

Study of Thermal Reduction of Barium Sulphate for Barium Sulphide Preparation

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Abstract. Industrial wastewaters, particularly those associated with mining and mineral processing, can contain high concentrations of sulphate. There are various methods of sulphate removal e.g. reverse osmosis, ion exchange, precipitation by lime, cements, and salts of barium and the biological removal process. The soluble salts of barium are most commonly used for precipitation of sulphate from aquatic acidic solutions to the insoluble product barium sulphate BaSO₄. Benefits of precipitation are high sulphate removal efficiency but limitations are toxicity of barium compounds and high economical costs. For this reason the recycling of BaSO₄ to barium sulphide BaS (the precipitating reagent) is very important.

The paper deals with study of BaSO₄ reduction by activated carbon to BaS by thermal analysis and infrared spectrometry. DCS analysis indicated that conversion of BaSO₄ to BaS in the range of temperature 800–1,000 °C was performed. Thermal analysis and infrared spectra of the products confirmed the change in its composition, but process of reduction by carbon was incomplete and in sample was still present a part of BaSO₄. Presence of BaS was confirmed by colorimetric method.

Keywords: sulphate, precipitation, BaSO₄, thermal reduction.

Conference topic: Environmental protection.

Introduction

Most commonly used technique for removal sulphates from water solution is chemical precipitation with barium salts to form barium sulphate (Holub *et al.* 2014). Standard or innovative regeneration techniques of barium sulphate is actual problematic for many researcher for reusing in precipitation of sulphates. Luptakova *et al.* (2015) studied regeneration barium sulphate by sulphate reducing bacteria and observed low-cost potential in bio-regeneration technology in comparison with standards thermal methods.

Barite/Baryte (BaSO₄) a mineral consisting of barium sulphate. BaSO₄ is generally white or colourless, and is the main source of barium (Hanor 2000). It is highly insoluble, what is a suitable form for sulphate removal (Lorax 2003). However, barium salts are expensive, thus the barium sulphate sludge is often recycled to reduce costs and to provide additional income through the production of elemental sulphur and barium sulphide (Luptakova *et al.* 2015). Barium sulphide (BaS) is an important industrial material. Conventional method of preparation is based on high-temperature reduction (approximately 1,200 °C) of barite (natural barium sulphate or a waste from removal of sulphates) with carbon-containing compounds (mostly coal or CO, CH₄, etc.) to final production of BaS and carbon dioxide (CO₂). The industrial method for producing barium sulphide from barite is following. Barite is reduced by coal in a rotary kiln at about 1,100–1,200 °C (Kirk-Othmer 1991). This process is called as black ash method (Holleman, Wiberg 2001).

Reduction of barium sulphate (BaSO₄) to barium sulphide (BaS) is an important step in producing barium chemicals from barite (natural barium sulfate mineral). Barite ore is a basic starting material for manufacturing a variety of barium chemicals such as BaCO₃, Ba(OH)₂, Ba(NO₃)₂, Ba(HS)₂, BaO (Alizahed *et al.* 2010).

Studies on the kinetics of the reduction of barite are very limited. Only in a few studies have carried out mechanistic studies of the reduction of barite by carbon (Jagtap *et al.* 1990; Alizahed *et al.* 2010; Salem *et al.* 2010). Gokarn *et al.* (2000) studied the no isothermal carbothermic reduction of barite in the absence and presence of sodium vanadate catalyst. All studies have similar results an initial reduction of barium sulphate with carbon. In this reaction is produced a carbon monoxide, which is used for a reduction barium sulphide too. Final products are BaS and CO₂. Thus, in the solid-state reduction of barium sulphate, CO is the gaseous intermediate. Also, Pelovski *et al.* (1990) have studied the isothermal reduction of barite with hydrogen (H₂) and in this study the kinetic parameters of reaction were determined. Recently, Sohn *et al.* (2006) have studied the isothermal reduction of BaSO₄ with H₂ in the presence and absence of nickel catalyst and also the kinetic parameters of the reaction were determined. They developed a novel process for converting sulphur dioxide to elemental sulphur by a cyclic reaction scheme involving barium sulphide and barium sulphate.

Paper deals with a thermal analysis of pure BaSO₄ and its mixtures with an active carbon using DSC method to the temperature 1,200 °C. Change of a crystalline structure of a BaSO₄ was confirmed by TG/DSC at a temperature approximately 1,170 °C. Production of BaS was evaluated by TG/DSC and infrared spectrometry. Reduction BaSO₄ to BaS was observed at a temperature between 800–1,000 °C. Presence of BaS after thermal reduction was confirmed by colorimetry after dissolving of product in distillation water.

