THE STUDY OF COAL-DERIVED PYRITE USING ATMOSPHERIC PRESSURE TEMPERATURE PROGRAMMED REDUCTION (AP-TPR) AND TGA

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ABSTRACT

It is possible with AP-TPR to determine qualitatively as well as quantitatively the different organic sulfur forms in coal. The presence of pyrite might disturb an accurate sulfur determination by AP-TPR as is the case in other thermal techniques. Therefore it is important to have an insight into the behaviour of pyrite under the reducing experimental conditions. This study presents an explanation for the behaviour of pyrite subjected to a linear temperature increase up to 1000°C in an inert (TGA) as well as reducing (AP-TPR) atmosphere. Two pyrite samples were extracted from coal of the Halemba and Jastrzebie mine. As an example of the consequences of the presence of pyrite in coal, a discussion of the AP-TPR kinetogram of the Siersza coal of high pyritic sulfur content is included.

INTRODUCTION

Pyritic and organic sulfur are the two major sulfur forms in coal. Pyritic sulfur occurs mainly as iron sulfide, FeS_2. There are two naturally occurring forms of FeS_2, pyrite and marcasite of which pyrite is a major contributor to the total sulfur content of coals.

The AP-TPR technique is used to determine the organic sulfur functionalities in coal-derived materials. It is recommended to record pyrite free samples in order to overcome interference and to have an accurate view of the organic sulfur functionalities present in the raw coal. In the past, extraction with diluted nitric acid was commonly used to obtain pyrite free coal samples. Nevertheless, using this method, a complete removal is not always achieved when the pyrite is highly disseminated and present in particles of < 5 μm [1]. In addition, it has been demonstrated that the nitric acid treatment may have an influence on the coal structure and consequently some other organic sulfur functionalities might be changed [2]. More and more this treatment has been replaced by the lithium aluminium hydride procedure [3,4]. At the moment, $LiAlH_4$ is thought to cause selective desulfurization of the pyrite, although there is still a possibility that cleavage of di- and polysulfide linkages can occur. Moreover, a reduction of other organic sulfur compounds is not excluded.

The AP-TPR technique proved to be very promising for monitoring the consequences of different types of selective chemical treatments on coal [5]. In those cases, the ability in distinguishing pyritic sulfur from organically-bound sulfur is very desirable. The AP-TPR analysis has appeared to be useful in following the changes in the organic sulfur functionalities induced by heat treatment of coal as well [6].

The purpose of this paper is to present results of our study on the conversion of coal pyrite during the AP-TPR experiment. For this purpose coal pyrite was chosen to avoid a discrepancy which could be arised from the use of mineral pyrite. Moreover, coal-derived pyrite can be enriched in trace elements which can affect on its reactivity [7].

EXPERIMENTAL

a) Samples

The two pyrite samples studied in this paper are extracted from the Halemba and Jastrzebie coal. The pyrite concentrates are firstly cleaned by means of gravity separation and consequently by magnetic separation. The obtained coal-derived pyrites show a high degree of purity, which is determined by X-ray diffraction analysis.

The subbituminous coal sample originates from the Siersza mine (Poland) and is chosen for its high pyritic sulfur content of 4.17 wt%.

b) Used Techniques

Powder X-ray diffraction (XRD) with Mo K_α radiation was used for identification and purity control of the extracted pyrite samples.

Atmospheric Pressure-Temperature Programmed Reduction (AP-TPR) experiments are recorded

according to the procedure mentioned in previous papers [5,8,9]. A further optimization is performed by using a MKS flow controller (Model 2476). This set-up guarantees a flow of 50 cm^3 min^{-1} H_2-gas through the reactor during the entire AP-TPR experiment. All experiments are recorded with a heating rate of 5 °C min^{-1} and without the use of a reducing mixture. In this study the experimental AP-TPR data are smoothed by a more narrow 11 point Savitsky-Golay-Gorry filtering algoritm [10,11]. This change results in sharper signals and more detailed AP-TPR profiles. All samples were grounded before analysis to a particle size of less than 147 µm.
The Thermographical Analysis (TGA) experiments are performed with a TA Instruments (formerly Du Pont) Model 2000-951 apparatus. The samples (20-30 mg) are heated up to 1000°C at a heating rate of 5 °C min^{-1} in a pure argon gas stream of 50 cm^3 min^{-1}. The TGA data manipulation was performed using a 13 point smoothing filter of the Savitsky-Golay procedure.

