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DEMINERALISATION OF A SEMIANTHRACITE CHAR WITH MOLTEN SALTS.

A STUDY BY FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

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Resumen

Los efectos de los tratamientos químicos y térmicos en una semiantracita (AN) y en una semiantracita carbonizada (AC) sobre la composición de la fracción mineral del material son investigados. La muestra AC, fue primero tratada con una mezcla de LiCl/KCl o bien una mezcla de LiCl/KCl y un óxido metálico M_n= 1 o 2O (MgO, CaO, FeO, CoO, NiO, C_u2O or ZnO), a 470, 600 o 900 ºC y los productos obtenidos fueron entonces cuidadosamente lavados con agua destilada. Los cambios en la composición fueron estudiados por FTIR. Los componentes minerales inicialmente presentes en la semiantracita (AN) son moscovita y/o caolinita, cuarzo y anquerita, y en la semiantracita carbonizada (AC) son cuarzo, mullita, moscovita y/o caolinita. Los tratamientos de AC dan lugar a cambios significativos en la fracción mineral del material, en particular cuando la mezcla usada fue LiCl/KCl/MgO o LiCl/KCl/CaO a la más alta temperatura, 900 ºC.

Abstract

The effects of chemical heat treatments of a semianthracite (AN) and a semianthracite char (AC) on the composition of the mineral fraction of the material are investigated. Sample AC was first treated with a mixture of LiCl/KCl or a mixture of LiCl/KCl and a metallic oxide, M_n= 1 o 2O (MgO, CaO, FeO, CoO, NiO, C_u2O or ZnO), at 470, 600 or 900 ºC and the products obtained were then washed thoroughly with distilled water. The composition changes were studied by FTIR. The predominant mineral components initially present in the semianthracite (AN) are muscovite and/or kaolinite, quartz and ankerite, and in the semianthracite char (AC) are quartz, mullite, muscovite and/or kaolinite. The treatments of AC resulted in significant changes in the mineral fraction of the material, in particular when the mixture LiCl/KCl/MgO or LiCl/KCl/CaO was used for the highest temperature, 900 ºC..

1.Introduction

Generally, the methods of demineralisation of the coal are based on physical and chemical processes. The simplest and economic method consists of warming up the material in the presence of water. The operation of extraction of components minerals of the coal can be made in a Soxhlet system. Of this form they eliminate alkaline metal salts mainly. Like a variant of the method, it would be possible to be warmed up to the temperature of boiling of the water and to be used changers of ions. With glacial acetic acid, alkaline metal salts and of iron are extracted. On reduced scale of laboratory, and the object to obtain its demineralisation, the coals are treated frequently with dissolutions of acids HCl and HF to 15 ºC . Using HF it is possible to eliminate all the components almost completely minerals of the coal. A form to come, that was recommended [1-2] does already enough time for a carbonaceous material like the activated charcoal, consists of to mix 1 kg of coal with 4 l of HF of 35% (appropriate container can be bottle or a plastic bottle, that is covered with paper with paraffin) and in leaving later to react the mixture during several days. Next the residual liquid separates by movement and successively washes the coal with dissolution of HC1 and NH4OH and with water distilled until chloride absence.

2. Material and methods

2.1. Materials, reagents and experimental procedures

In this study, a semianthracite (AN) from Peñarroya (Córdoba, Spain) was used. Its ash content was 42.5 wt. % dry basis [3]. The as received coal was oven dried, ground, and sized, between 0.15 and 0.20 mm being chosen. After these operations the material was first carbonised at 1000 ºC for 2 h in N^2 (purity > 99.998 vol %, flow rate = 100 cm3min-1). Subsequently, around 5 g of the carbonised product (AC, hereafter) were treated with 5 g of either LiC^1/KC^1 (60/40 mol %, mp = 450 ºC) or 5 g of LiCl/KCl/metallic oxide [4 g Cl-/1 g metallic oxide, $M_n=^1$ o ^1O (MgO, CaO, FeO, CoO, NiO, Cu^2O or ZnO)] at 470, 600 or 900 ºC for 5 h in N^2. After that, the product obtained was thoroughly washed with distilled water until absence of C^1- ions from residual liquid and oven-dried a 110 ºC for 24 h. The samples were given the symbols AC-LiC^1-KCl-T, AC- $M_n=^1$ o^2O-T (T, maximum heat treatment temperature = 470, 600 or 900 ºC) depending upon whether the preparation was carried out with the LiCl/KCl mixture or with the $LiC^1l/KC^1/$ M_n = 1 o 2O.