Material and methods

Powdered BaSO₄ (p.a.) and a powdered activated carbon (p.a.) were used for experiments. Based on chemical Eqn (1) mixture of BaSO₄ and C in the ratio 1:2 and 1:4 was prepared. Samples of BaSO₄ (reference sample) and mixtures was analysed by thermal analysis Thermal properties of samples were studied by using STA 449F3 Jupiter thermoanalyser (Netzsch, Germany) in the temperature range from 25 to 1,200 °C with the heating rate of 10 K/min using DSC/TG mode. The samples of weight about 40 mg were heated in Al₂O₃ crucibles.

FTIR measurements of all products after thermal analysis were carried out on Bruker Alpha Platinum-ATR spectrometer (BRUKER OPTICS, Ettingen, Germany). A total of 24 scans were performed on each sample in the range of 400–4,000 cm⁻¹.

For confirmation presence of BaS after thermal reductions the samples were soluble in distillation water and dissolved S²⁻ was determined by colorimetric method with methylene blue reagent using Colorimeter DR890 (HACH LANGE, Germany).



Results and discussion

Thermal analysis

The study of thermal behaviour of the samples was based on determination of the weight losses and thermal gradients through the analysis of DCS (Differential Scanning Calorimetry). As seen from the DSC curve of BaSO₄ (reference sample) only one peak presents change in the structure at temperature 1,168.5 °C. The mass change was not confirmed due to a high purity of sample. Thermal transformation of crystal modification β to γ according chemical Eqn (2) (Qi *et al.* 2000) is shown in Figure 1. The enthalpy values of this process for interpretation of BaSO₄ reduction were used.

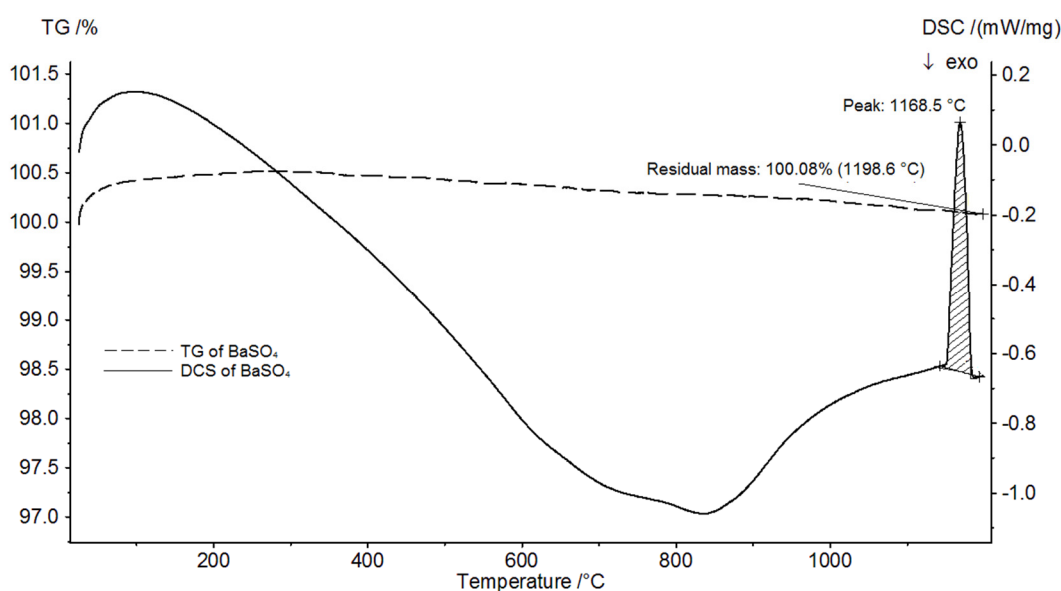


Fig. 1. TG/DSC curves of BaSO₄

In contrast to DSC curve of BaSO₄ for the mixtures of BaSO₄ with C two peaks were observed for every sample (shown in Figs 2 and 3). This result is in accordance with Salem *et al.* (2010) where DSC analysis showed an endo-

thermic reaction at about 900 °C. This process can be described as a reduction of BaSO₄ according to the Eqns (3) and (4), where the primary reducing agent is carbon, and carbon monoxide (an intermediate in the reduction process). In comparison to thermal analysis of reference BaSO₄ this thermal process was connected with lost weight. Peaks shifting to higher temperature during reduction are caused by overage amount of carbon. Results from analysis are summarized in Table 1.

