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The effect of vapour pressure on the reaction of water vapour with siderite and its relevance to retorting of Australian Tertiary oil shales

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Abstract

The thermal decomposition reaction of siderite mineral samples in water vapour/nitrogen atmospheres was studied using thermogravimetry. A reduction of about 120 °C in the decomposition temperature in 60 kPa water vapour, compared to that in nitrogen, was found for both siderite and ferroan magnesite. A different reaction mechanism in water vapour accounts for the differences in temperature. The effect of water vapour pressure between 0 and 80 kPa was non-linear, being relatively greater at low vapour pressures, and the inverse relationship between the peak decomposition temperature and water vapour pressure has been established. The results imply that the siderites and magnesian siderites present in Australian Tertiary oil shales will decompose during steam-retorting, although the possible countervailing effect of carbon dioxide remains to be defined.

INTRODUCTION

Many aspects of the retorting of Australian Tertiary oil shales to liquid fuels are influenced by the minerals which represent the greater part of the oil shale. Work in these laboratories has examined the reactions of such minerals [1–5]. The thermal decomposition reactions of siderite, $FeCO_3$, were included in this program because siderite is the dominant carbonate mineral in the majority of these deposits, where concentrations generally range from 2 to 10%, with variability both between and within seams [4].

Naturally occurring siderites exhibit a wide variability in chemical composition. Isomorphous substitution of Mg, Mn and, to a lesser extent, Ca, is so common that a pure siderite is seldom found [6]. For siderites in Australian Tertiary oil shales, mineralogical studies [4,5] have shown this diversity: for example, Nagoorin shales generally contain siderite with low concentrations of other cations, whilst the shales in the Rundle, Stuart and Nagoorin South deposits contain iron carbonates with magnesium contents reaching 50% $MgCO_3$ and are better described as magnesian siderites. The

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deposits at Yaamba and Duaringa contain manganoan siderites. Previous thermoanalytical work by Warne [7] has shown that variations in composition exercise a considerable effect, in that isomorphous replacement of Fe by Mg markedly alters the temperature of the decomposition which occurs in a single stage in either N_2 or CO_2 atmospheres [8].

Siderite decomposition in nitrogen [8] occurs in the same temperature range (450–550 ° C) as that planned for retorting the Australian Tertiary oil shales. Siderite decomposition is endothermic and is important as it represents a heat loss from the process. During retorting, water vapour is produced from the shale, or additional steam may be introduced to the retort as part of the process. Consequently, the reaction of siderite with water vapour, and the temperature range in which it occurs, is relevant. Previous work by Mel'nik [9] showed that siderite is oxidised to magnetite at lower temperatures in steam than in an inert gas. This study further investigates this reaction, using an almost pure siderite, a ferroan magnesite and a magnesian siderite more typical of those found in several Australian Tertiary oil shales.

EXPERIMENTAL

Thermogravimetric (TG) data were obtained using a Cahn RG thermobalance. The sample enclosure was designed to allow the study of reactions in water vapour/gas atmospheres up to partial pressures of water vapour of 80 kPa. It consisted of a silica and glass enclosure with a steam generator attached via heated tubing. This allowed water vapour to be introduced without having to heat the complete balance to prevent condensation. The enclosure was attached vertically about the sample hangdown wire and platinum sample pan. The silica furnace tube was heated with a vertical tube furnace. The sample temperature was measured with a type K thermocouple, located about 2 mm below the sample pan.

The amplified mass and temperature signals were fed to a 12 bit analogue-to-digital converter and thence to a DEC PDP-11/23 computer. Experimental TG data were stored within the data system. Derivative thermogravimetric (DTG) curves were obtained from the TG data by applying a recursive digital filter in a smoothing routine [10].

Samples of siderite were freshly crushed in a mortar and pestle. Samples of about 10 mg were spread thinly on the bottom of the pan and heated at 10 ° C min^{-1} in nitrogen flowing at 130 $\mathrm{cm}^3\ \mathrm{min}^{-1}$, with water vapour pressures of 0, 5, 10, 20, 40 and 80 kPa. The nitrogen supply was reticulated from a bulk liquid nitrogen tank, and oxygen and moisture impurities were each less than 10 vpm. Three members of the isomorphous siderite–magnesite series and their chemical analyses (Table 1) were kindly made available by Professor S.St.J. Warne of Newcastle University.