2.2. Analysis tools

All of the samples were characterized by FTIR. The FTIR spectra were obtained from KBr discs (1.2 mg of sample per 250 mg of KBr) by co-adding 20 scans at a resolution of 4 cm-1. Spectra were recorded between 5000 and 370 cm-1, using a Perkin-Elmer 1720 spectrometer. The spectrum of a similar mass KBr disc was subtracted from the spectrum of each sample.

3. Results and discussion

In this section it will be come to the study of the influence of the temperature from sample preparation on the chemical composition of the inorganic fraction of the same ones. The symbols, formulas and the inorganic components in the samples which were identified by FTIR appear in Table 1. It may also be inferred that chemical heat treatments of the AC produce important changes in the inorganic fraction of the material. Their magnitude depends upon whether the mixture was used LiC^1/KC^1 or $LiC^1/KC^1/$ $M_n=$ ^{1} o ^2O, upon the heat treatment temperature used.

In order to facilitate their comparison, in the Fig. 1 the spectra AN and AC are imagining together. At sight of this figure it can be verified that certain absorption bands or disappear completely of the AN spectrum or experience a very important diminution in their intensity in the AC spectrum. Between first is the band to 1437 cm-1, that has been associated with present carbonates in the coal. Logically, these results were to anticipate considering that the carbonates disturb thermally when AN is warmed up to 1000 °C during 2 h in the preparation of AC, and they are transformed into corresponding metallic oxides.

The effects on the chemical composition of the mineral fraction of the product carbonised, AC, they are, as a rule, more important when a metallic oxide is added to the mixture of chlorides, and in special when this oxide is CaO. In this case, with the increase of the temperature favours the formation of a series of different chemical species, dominating the spurrite one in the prepared sample to 470 ºC and the kaolinite in the sample warmed up to 900 ºC. The presence of this silicate in last sample seems much more to be elevated that the one of the quartz.

Table 1
Symbols, formulas and the inorganic components in the samples which were identified by FTIR.

Symbols, formulas and the inorganic components in the samples which were identified by FTIR.		
Components	**Symbols**	**Formulas**
Ankerite	A	$Ca(Fe,Mg)(CO_3)_2$
Bunsenite	B	NiO
Calcite	Cc	$CaCO_3$
Calcium orthosilicate	SC	Ca_2SiO_4
Cobalt monoxide	OM	CoO
Cobalt tetroxide	OT	Co_3O_4
Dolomite	D	$CaMg(CO_3)_2$
Forsterite	F	Mg_2SiO_4
Hydromagnesite	H	$Mg_5(OH)_2(CO_3)\cdot 4H_2O$
Kaolinite	Ca	$Al_2Si_2O_5(OH)_4$
Lime	Cl	CaO
Magnesioferrite	Mf	$MgFe_2O_4$
Mullite	Mu	$Al_2Si_2O_{13}$
Muscovite	Mo	$KAl_2(Si_3Al)O_{10}(OH,F)_2$
Periclase	P	MgO
Quartz	C	SiO_2
Spurrite	E	$Ca_5(SiO_4)_2CO_3$
Tenorite	Te	CuO
Zincite	Z	ZnO

