



HOKKAIDO UNIVERSITY

Title	A Preliminary Experiment of Volatilization of Minerals in Coal Ash by Chlorination Treatment
Author(s)	Shimada, Taihei; Kumagai, Takehiko; Tsurue, Takashi et al.
Citation	日本エネルギー学会誌, 76(2), 134-144 https://doi.org/10.3775/jie.76.134
Issue Date	1997-02-20
Doc URL	https://hdl.handle.net/2115/74951
Rights	著作権は日本エネルギー学会にある
Type	journal article
File Information	energy 76(2) 134.pdf



A Preliminary Experiment of Volatilization of Minerals in Coal Ash by Chlorination Treatment

Taihei SHIMADA^{*1}, Takehiko KUMAGAI^{*2}, Takashi TSURUE^{*3}, Yoshinori NAKATA^{*3}
Takeshi OKUTANI^{*3}, Shohei TAKEDA^{*3}, Jun-ichiro HAYASHI^{*1} and Tadatoshi CHIBA^{*1,4}

***1** Center for Advanced Research of Energy Technology, Hokkaido University,
N-13 W-8, Kita-ku, Sapporo, 060, Japan

***2** Division of Material Science and Engineering, Graduate School of Engineering, Hokkaido University,
N-13 W-8, Kita-ku, Sapporo, 060, Japan

***3** Hokkaido National Industrial Research Institute,
2-17 Tsukisamu-Higashi, Toyohira-ku, Sapporo, 062, Japan

Chlorination and volatilization characteristics of minerals in coal ashes were studied for chemical modification of the ash composition and properties. The ash samples were prepared by burning three bituminous coals, a lignite and a brown coal in a muffle furnace at 1088 K (high-temperature ash; HTA) and in an O₂ plasma asher (low-temperature ash; LTA). On heating the ashes at 10 K/min to 1273 K in atmospheric chlorine gas flow in a thermobalance reactor, chlorination of minerals was found to take place even without oxygen sink and was followed by vaporization of the metal chlorides formed. Elemental analysis of the original and chlorine-treated HTAs revealed that most of K, Na, Mg and Fe and a portion of Ca were extracted while others such as Si and Al were hardly volatilized. Some pure metal oxides and a carbonate abundant in the ashes were treated at the same conditions. The result showed that Fe₂O₃ and Fe₃O₄ were rapidly volatilized in a temperature range of 900 to 1200 K. MgO was slowly but completely volatilized at 1273 K. Chlorination of CaO and CaCO₃ occurred at much lower temperatures but vaporization of CaCl₂ proceeded very slowly even at 1273 K. Changes in the ash weight with increasing temperature widely varied for the type of the initial ash. The variation was explained on the basis of the initial contents of metal oxides and carbonates. The chlorination treatment resulted in a significant reduction of differences in the mineral compositions, melting point temperatures and acid-base indices of residual solids from HTAs derived from the bituminous coals.

Key Words

Volatilization, Coal ash, Chlorination, Metal chlorides

1. Introduction

Coal utilization inevitably results in discharge of ash containing various kinds of minerals. The

per-year amount of the discharge in Japan is about 6 Mt in 1995 and is predicted to increase to more than 12 Mt in the early 2000's. At present, about 60 % of coal ash is utilized as raw material

***4** To whom all correspondence should be addressed

in cement industries and the rest is disposed by land reclamation which now gives rise to significant environmental impacts¹⁾. The composition of minerals in coal ash widely varies from coal to coal and the variety has been responsible for difficulties in utilizing coal ash as raw material, leading to a thought that coal ash is a solid waste troublesome to be treated. It is hence necessary to find its alternative utilization into useful materials and the present study aims to examine a possible method of utilization of coal ash.

In the field of metallurgical engineering, chlorination is a well-established technique to extract or purify metals, using chlorine and carbon as chlorinating and reducing agents, respectively. Okutani *et al.*²⁾ investigated chlorinating extraction of silica in rice hull ash as silicon tetrachloride. Landsberg *et al.*^{3)~6)} studied chlorination of aluminum bearing minerals such as bauxite and clay in the presence of carbon. In addition, there have so far been a few reports of chlorination treatment of coal ash and ash in coal. Mehrotra *et al.*^{7)~10)} calculated the free energy for 135 chemical species involving 12 elements such as Al, C, Ca, Cl, Fe, K, Mg, Na, O, S, Si and Ti in a temperature range of 298 to 1700 K and suggested that chlorination treatments with reducing agents such as carbon (fluid coke) and carbon monoxide would produce aluminum and other metal chlorides. They carried out an experimental study of extraction of Al, Fe, Ti and Si by a chlorination treatment of Alberta coal ash in a fluidized-bed reactor at temperature ranging from 703 to 1248 K. The best conversions achieved were 25 % of Al, 100 % of Fe, 5 % of Si and 25 % of Ti above 1173 K. Adelman *et al.*¹¹⁾ also studied a chlorination treatment of a fly ash with phosgene (COCl_2) which is expected to have dual functions for reduction and chlorination. However, the primary purpose of these studies was to extract specific metals and hence little attention was paid to composition and properties of residual solid, mass of which amounts 90 % of the initial one, as well as to applicability of their methods to other types of coal ashes.