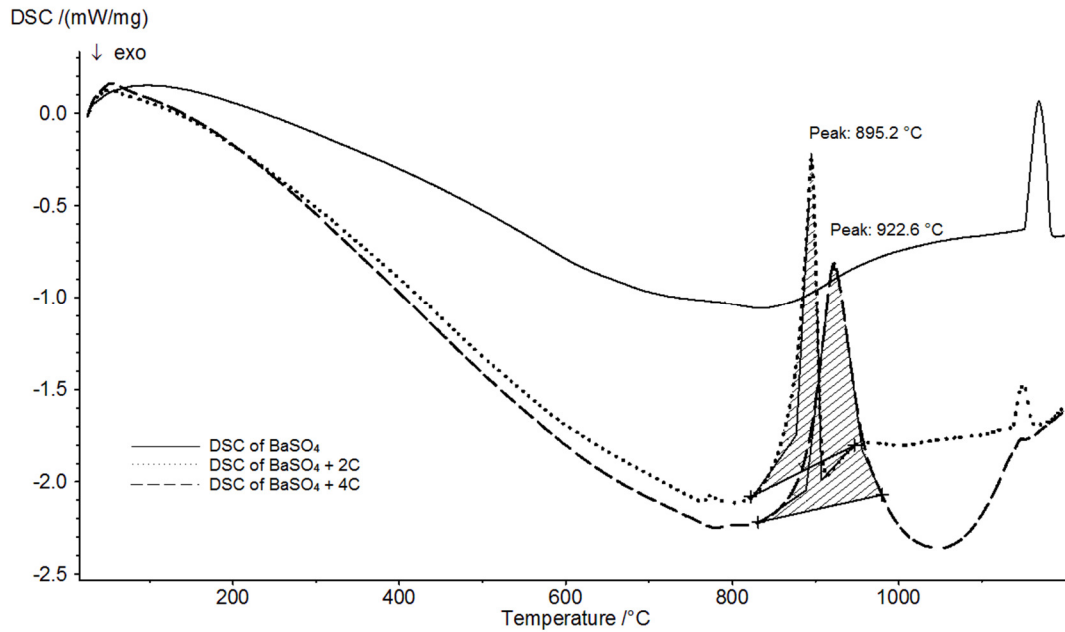


Fig. 2. Comparison of endothermal reaction of mixtures BaSO₄ with activated carbon (ratio 1:2 and 1:4)

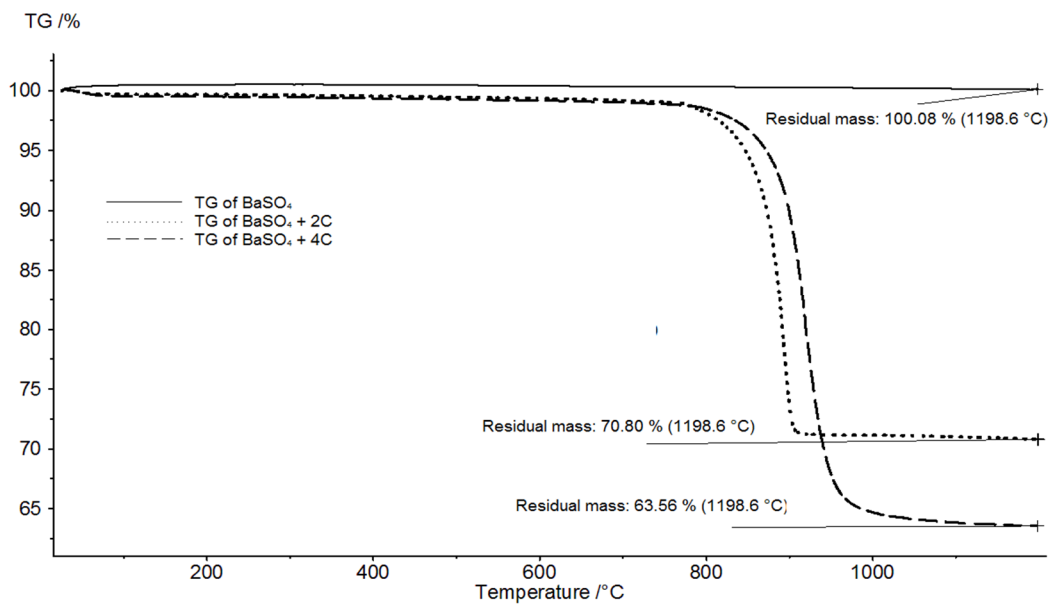


Fig. 3. Mass changes of BaSO₄ and mixtures with activated carbon (ratio 1:2 and 1:4)

