Behavior of chlorine during co-carbonization of coal and chloride compounds in cokemaking process

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ARTICLE INFO

ABSTRACT

The behavior of chlorine during co-carbonization of coal and chloride compounds such as PVC in cokemaking process both on a laboratory scale and commercial scale was investigated. On a laboratory scale test, the chlorine residue ratio in coke derived from PVC was only 0.04%, which was much lower than that derived from the coal tested (35.1%) and NaCl (52.9%). The chlorine residue ratio derived from PVC reached near zero at about 400 °C and it decreased at lower temperature range than that derived from $MgCl_2$, NaCl and $CaCl_2$. CaO addition helped the chloride derived from coal, PVC and NaCl to be fixed in coke. In the commercial scale coke oven, the addition of PVC to coal hardly affected the chlorine content in coke and COG. Most of the released chlorine was absorbed by the ammonia liquor spray for cooling hot COG. The chlorine in PVC was distributed to the coke, the ammonia liquor and the COG by 7%, 92% and 1% respectively, while the chlorine in coal was distributed by 43%, 56% and 1% respectively. The chlorine residue ratio in coke derived from PVC was much lower than that derived from coal since the decomposition of PVC added to coal was much faster than the release of chlorine from coal during carbonization.

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1. Introduction

High levels of chlorine in coal may cause boiler corrosion problems in coal combustors and the coal conversion process (Cross et al., 1996; Hodges et al., 1983; Huggins and Huffman, 1995). Thus there have been many studies on the mode of occurrence of chlorine in coal (Caswell et al., 1984; Chou, 1991; Dai et al., 2008; Fynes et al., 1988; Hower and Gayer, 2002; Huggins, 2002; Vassilev et al., 2000; Wei et al., 2004; Yudovich and Ketris, 2006) and the removal of chlorine from coals by heating to a relatively low temperature (200 to 300 °C) under nitrogen or air (Daybell and Pringle, 1958; Edgecombe, 1956; Fynes et al., 1988; Herod et al., 1983). In the steel industry, bituminous coals are carbonized into coke in coke ovens and coke is charged into blast furnaces with sintered iron ore to produce pig iron. In this process chlorine in coke is released as HCl and could cause corrosion problems in blast furnace facilities, then it is important to know the chlorine content in coke and the behavior of coal chlorine in the cokemaking process. In the previous paper (Nomura, 2010), we reported on the determination of chlorine in bituminous coals commercially used for cokemaking and in the resultant coke. Furthermore, we investigated the behavior of chlorine in coal during carbonization in coke ovens.

On the other hand, the waste plastic recycling process using coke oven was developed and several commercial scale plants have been operating (Nomura and Kato, 2006). In this process, the agglomerated waste plastics are blended with coal and carbonized in a coke oven chamber. The waste plastics are converted to coke, tar, light oil and coke oven gas (COG) and recycled. To date, NSSMC (Nippon Steel & Sumitomo Metal Corporation) has established waste plastic recycling facilities at five steelworks throughout Japan. Approximately 200,000 tons a year of plastic containers and packaging collected from general households is recycled using a coke oven and an addition of waste plastic in the coal blend is about 1 wt.%. Since household waste plastics include a small amount of poly(vinyl chloride) (PVC), chlorine in waste plastics as well as in coal has become an important subject. This paper reports the behavior of chlorine during co-carbonization of coal and chloride compounds such as PVC in cokemaking process both on a laboratory scale and commercial scale.

2. Experimental

2.1. Sample used

In fundamental experiment on a laboratory scale, coals F and H were used with similar average random vitrinite reflectance (1.22 and 1.18%) and the same volatile matter (23.8%). The characterization data and chlorine content are given in Tables 1 and 2. These are bituminous coals commercially used in the steel industry for cokemaking. Blended coal samples B1, B2 and B3 were used in a commercial scale coke oven test and a pilot scale coke oven test. The chlorine contents in B1,

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Table 1
Characterization data for the coals used.

Coal	Country	Proximate analysis (mass% db)		Ultimate analysis (mass% daf)		Dilatometry Total dilatation (vol.%)	Gieseler plastometry Maximum fluidity (log MF/ddpm)	Petrographic analysis	
		VM	Ash	C	H			Reflectance (av.) (%)	Total inerts (vol.%)
F	Australia	23.8	9.1	90.0	4.9	119	2.82	1.22	31.0
H	Australia	23.8	9.9	89.5	5.0	106	2.99	1.18	35.1

Table 2
Chlorine content in coal and coke. (n.a. : no data available; * heat treatment condition : N_2, 10 °C/min, 900 °C).

