HYDROTHERMAL REACTION OF $CA(OH)_2$ WITH QUARTZ IN COAL

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ABSTRACT

Quartz is generally most abundant as mineral matter in coal. In order to obtain fundamental information for chemical demineralization of coal with $Ca(OH)_2$, the hydrothermal reaction of $Ca(OH)_2$ with reagent quartz has been studied in detail. The results showed that the quartz was converted to various silicates, depending on autoclaving conditions. At a CaO/SiO_2 ratio of about 1, quartz was initially converted to $Ca_2SiO_4 \cdot H_2O$, then to tobermorite-like compounds, and finally to xonotlite. Higher temperature and longer reaction time are preferable to the complete conversion of quartz. The formed calcium silicates were susceptible to dissolution in acid.

INTRODUCTION

The presence of minerals in coal causes many serious disadvantages in coal utilization. A great deal of effort has been concentrated on removal of mineral matter from coal. Chemical cleaning has attracted much attention because of its high removal efficiency[1,2]. In general, however, high processing costs have been a major barrier to commercialization of these processes. We proposed a chemical leaching method by using a cheaper and less corrosive reagent, lime, for coal demineralization and found that 75% of the ash in Newstan coal could be removed from coal[3].

Among numerous mineral species present in coal, quartz, together with clays, carbonates and sulfides constitute the most common species[4]. Therefore, the understanding of the reaction between $Ca(OH)_2$ and quartz is of fundamental significance as far as coal demineralization by $Ca(OH)_2$ leaching is concerned. Although the reactions in the system of quartz/lime/water have been investigated in relation to cement and concrete production[5,6], the reactions were extremely complex and the products considerably varied with the hydrothermal conditions. The principal aim of this paper is to study the hydrothermal reaction between $Ca(OH)_2$ and reagent quartz from the standpoint of coal demineralization. On the basis of the results obtained by using pure quartz, the reaction between $Ca(OH)_2$ and quartz in coal is further examined.

EXPERIMENTAL

Pulverized lime used in this study contained 40 ± 15 % of $Ca(OH)_2$ (estimated by TG analysis) with other impurities of less than 2 %. α-Quartz (Kanto Chemical Co.) had a particle size distribution of -325 mesh: 30 %, 325-200 mesh: 68 % and 200-100 mesh: 2%.

Hydrothermal reactions were carried out at saturated steam pressures using an autoclave equipped with a stirrer. About 2.5 g of quartz powder with a pulverized lime was used for each run with 150 ml of distilled water. After being autoclaved, all specimens were dried at 105°C under a nitrogen atmosphere. The specimens were stored in tightly stoppered bottles. The coal demineralization method was in detail described elsewhere[3].

The assignment of products by X-ray diffraction (XRD) was carried out after drying at 105°C, whereas the semi-quantitative XRD analysis to determine the amount of unreacted quartz was made after heat treatment at 850°C. After this treatment, most of calcium silicates were nearly free of water and this procedure enables to evaluate the exact weight of sample on

an XRD sample holder. X-ray photoelectron spectroscopy (XPS) analysis was accomplished with Shimadzu ESCA 750 spectrometer. Scanning electron microscopes (SEM) used were Cambridge S360 with Tracor Northern EDAX equipment and Hitachi S2250N with Link System EDAX equipment.