Table 2

Samples	**Components***
AN	Mo/Ca, C, A
AC	C, Mu, Mo/Ca
AC-LiCl-KCl-470	C, Mo, Mu, Mf
AC-MgO-470	C, P, Mu, Mg, Mf
AC-CaO-470	E, C, Mo/Ca, Mu, Mf
AC-FeO-470	C, Mu, Mo, Mf, Cc
Ac-CoO-470	C, OT, Mu, OM
AC-NiO-470	C, B, Mo, Mf, Mu
AC-Cu_2O-470	C, Te, Mu, Mo, Mf
AC-ZnO-470	Z, C, Mu
AC-LiCl-KCl-600	C, Mo/Ca, Mu, Mf
AC-MgO-600	C, F, P, Mu, Mo, Ca, Cc, Mf
AC-CaO-600	C, SC, Mo/Ca, Mu, Cc, Cl
AC-FeO-600	C, Mo/Ca, Mu, Cc, Mf
Ac-CoO-600	C, OT, Mo/Ca, Mu, OM
AC-NiO-600	C, B, Mo/Ca, Mu, Mf
AC-Cu_2O-600	C, Mo/Ca, Mu, Mf
AC-ZnO-600	C, Z, Mo/Ca, Mu, Mf
AC-LiCl-KCl-900	C, Mo/Ca, Mu
AC-MgO-900	C, F, Mo/Ca, H, P
AC-CaO-900	C, Mo/Ca, Mu, Cc, D
AC-FeO-900	Mo/Ca, C, Mu, Mf, Cc
AC-CoO-900	C, Mo/Ca, Mf, Cc
AC-NiO-900	C, B, Mo/Ca, Mf, Cc
AC-Cu_2O-900	C, Te, Mo/Ca, Cc
AC-ZnO-900	C, Mo/Ca, Mf, Cc

*The different components appear ordered for each in sequence descendant sample with respect to their amount, thus for sample AN, Mo/Ca > C > A. When symbol / is put, it means that a component exists as much as another one and in similar amount.

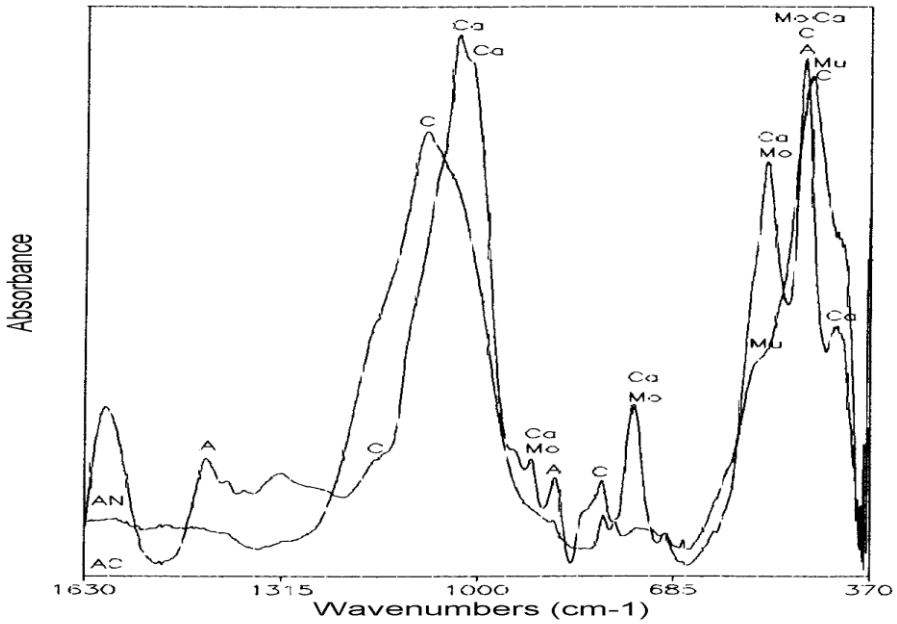

Fig1: FTIR.spectra.samples: Anand AC.

It stops most of remaining metallic oxides and in individual for FeO and ZnO, the changes of composition are also very important to 900 ºC. In the case of the FeO one a diminution accused in the content takes place very of some of main components, like the quartz. For some oxides, like FeO and Cu^2O, these changes are already of a certain importance to 600 ºC.

4. Conclusions

According to the results of FTIR, the treatment of the product carbonised, AC, with the LiC1-KC1 mixture to 600 and 900 ºC, due to the interaction chemistry of the chloride mixture with mineral components of the material, gives rise to formation of silicates of different composition. When a metallic oxide to this mixture is gotten up detects the presence of one or more metallic oxides in excess. The samples also can contain other species chemistries, like for example magnesioferrite (Mf, MgFe2O4).

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