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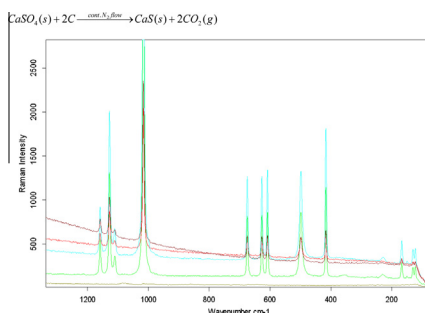
## Raman spectroscopic study of phosphogypsum thermal reduction with the carbonaceous material

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### HIGHLIGHTS

- REDOX pathway for phosphogypsum with graphite was established using TGA and *in situ* Raman.
- An intermediate was determined to be dehydrated orschallite type compound.
- Metal impurities did not lower than previously reported onset temperature or activation energy.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Elemental sulphur (S) can be produced from hydrogen sulphide (H<sub>2</sub>S) in a PiPco or Iron process. In turn H<sub>2</sub>S can be stripped with carbon dioxide (CO<sub>2</sub>) from calcium sulphide (CaS) obtained from the thermal reduction of phosphogypsum with carbon. The reaction pathway for the thermal reduction of the phosphogypsum with graphite was studied using thermogravimetric analysis and *in situ* Raman spectroscopy. The dehydration of the phosphogypsum to anhydrite was completed at about 142 °C. The dehydration was followed by the formation of the intermediate compound at about 860 °C which is characterised by a mass loss of about 11%. The intermediate compound, identified using the *in situ* Raman spectroscopy to be a dehydrated orschallite-type compound (Ca<sub>3</sub>[SO<sub>4</sub>][SO<sub>3</sub>]<sub>2</sub>), converted to CaS at about 935 °C. The presence of the metal impurities in the phosphogypsum: Ni<sup>2+</sup> (4 mg kg<sup>-1</sup>); Co<sup>2+</sup> (2 mg kg<sup>-1</sup>); Mn<sup>2+</sup> (5 mg kg<sup>-1</sup>); Cu<sup>2+</sup> (14 mg kg<sup>-1</sup>); Fe<sup>2+</sup> (200 mg kg<sup>-1</sup>) and Mg<sup>2+</sup> (300 mg kg<sup>-1</sup>) showed no influence the onset temperature for the reduction reaction.

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### Introduction

The association of the dissolved sulphate and hydrocarbons is thermodynamically unstable in virtually all diagenetic environments [15]. Hence redox reaction occurs where sulphates are reduced by the hydrocarbons either bacterially (bacterial sulphate reduction – BSR) or inorganically (thermal sulphate reduction –

TSR). Although TSR is thermodynamically possible at temperatures as low as 25 °C; there is evidence that BSR and TSR occurs in two mutually exclusive thermal regimes. BSR predominantly occurs at shallow depth ( $T < 100$  °C) and TSR in deeper evaporitic or carbonate reservoirs ( $T > 100$  °C) [15]. BSR by various electron donors is documented in literature by [4,12]. The electron donors include hydrogen gas, synthetic gas, methane, methanol, ethanol, glycerol, acetate, lactate and organic waste [4]. In addition to these, other e-donors have been evaluated in the laboratory studies of reduction of solid calcium sulphates (anhydrite and gypsum): C<sub>1</sub>–C<sub>3</sub> hydrocarbons [7], CO and coal dust [18] and C<sub>1</sub>–C<sub>6</sub> hydrocarbons [6]. Yue et al. [24],

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reported methane as the most non-reactive hydrocarbon in the TSR reaction in the range of hydrocarbons tested. This is in line with the finding by [15]. Machel suggested that the order of reactivity in hydrocarbons is: branched alkanes + *n*-alkanes > cyclic + mono aromatic compounds > methane. A common challenge in all the work carried out so far on TSR has been to reduce the activation energy of the redox reactions involved.

There have been many attempts to explain the redox reaction mechanism involved in the reduction of sulphate. Machel [15] singled out temperature to be the most important factor that governs the redox reactions involved in the TSR. However there are other potential factors that enhances or reduces the rate of TSR in natural environment such as: (i) initial total sulphur concentration; (ii) pH; (iii) salts (soaps) of inorganic acids; (iv) organic acids; (v) metal complexes; (vi) catalytic action of Ni<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>; (vii) organic compounds such as phenols, aldehydes aniline, urea, and vanillin; (viii) clay minerals particularly montmorillonite; and silica gel. The effect of the many of these factors is not well understood but it is clear that the increase in temperature and the initial concentration of H<sub>2</sub>S enhances the rate of TSR [7].

Ma et al. [14] in the theoretical study of the mechanism of TSR, elucidated the catalytic function played by the H<sub>2</sub>S in reduction of sulphate. Sulphate anions are symmetric tetrahedrons with S–O bond lengths of 1.47 Å and O–S–O bond angle of 109° [14,7]. This makes sulphate extremely un-reactive to reduction by hydrocarbons with the activation energy of 318 kJ mol<sup>-1</sup>. H<sub>2</sub>S dissociates in water to form HS<sup>-</sup> and H<sup>+</sup>. The acidification of water by the dissociation of H<sub>2</sub>S encourages the formation of protonated sulphate (HSO<sub>4</sub><sup>-</sup>). The more acidic the water is the more bisulphate forms. The resulting protonated S–O bond is longer (weaker); 1.71 Å and the resulting molecule is polar with a total dipolar moment of 3.02 Debye. The presence of H<sub>2</sub>S therefore lowers the activation energy for sulphate reduction to 222 kJ mol<sup>-1</sup>. This mechanism required H<sub>2</sub>S to dissociate for the H<sup>+</sup> to protonate the sulphate, which in turn has to be in its dissolved anionic form. The wettability of calcium sulphate therefore becomes an important parameter to be considered.