Table 1. Thermal characterization of reduction process

Mixture	BaSO ₄ + 2C	BaSO ₄ + 4C
Enthalpy	231.0 J.g ⁻¹	382.8 J.g ⁻¹
Peak	895.2 °C	922.6 °C
Onset	876.9 °C	888.9 °C
End	907.2 °C	956.3 °C
Residual mass	70.8%	63.7%

Crystallization changes of reference BaSO₄ and mixtures with activated carbon (ratio 1:2 and 1:4) are illustrated in Figure 4. For confirmation of BaSO₄ amount decreasing in the tested samples, the values of enthalpy for the endothermic DSC peaks at about 1,150 °C were used. As it is seen from the values of enthalpy in Table 2, for mixture BaSO₄ and C (1:4) was efficiency of BaSO₄ reduction 91.36%.

As it results from Figure 4 endothermic peaks of BaSO₄ are shifted to the lower temperature with a decreasing amount of BaSO₄.

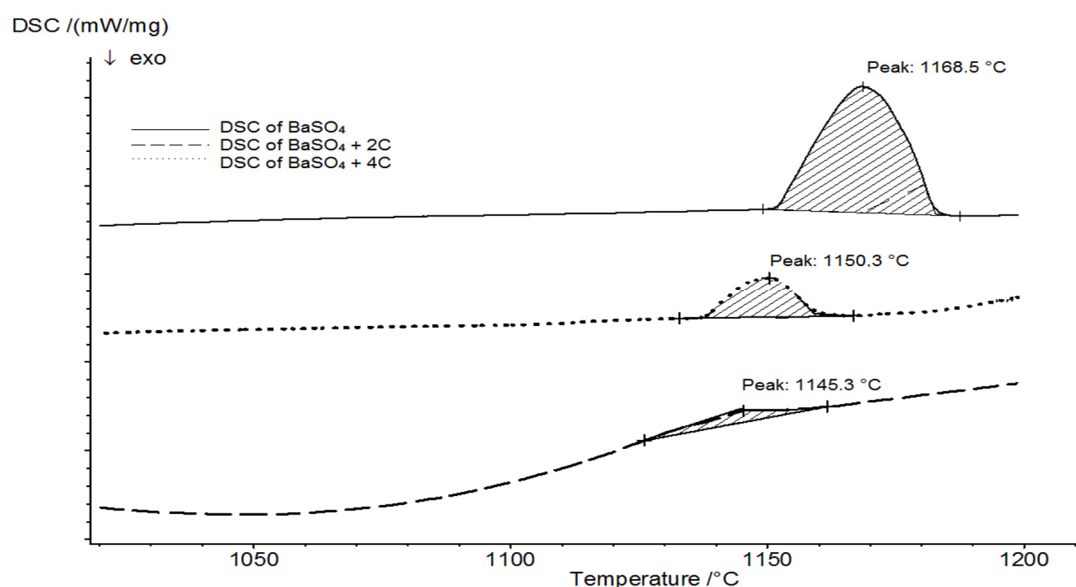


Fig. 4. Crystallization changes of reference BaSO₄ and mixtures of BaSO₄ with activated carbon (ratio 1:2 and 1:4)

Table 2. Transformation in crystalline structure of BaSO₄

Compound/Mixture	BaSO ₄	BaSO ₄ + 2C	BaSO ₄ + 4C
Enthalpy	80.9 J.g ⁻¹	18.85 J.g ⁻¹	6.99 J.g ⁻¹
Peak	1,168.5 °C	1,150.3 °C	1,145.3 °C

Characterization of chemical changes of BaSO₄

The chemical changes before and after thermal processes were studied by Infrared spectrometry. Figure 5 shows infrared spectra of BaSO₄ before and after thermal analysis. According to Ramaswamy *et al.* (2010) the sulphate group has 4 fundamental vibrational modes. One non degenerate (ν_1), one doubly degenerate (ν_2) and two triply degenerate (ν_3 and ν_4). Generally frequency characteristic vibrations of ν_3 appear between 1,200–1,080 cm⁻¹. The peaks obtained in both cases at 634 cm⁻¹ and 603 cm⁻¹ are due to the out of plane bending ν_4 vibrational mode in sulphate group (Lopez Perez *et al.* 1997). The peak at 982 cm⁻¹ is attributed to ν_1 vibrational mode. The peaks at 460 cm⁻¹ corresponds to symmetrically bending ν_2 (out of scope). From the comparison of FTIR spectra in Figure 5 resulted that due to the change of the crystal modification BaSO₄ ($\beta \rightarrow \gamma$) intensity of peaks at 1,179 and 634 cm⁻¹ were decreased.