RESULTS AND DISCUSSION

Hydrothermal reaction between $Ca(OH)_2$ and reagent quartz

Selected X-ray diffraction patterns for the samples obtained at 300°C are illustrated in Figure 1. Table 1 lists the reaction products obtained at various temperatures with a CaO/SiO_2 molar ratio of 0.93 ± 0.02. At 175°C, the major product was $Ca_2SiO_4 \cdot H_2O$ ($C_2\bar{S}\bar{W}(A)$ according to Eitel's nomenclature[7]). Some other weak peaks were difficult to be identified, however they were probably due to compounds similar to tobermorite ($Ca_4Si_5O_{14} \cdot 5H_2O$)[5]. At 250°C and 300°C, the major product was also $Ca_2SiO_4 \cdot H_2O$ during a relatively short period of time, but tobermorite-like compounds were more distinct than at 175°C especially after 5 h. At 7 h, the XRD intensity for a new phase, xonotlite, became very strong and the peak for $Ca_2SiO_4 \cdot H_2O$ almost disappeared at both temperatures. When the temperature was raised up to 340°C, the tendency of the changes of products with time was virtually the same as observed for 300°C, although the reaction became more prompt. Only xonotlite was observed after 5 h.

The variations of quartz conversion with time during autoclaving at different temperatures are shown in Figure 2. When the autoclaving at 175°C was prolonged up to 12 h, about half of quartz was converted and $Ca(OH)_2$ disappeared completely (Table 1). A higher temperature is necessary to convert the rest of quartz. At higher temperatures, the quartz conversion took place in two stages. The first stage was a relatively rapid reaction in which the main reaction was the formation of $Ca_2SiO_4 \cdot H_2O$. Thus, it can be said that at a CaO/SiO_2 molar ratio of about 1, this stage roughly terminated when half of quartz was converted. In the second stage, the main reactions were the transformation of $Ca_2SiO_4 \cdot H_2O$ to tobermorite-like compounds and/or xonotlite. These reactions were relatively slow compared with the formation of $Ca_2SiO_4 \cdot H_2O$.

XPS analysis was used to determine the binding energy of Si_{2p} in reagent quartz and in two treated samples (No. 9 and No. 13 presented in Table 1). The XPS spectra showed that the chemical environment of Si greatly changed due to the formation of $Ca_2SiO_4 \cdot H_2O$ and xonotlite. This change may be related to greater solubility of the products in acidic solution.

Interaction between $Ca(OH)_2$ and quartz in coal

Newstan coal was taken as an example. The properties of this coal were presented previously[3]. The examination of this coal, by XRD analysis and SEM-EDAX analysis, showed that quartz and clay were dominated mineral phases in the original coal. When the coal was subjected to $Ca(OH)_2$ leaching followed by a dilute HCl washing, the XRD analysis showed that most of quartz could be removed. Figure 3 is the SEM-EDAX analysis of a treated sample obtained at 320°C and 1.5 h by use of 5% CaO before acid washing. The observed particle was strongly attacked by $Ca(OH)_2$, forming Ca-bearing phases. Elements in spot A were mainly Ca and Si, which might be a calcium silicate derived from the reaction between $Ca(OH)_2$ and quartz. The rich elements in Spot B were Ca, Si and some Al. This observation suggests another important reaction occurring between $Ca(OH)_2$ and clays in coal. The SEM analysis of the acid-washed sample indicated that the Ca-bearing silicate products were removed by the acid solution. After the acid-washing of the treated sample, the ash content was reduced from 9.2 % of the original coal to 2.6 %. As can be seen from Figure 2, the above autoclaving condition (320°C, 1.5 h) was not enough for a complete removal of quartz. Thus we tried to use a longer reaction time for demineralization of Newstan coal. The treatment at 300°C for 7 h produced a clean coal with much lower ash content, 1.0 %.

CONCLUSION

1. Upon the hydrothermal reaction with $Ca(OH)_2$, quartz formed various hydrated calcium silicates, depending on the autoclaving conditions. Increasing temperature from 175°C to 340°C significantly accelerated the reaction.

2. At a CaO/SiO_2 ratio of about 1, the reaction between $Ca(OH)_2$ and quartz initially resulted in $Ca_2SiO_4 \cdot H_2O$. As the reaction proceeded, $Ca_2SiO_4 \cdot H_2O$ progressively reacted with residual SiO_2 to form tobermorite-like compounds. Final product at higher temperature and longer time was xonotlite. Through these reactions, quartz could be completely converted to calcium silicates.