RESULTS AND DISCUSSION

In Figure 1 the AP-TPR kinetogram of the Halemba pyrite sample is presented. The profile consists of two well separated maxima. The first temperature maximum is found at approximately 570 °C and the second at 690 °C. From this point it is clear that the pyrite (FeS_2) is not reduced in one step, but in two. The difference in shape between the two peaks also suggests a difference in reducing conditions. For the pyrite extracted from the Jastrzebie coal, the AP-TPR profile is comparable, as can be seen in Figure 1. In this kinetogram the maximum reducing temperatures are at 575 °C and 675 °C. Here the difference between the two reducing step mechanisms is even more obvious. Relatively, the first reducing peak has gained in intensity and the second peak has broadened even more in comparison to the Halemba pyrite curve.
In order to understand better the reason for this phenomenon, a TGA experiment is carried out under an argon atmosphere on the Halemba pyrite sample. The TGA plot is shown in Figure 2. Undoubtly, there is only one sharp peak at 600 °C visible. Calculations have proven that the mass decrease of 27.73 % during the experiment corresponds with a loss of 0.19 mmol sulfur for an amount of 0.18 mmol pyrite which was originally present in the examined sample. Taking into account the experimental error, this calculation illustrates that indeed only one sulfur is liberated for each FeS_2 molecule. Consequently, the signal in Figure 2 has to result from the thermal decomposition of pyrite into troilite (FeS) and elemental sulfur. The corresponding chemical reaction can be written as follows:

$$FeS_2\,(s) \xrightarrow{T\nearrow,\ Ar} FeS\,(s) + S\,(g)$$

In an inert atmosphere this reaction takes place at approximately 600 °C. The first Halemba pyrite maximum reduction temperature of the AP-TPR kinetogram in Figure 1 is found at 570 °C. From non-isothermal kinetic studies it is known that the removal of sulfur from pyrite under hydrogen is more favorable than under an inert atmosphere [12,13]. This can explain the 30 °C temperature difference between the thermal decomposition under argon and the AP-TPR reduction under H_2 atmosphere. Consequently, this means that probably the first reduction step of pyrite takes place after thermal liberation of the elemental sulfur. In the gaseous phase this sulfur will then react with the H_2-gas forming H_2S and is as such detected. This gas phase reaction proceeds rapidly, which is translated in a corresponding sharp, high peak in the AP-TPR kinetogram. The same profile characteristics can be seen in the Jastrzebie pyrite kinetogram in Figure 1. It also seems that the first reduction peak of both pyrite samples is at almost the same temperature.
The TGA experiment shows that the troilite does not decompose thermally at temperatures up to 1000 °C. In consequence, the second reduction peak in both pyrite AP-TPR kinetograms can thus be attributed to the direct reduction of FeS. In contrast with the first reduction peak, this reaction occurs between the H_2-gas and FeS in the solid phase according to:

$$FeS\,(s) + H_2\,(g) \xrightarrow{T\nearrow} Fe\,(s) + H_2S\,(g)$$

This solid phase mechanism causes the broadening of the second pyrite reduction peak. The H_2-gas reacts with the surface of the solid troilite which causes a slower reduction and consequently a broader reduction peak in comparison to the former gas-gas reaction. Consequently, the second reduction peak of the Halemba and Jastrzebie kinetograms are not so similar as the first. The peaks do not have the same maximum reduction temperatures, nor the same shape. Assumed is that this reduction in the solid phase is strongly dependent on the morphology. Minor physical differences of the troilite surface can affect the course of the reduction process. In consequence, the AP-TPR kinetogram can look a little different for each experiment if the troilite particles originating from the thermal decomposition of pyrite have a different particle size or different surface characteristics. Because of the nature of the solid-gas reduction, the peaks exhibit a broad contour. Depending on the relative concentrations, this band can usually be seen as a background on which possible reducing peaks of other sulfur groups present in for instance coal are superimposed.

