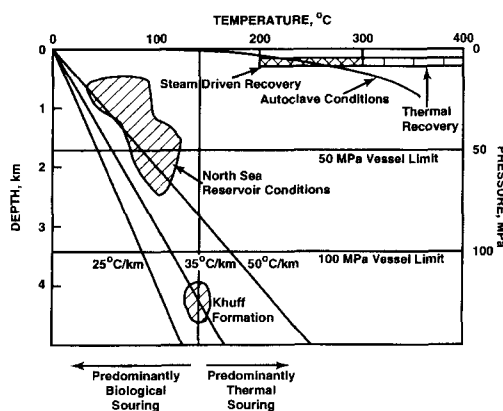


FIG. 1. A schematic P-T graph illustrating the conditions utilised in the experimental work (After Manning *et al.* 1994).

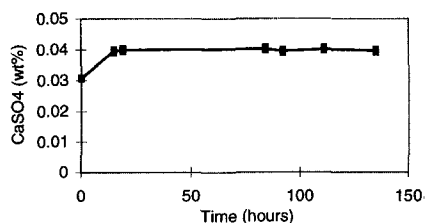


FIG. 2. A graph to show the variation in anhydrite solubility in response to an increase in pressure, from 250 to 500 bars, at 145°C.

approximately 1750 m, and therefore this project represents a better simulation of the conditions controlling the natural TSR reaction than previous work (Fig 1). Furthermore the reactants are held within an inert reaction system, consisting of a gold reaction cell, with titanium closure and exit tube, which leads to a titanium external sampling valve. This system allows fluid samples to be taken periodically during long experiments, to monitor reaction progress without quenching the reaction vessel to room conditions.

Anhydrite dissolution reactions have been performed with natural anhydrite (Wards) and de-ionised water. Equilibrium solubility is achieved at the run temperature, and then an instantaneous change in pressure is used to disturb the equilibrium. New equilibrium solubility values are then approached either from undersaturated or supersaturated conditions at constant temperature. This prevents uncertainties due to thermal lag.

TSR reactions have been performed with reagents in aqueous solution. Generally analytical grade sodium sulphate has been adopted as a source of sulphate. When sulphate with a heavy $\delta^{34}\text{S}$ value (+27 per mil) is required for isotope analysis, it is obtained from the conversion of natural anhydrite to sodium sulphate by ion exchange. Acetic acid/sodium acetate buffer solutions or dextrose solutions have been used as analogues for the organic species present in reservoirs.

Analyses of experimental samples have been principally performed using Ion Chromatography (IC), although ICP-AES has also been used to determine cation concentrations, and XRD used to characterise solid reaction products. Analyses of natural samples have been performed using XRD, and analytical SEM/TEM. This investigation of natural samples is focused on observing reaction textures, using optical and electron microscopy (SEM/ATEM), to assess the possibility of using core material as a petrographic indicator of probable extent of TSR reaction. This information might not

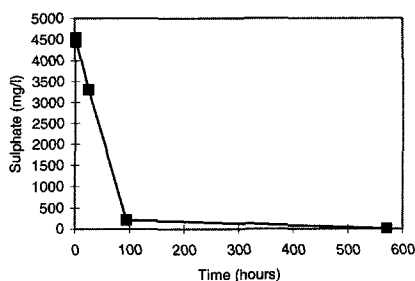


FIG. 3. A graph illustrating a TSR experiment between acetic acid, sodium sulphate and sulphur at 500 bars and 250°C.

be obtained from reservoir fluid compositions.

Results. The anhydrite dissolution reactions have confirmed that the equilibrium solubility values for anhydrite (Blount and Dickson, 1969) are reproducible and indicate that anhydrite dissolution rates are rapid at temperatures above 100°C (Fig. 2). Therefore anhydrite dissolution is not likely to be rate-limiting in the natural TSR reaction.

TSR reactions have been performed under a variety of experimental conditions. A proportion of these reactions show significant decreases in sulphate concentration during the experimental runs. The remainder of experimental runs show little or no decrease in sulphate concentration during the experiments. This second group of unsuccessful TSR reactions serves to demonstrate the inert containment of reactants within the experimental apparatus for very long experimental durations of up to four months. The unsuccessful TSR reactions demonstrate sulphate half-lives as short as 50 hours at 250°C (Fig. 3). The data suggest that a catalytic quantity of low valence sulphur species, for example elemental sulphur, is required for reduction to occur. Sulphur ($\delta^{34}\text{S}$), carbon ($\delta^{13}\text{C}$) and sulphate-oxygen ($\delta^{18}\text{O}$) isotope data will further elucidate the mechanism of reaction.

SEM/TEM analyses of heavily reacted and apparently unreacted natural anhydrite have been undertaken. TSR reaction textures are visible on a very small scale (TEM) even within apparently unreacted (optical/SEM) anhydrite nodules. Increasing extent of reaction correlates with increasing depth and temperature. TEM study of crystal boundaries between the phases present suggests that the secondary calcite, formed during TSR, nucleates on the surface of the anhydrite nodules undergoing reaction.

It is hoped that the geochemical data, isotopic analyses and petrographic study will lead to a greater understanding of the processes by which TSR occurs.