3. Quartz was a major mineral phase in Newstan coal. During the leaching of this coal, the quartz was reacted by $Ca(OH)_2$ forming Ca-bearing phases, which was removed by dilute HCl washing. The ash content could be reduced from 9.2 % to 1.0 %.

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Table 1. Products of hydrothermal reactions of $Ca(OH)_2$ with quartz at a CaO/SiO_2 molar ratio of 0.93.

	Conditions		Products*				
No.	Temp. (°C)	Time (h)	SiO_2	$Ca(OH)_2$	A	T	X
1	175	3	vs	m	s	w	-
3	175	7	vs	s	s	w	-
4	175	12	s	-	vs	w	-
5	250	1.5	vs	s	s	w	-
6	250	3	vs	w	s	m	-
7	250	5	s	-	vs	m	-
8	250	7	s	-	-	m	vs
9	300	1	vs	s	s	w	-
11	300	3	s	w	vs	w	-
12	300	5	m	-	s	m	s
13	300	7	-	-	-	-	vs
14	340	0.75	vs	w	s	s	-
17	340	5	-	-	-	-	vs

* A: α-Dicalcium silicate hydrate ($Ca_2SiO_4 \cdot H_2O$); T: Tobermorite-like compounds; X: Xonotlite ($Ca_6Si_6O_{18} \cdot H_2O$). vs: very strong; s: strong; m: medium; w: weak.

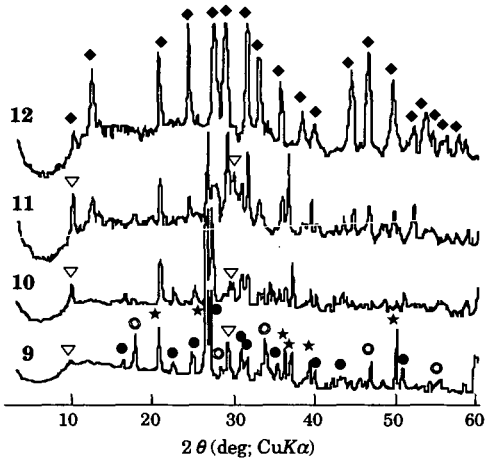

Figure 1 XRD patterns of the specimens obtained at 300°C. The sample numbers indicated correspond to those in Table 1. ●: $Ca_2SiO_4 \cdot H_2O$; ★: Quartz + $Ca_2SiO_4 \cdot H_2O$; ◎: $Ca(OH)_2$; ▽: Tobermorite-like compounds.

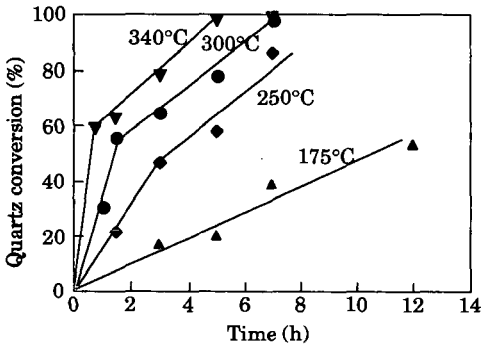

Figure 2 Quartz conversion during the hydrothermal reaction at a CaO/SiO_2 molar ratio of 0.93.

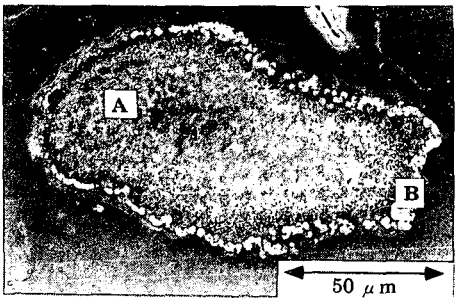

Figure 3 Scanning electron micrograph of mineral matter in coal after the reaction with $Ca(OH)_2$.