Coal	Inorganic constituents in coal				Inorganic constituents in coke*		Coke yield* ($-$)	Chlorine residue ratio (%)
	Na_2O (ppm)	CaO (%)	Cl_{coal} (ppm)	Water soluble chlorine ratio (%)	Cl_{coke} (ppm)	Water soluble chlorine ratio (%)		
F	278	0.194	210	84.3	97	90.7	0.759	35.0
H	438	0.078	471	n.a.	179	n.a.	0.781	29.7

B2 and B3 were 450, 455 and 550 ppm respectively. In order to investigate the behavior of chlorine during co-carbonization of coal, PVC powder, NaCl (Kanto Kagaku, >99.0%), $CaCl_2$ (Kanto Kagaku, >95.0%), $MgCl_2$ $6H_2O$ (Kanto Kagaku, >98.0%) and CaO (Kanto Kagaku, >98.0%) were used as additives. The main objective of using thermally stable and water-soluble metal chlorides is for comparison with PVC that it has opposite properties, organic chlorine water-insoluble and thermally unstable during the first stages of pyrolysis.

2.2. Analyses of chlorine in coal, heat-treated coal and coke

The chlorine content of the various coal samples was determined by the high temperature tube furnace combustion and ion exchange chromatography method. The high temperature tube furnace combustion method was based on the sulfur determination method, JIS M8813, where 0.2 g of the sample was subjected to combustion under oxygen flow at 1350 °C. The combustion gas was made absorbable by 80 ml of 1/500 N NaOH aqueous solution. After the solution was diluted, the chlorine concentration was measured with ion exchange chromatography (DIONEX, 2000 i/sp). Measurement range of chlorine concentration was 0.1 to 10 ppm and was made to three significant figures. Measurement was carried out twice for each sample and analysis error was within 5%.

2.3. Thermogravimetric analysis

The weight loss was measured as a function of temperature using TGA for coal H and poly(vinyl chloride) (PVC). The instrument used was a Seiko SSC5200 series thermal analyzer. Coal sample was crushed to less than 150 μm. About 10 mg of the sample was put into the sample cell of the TGA and carbonized at a constant heating rate of 3 °C min^{-1} from room temperature to 1000 °C in a nitrogen atmosphere of which the flow rate was 200 cm^3 min^{-1}.

2.4. Preparation of coke and heat-treated coal sample

The coal samples crushed to <1 mm and with a weight of 1.5 g were put in an alumina combustion boat (85 mm in length, 10 mm in width and 10 mm in depth) and the boat was set in a quartz tube (63 mm in diameter and 600 mm in length). The sample was heated in a stream of nitrogen (1 Nl min^{-1}) in an infrared gold image furnace (ULVAC-RIKO, Inc., type RHL-P610, heating zone length 265 mm) as shown in Fig. 1. The temperature was controlled by a thermocouple placed on the sample. The sample was heated to 900 °C at a heating rate of 10 °C min^{-1} and quenched soon after the temperature reached the desired value. In this report the sample heat-treated to 900 °C is called the "coke" sample.

The ratio of the chlorine content in the heat-treated sample to that in the coal was defined as the chlorine residue ratio derived from coal ($ClRR_{coal}$ (%)) and obtained by the following equation. The chlorine concentration in a solid sample (mg-chlorine/kg-solid on a dry basis) is expressed by ppm.

$$ClRR_{coal} = (Cl_{heat-treated} \times m_{heat-treated})/(Cl_{coal} \times m_{coal}) \times 100$$

where $Cl_{heat-treated}$ (ppm) is the chlorine concentration in the heat-treated sample, $m_{heat-treated}$ (g) is the mass of the heat-treated sample, Cl_{coal} (ppm) is the chlorine concentration in the coal and m_{coal} (g) is the mass of the coal.
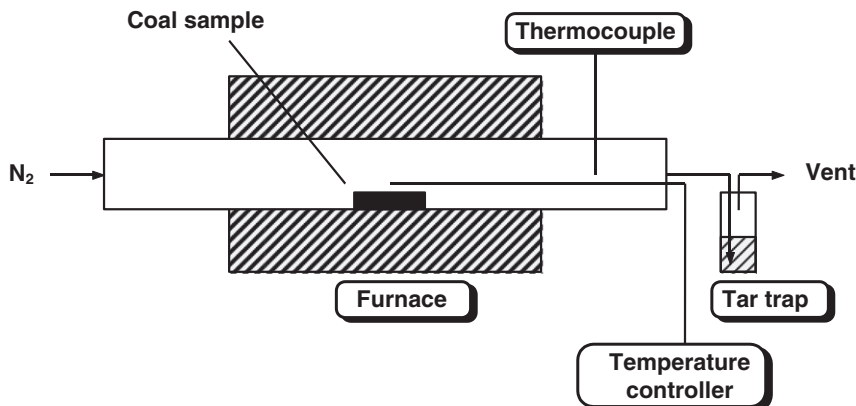
Fig. 1. Experimental apparatus for carbonization.