Ellis et al. [7] carried out experiments that confirmed catalysis of TSR by H<sub>2</sub>S. They further suggested that magnesium played a significant role in a two-stage reduction of sulphate. Therefore they proposed that the mechanism involved the formation of contact ion-pairs between Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> ions in solution. The formation of MgSO<sub>4</sub> contact ion pairs by Mg<sup>2+</sup> bidentate coordination changed the symmetry of the SO<sub>4</sub><sup>2-</sup> ion from T<sub>d</sub> to C<sub>2v</sub>. This coordination results in increased S–O bond length. The longer S–O bond is weaker and easier to reduce.

Ding et al. [6] studied the role of labile sulphur compounds in TSR, and proposed a different mechanism. They proposed that the mechanism occurs via the formation of sulphur radicals that enhances the formation of alkene compounds. The alkenes are easier to oxidise than alkanes. Prior to 1991 it was believed that the oxidation of hydrocarbons under geological conditions would not proceed unless the lower oxidation state sulphur, such as H<sub>2</sub>S is present [9]. The geological conditions are characterised by, amongst other factor, the dissociated SO<sub>4</sub><sup>2-</sup> salts in aqueous solution [7,25,26,2]. The presence of initial low oxidation state sulphur has been shown to increase the rate of TSR and lower the activation energy of the S–O bond rupture [25,26]. Amrani et al. [2] carried out experiments to understand the role of labile sulphur compounds in TSR. Their findings disputed the mechanisms via (a) the thermal release of H<sub>2</sub>S from the thiols, (b) generation of alkenes by leaving H<sub>2</sub>S compounds and (c) the radical formation followed by chain reaction of active compounds formation. They instead suggest that the thiols react directly with the sulphate resulting in the formation of sulphate ester. The ester formation results in the lower activation energy for the rupturing of the S–O bond.

But the conditions required for TSR in geological environment have been shown not to be essential for solid/liquid or solid/gas such as reactions C<sub>1</sub>–C<sub>6</sub> hydrocarbons [6]; C<sub>1</sub>–C<sub>3</sub> hydrocarbons under pressure [24]; and solid–solid reaction such as coal dust and CO at ambient pressure [18,19]. These studies reported no dissociation of sulphate, acidification or H<sub>2</sub>S initiation but showed that different carbon sources required different amount of energy to reduce the sulphate. The activation energy (*E<sub>a</sub>*) for the reactions between solid gypsum and C<sub>1</sub>–C<sub>3</sub> hydrocarbon were 152.9, 131.0 and 120.6 kJ mol<sup>-1</sup> for C<sub>1</sub>–C<sub>3</sub> respectively, whereas the reaction of coal and carbon monoxide with gypsum the *E<sub>a</sub>* was 14,340 and 28,680 kJ mol<sup>-1</sup>.

It is evident from literature reports that the reaction mechanism of TSR in aqueous solution is not the same as those in solid/solid reaction. The study by Nengovhela [19], which focused on the reaction of gypsum with coal dust and CO, proposed that the mechanism is complex and it results in the formation of CaS. In this study the authors follow the reaction mechanism pathway between graphite and phosphogypsum, a by-product from a phosphoric acid facility in the Lowveld region of South Africa. Thermogravimetric analysis and *in situ* Raman spectroscopy will be used similar reaction conditions to those previously described by Mihara et al. [16] and optimised by Nengovhela [19].

## Materials and methods

The concentrations of inorganic impurities in phosphogypsum were determined using an Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). A stoichiometric carbon rich mixture of gypsum and the carbonaceous material (1:3 M ratio) was prepared by mixing 17.2 g of gypsum with 3.6 g of carbon. The mixture was finely grinded with the mortar and pestle. Thermo-gravimetric measurements were done using a TG-DSC analyzer SDT Q600 instrument. About 6 mg of sample was heated from ambient temperature to 1200 °C at 20, 25 and 30 °C min<sup>-1</sup>, under constant flow of nitrogen (100 cm<sup>3</sup> min<sup>-1</sup>).

*In situ* Raman measurements were carried out in a TS 1500 reactor controlled by the Linkam™ stage TMS 94. A stoichiometrically carbon rich mixture of graphite:gypsum (3:1 M ratio) was reacted up to 1080 °C, under a 100 cm<sup>3</sup> min<sup>-1</sup> continuous nitrogen flow. The mixture was heated up at the rate of 20 °C min<sup>-1</sup> to set temperatures then quenched before Raman scan were taken on the Bruker Raman spectrometer equipped with charge-coupled device detector (CCD) detector and a green laser (λ = 532 nm). Blank runs for gypsum and the carbonaceous material was also carried out under the same conditions. The commercial grades of likely products of gypsum decomposition and gypsum reduction with carbon such as, calcium sulphite in the form of hannebachite (CaSO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O and calcium oxide were analysed under ambient conditions.

## Results and discussion

### *Raman characterisation of the reactants: phosphogypsum and the carbonaceous material – before and after heating*

Gypsum crystallises in monoclinic crystal system, space group C2/c [20]. Each sulphate is tetrahedrally bonded to the calcium ion although a distinct distortion of the shape commonly occurs which gives rise to band splitting in Raman spectroscopy (Sarma et al. [22]). Factor group analysis predicts 72 vibration modes for gypsum belonging to the irreducible representations: 17A<sub>g</sub><sup>R</sup> + 17A<sub>u</sub><sup>R</sup> + 19B<sub>g</sub><sup>R</sup> + 19B<sub>u</sub><sup>R</sup> (Sarma et al. [22] and [3]). In this study 8 peaks are observed. The observed Raman bands are assigned and compared to the published data on Table 1.

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