TABLE 1

Description of siderite samples

Sample	Description	Structural formula
401	Siderite	$Fe_{0.95}Mg_{0.005}Mn_{0.04}CO_3$
559b	Magnesian siderite	$Fe_{0.83}Mg_{0.11}Mn_{0.05}Ca_{0.01}CO_3$
HH1	Ferroan magnesite	$Fe_{0.17}Mg_{0.82}Mn_{0.01}CO_3$

Determination of the gaseous products from the reaction of siderite with water vapour was carried out as follows. A small sample (≈ 30 mg) of siderite 559b and excess water were placed in a sealed glass reaction tube, frozen with dry ice ($-80\,°C$) and evacuated. The sample at the base of the tube was heated to 525 °C at 10 °C $\min^{-1}$ and soaked isothermally for 10 min while the rest of the tube was heated to 110 °C to prevent condensation. The tube was then cooled, filled with nitrogen and a gas sample taken for gas chromatographic analysis.

RESULTS AND DISCUSSION

Initially, a siderite (401) and a ferroan magnesite (HH1) were selected for study. These represent each end of the isomorphous siderite–magnesite series, and were examined under dry conditions in nitrogen and in 60 kPa pressure of water vapour in nitrogen. The reactions proceeded in a single stage in both environments. The TG curves illustrated in Fig. 1 show that a large shift to much lower reaction temperatures occurs for both samples in the water vapour atmosphere. The DTG plots clearly show a decrease in peak temperature of about 125 °C for the siderite decomposition reaction: from 455 to 330 °C. A similar reduction is also observed for the reaction of the ferroan magnesite: from 640 to 520 °C. This reflects the ability of water vapour to provide an alternate pathway to the end products. The greater mass loss observed for the ferroan magnesite sample is expected from the proportionally higher mass content of carbonate in this sample.

Sample 559b, with a composition more typical of the magnesian siderites from the Tertiary oil shales was used to investigate the effect of varying water vapour pressure. Selected TG curves are illustrated in Fig. 2. Again, a large shift to much lower reaction temperatures occurs in the presence of water vapour. The temperatures of the reaction maxima in the DTG curves derived from these TG curves are plotted in Fig. 3 which shows that the effect of water vapour is markedly non-linear. At 5 kPa there is a 53 °C decrease in the temperature of maximum decomposition rate to 467 °C, compared with that in dry nitrogen. This inverse relationship between reaction temperature and water vapour pressure continues, but with a reduced rate, to at least 80 kPa where the decomposition peak is observed at 416 °C: a reduction of 104 °C.

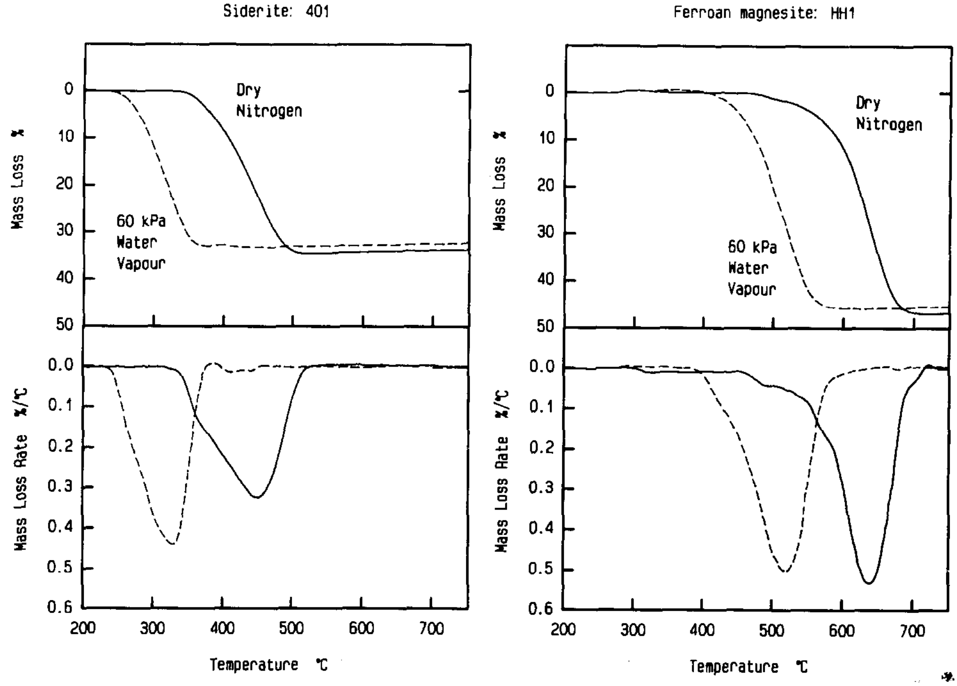

Fig. 1. Comparison of TG and DTG curves for the decomposition of siderite and ferroan magnesite heated at 10 °C min^{-1} in dynamic atmospheres of nitrogen and 60 kPa water vapour in nitrogen.