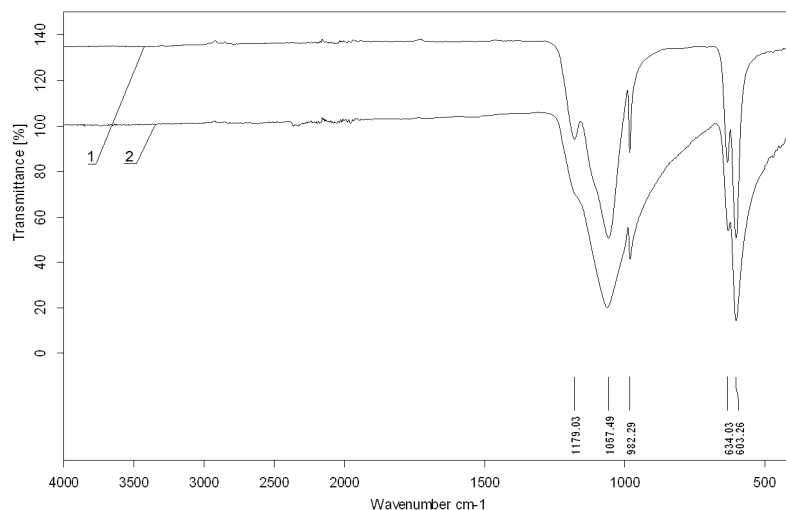


Fig. 5. FTIR of reference BaSO₄ (1) and BaSO₄ after thermal analysis (1,200 °C) (2)

Decreasing of intensity of the typical sulphate FTIR peaks after thermal reduction of sulphate is evident in Figure 6. The intensity of BaSO₄ peaks after reduction of mixture (2) is decreased but for the mixture (3) the peaks almost disappeared.

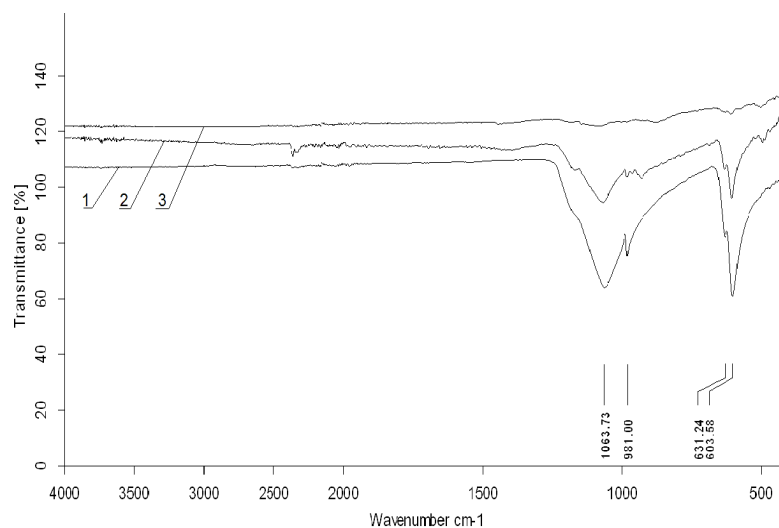


Fig. 6. Comparison of FTIR spectra of BaSO₄ (1), BaSO₄ + 2C (2), BaSO₄ + 4C (3), after thermal analysis (1,200 °C)

The presence of BaS after reduction of BaSO₄ was confirmed by colorimetric analysis using methylene blue method.

Conclusions

Precipitation of sulphates from water solution by the barium salts is most commonly used technology for treatment contaminated water. Due to the high cost of barium salts the methods for regeneration of BaSO₄ are examined. This research was oriented to the study of thermal reduction of BaSO₄ by powdered activated carbon. For reduction were used two mixtures in ratio 1:2 and 1:4.

It was found that the process of BaSO₄ reduction is running in the temperature range 800–900 °C and it is affected by the amount of carbon. The presence of larger amount of carbon shifts the peak of the endothermic process about of 27.4 °C to a higher temperature. For identification of reduction efficiency the amount of enthalpy for the endothermic peak belonging to the BaSO₄ modification changing was used. These results confirmed the formation of BaS too.

The reduction process was observed also by infrared spectrometry and colorimetry. The methods confirmed the presence of BaS after thermal analysis of mixture BaSO₄ with carbon.

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