As an example, the kinetograms of two AP-TPR experiments of the same Siersza coal sample are shown in Figure 3 and 4. Both profiles exhibit one sharp, intense peak that can easily be recognised as the first reduction peak of pyrite: the reduction of elemental sulfur in the gaseous phase. The Siersza coal was chosen for its high pyrite content (4.17 wt%) which explains the rather stupendous appearance of the first pyrite reduction peak in the kinetogram. As predicted, the second reduction peak is not so reproducible. This does not disturb the organic sulfur reduction peak characterization at 750-760 °C. The coal sample kinetograms prove that a qualitative analysis can be possible, even though the troilite reduction peaks are not exactly reproducible and the reduction conditions are hard to control. Also, it can be stressed upon that these experiments also suggest that most of the elemental sulfur, thermally liberated from pyrite, is reduced by the H_2-gas under AP-TPR conditions. However, still a smaller amount of elemental sulfur could have reacted with the organic matrix to form organic sulfur groups which will be reduced at higher temperatures. The extend of this taking place is not known at this point, but will be the subject of further investigations. If the objective of the AP-TPR analysis is to study the organic sulfur distribution in coal, than it may be opportune to remove the pyrite in advance. In this way, no elemental sulfur can react with the organic matrix and the troilite reduction peak can not interfere with the organic sulfur reduction peaks.

CONCLUSIONS

In this study the mechanism of pyrite reduction is explained. It is demonstrated that in the first reduction step sulfur is thermally liberated from FeS_2. In the AP-TPR experiment this S-gas is then reduced into H_2S at approximately 570 °C. Around 680 °C, the solid FeS is transformed under a reducing atmosphere into Fe and H_2S.

The kinetogram of a pyrite sample exhibits at first a sharp reduction peak followed by a broader and less intense reduction band. Because of the characteristic reduction peak at approximately 570 °C, pyrite can easily be recognised in the AP-TPR kinetogram of most coal samples. The troilite reduction peak at approximately 680 °C is in most cases too broad to be of great disturbance for the AP-TPR analysis of coal. The organic sulfur group reduction peaks will only be superimposed upon the FeS band.

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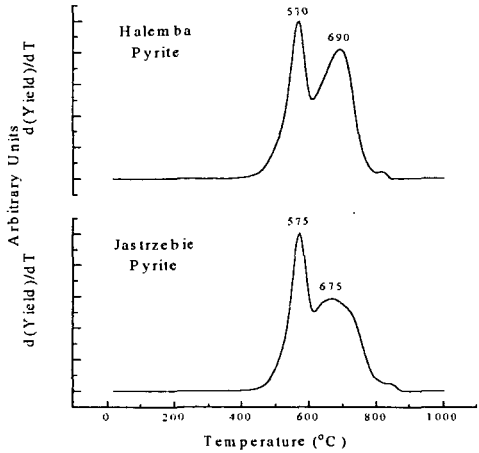

Figure 1 : AP-TPR kinetograms of the Halemba and Jastrzebie pyrite sample

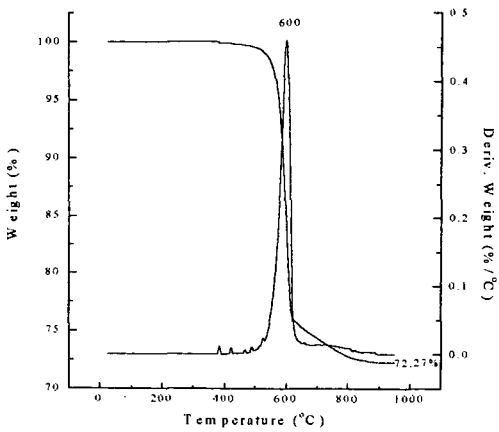

Figure 2 : TGA spectrum of the Halemba pyrite sample

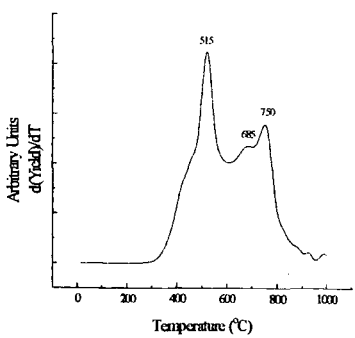

Figure 3 : AP-TPR kinetogram of the Siersza coal sample - I

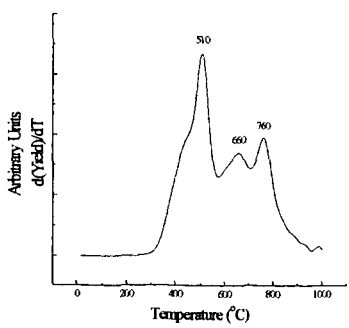

Figure 4 : AP-TPR kinetogram of the Siersza coal sample - II