Magnetite is the solid product of thermal decomposition in an inert atmosphere or vacuum when the reactant is relatively pure siderite, as Kubas and Szalkowicz [11] have shown with a definitive combination of simultaneous thermoanalytical techniques

$$3FeCO_3 \rightarrow 3FeO + 3CO_2 \rightarrow Fe_3O_4 + CO + 2CO_2 \qquad (1)$$

Mel'nik [9] used X-ray diffraction to show that magnetite is also the solid

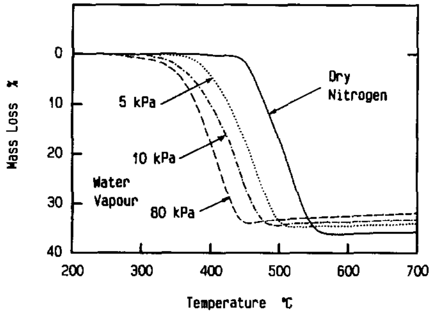

Fig. 2. Decomposition of magnesian siderite (559b) heated at 10 °C min^{-1} in dry nitrogen and in various pressures of water vapour in nitrogen.

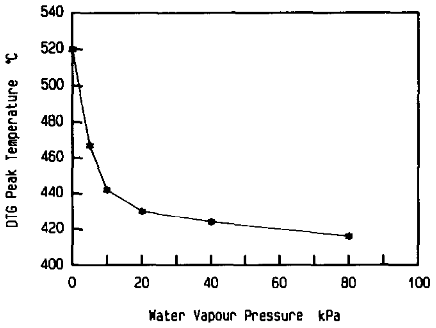

Fig. 3. The variation with water vapour pressure of the DTG peak temperature for decomposition of magnesian siderite (559b) heated at 10 °C min^{-1}.

product for the reaction of siderite with water vapour, this being thermodynamically favoured over hematite [12,13]. In inert atmospheres, isomorphous substitution in siderite leads to the formation of magnetic spinels of the type $(M,Fe)_3O_4$ on thermal decomposition [14]. Such spinels also form when these compounds react with water vapour [15]. Following the decomposition of the carbonate, the magnetite is slowly oxidised to hematite, resulting in the slow mass gain observed after the major reaction mass loss (Fig. 2). This probably arises by oxidation of the magnetite by traces of oxygen entering the system when water is added to the steam generator.

Mel'nik [12] calculated the thermodynamic parameters for the siderite reaction with water vapour, using the equation

$$3FeCO_3 + H_2O \rightarrow Fe_3O_4 + 3CO_2 + H_2 \qquad (2)$$

Magnetite was confirmed as the solid product but CO_2 and H_2 were not determined [9]. As outlined in the experimental section, gas chromatography showed that CO_2 and H_2 are the major product gases. Small amounts of CO were detected which probably arose from the water gas shift reaction

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad (3)$$

The reaction with water vapour to give these products is thermodynamically favoured over thermal decomposition. This probably arises from formation of a reactive intermediate between siderite and water, possibly a hydroxycarbonate species; hydroxide–carbonate compounds of iron have been isolated [16,17].

Inspection of Fig. 1 shows that, in nitrogen, the decomposition of siderite occurs at temperatures similar to that of oil evolution [18,19] from Australian Tertiary oil shale (450–550 °C), whereas the ferroan magnesite would be largely unaffected during retorting. With the introduction of water vapour and the consequent lowering of the reaction temperature, even the ferroan magnesite will decompose within the expected retorting range. It should be noted, however, that carbon dioxide will build up in the retort gases in the course of retorting, and this is expected to shift the reaction to higher temperatures [8]. Thus in retorting, a complex interaction occurs amongst temperature, variation in siderite composition, water vapour pressure and carbon dioxide pressure; and this complete system requires further definition.

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