Chlorination reactions of metal oxides and carbonates typically contained in coal ash are listed in Table 1. Equilibrium constants, K_{eq} , for the reactions at 1273 K were calculated from the Gibbs standard free energies¹²⁾ of the reactants and products by

$$K_{\text{eq}} = P_{\text{O}}^l P_{\text{X}}^m / P_{\text{Cl}}^n \quad (1)$$

where P_{O} , P_{X} and P_{Cl} are the equilibrium partial pressures of O_2 , metal chloride and Cl_2 , respectively. The exponents, l , m and n , are the orders of the reaction. For SiO_2 and CaCO_3 , K_{eq} respectively at 973 K and 1123 K were calculated because their standard free energies at 1273 K are not available and for CaCl_2 , MgCl_2 , KCl and NaCl their liquid-phase standard free energies were employed for the calculation because those for gaseous chlorides are not available, too. When P_{Cl} and the reaction temperature are 0.01 MPa and 1273 K, respectively, calculated values of $P_{\text{X}}/P_{\text{Cl}}$ from K_{eq} are as follows: 1.4×10^{-6} for SiCl_4 , 7.0×10^{-4} for AlCl_3 , 2.7×10^{-2} for Fe_2Cl_6 from Fe_2O_3 , 1.6 for Fe_2Cl_6 from Fe_3O_4 and 5.5×10^{-3} for TiCl_4 . These indicate that iron oxides can be chlorinated and volatilized much more easily than the other oxides. In the above-mentioned studies on high temperature chlorination treatment of metal oxides, carbon was added to promote chlorination by reducing metal oxides. However, the calculated result of P_{O} clearly shows that oxygen in metal oxides can be converted to molecular oxygen, suggesting that the chlorination is possible even in the absence of reducing agents. Further, large values of P_{O} calculated for MgO , CaO , K_2O and Na_2O mean that their chlorination is also possible.

In contrast to the chlorination reaction, little is known about vaporization characteristics of metal chlorides; although some phase equilibrium data have been reported, the data on the rate of vaporization are completely missing. Hence, in the present experimental study, simultaneous chlorination and volatilization characteristics have been observed for minerals contained in coal ashes with different compositions. Based on the equilibrium calculations, the experiments were

Table 1 Equilibrium constants for chlorination of metal oxides, carbonate and sulfate at 1273 K

Reaction	K_{eq}	Value/Temp. (K)
(1) $\text{SiO}_2(\text{s}) + 2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SiCl}_4(\text{g}) + \text{O}_2(\text{g})$	$P_{\text{SiCl}_4}P_{\text{O}_2}/P_{\text{Cl}_2}^2$	$2.0 \times 10^{-12}/973$
(2) $2/3\text{Al}_2\text{O}_3(\text{s}) + 2\text{Cl}_2(\text{g}) \rightleftharpoons 4/3\text{AlCl}_3(\text{g}) + \text{O}_2(\text{g})$	$P_{\text{AlCl}_3}^{4/3}P_{\text{O}_2}/P_{\text{Cl}_2}^2$	$3.0 \times 10^{-7}/1273$
(3) $2\text{CaSO}_4(\text{s}) + 2\text{Cl}_2(\text{g}) \rightleftharpoons 2\text{CaCl}_2(\text{l}) + 2\text{SO}_3(\text{g}) + \text{O}_2(\text{g})$	$P_{\text{SO}_3}^2P_{\text{O}_2}/P_{\text{Cl}_2}$	$1.1 \times 10^{-5}/1273$
(4) $\text{TiO}_2(\text{s}) + 2\text{Cl}_2(\text{g}) \rightleftharpoons \text{TiCl}_4(\text{g}) + \text{O}_2(\text{g})$	$P_{\text{TiCl}_4}P_{\text{O}_2}/P_{\text{Cl}_2}^2$	$3.0 \times 10^{-5}/1273$
(5) $\text{Fe}_3\text{O}_4(\text{s}) + 4\text{Cl}_2(\text{g}) \rightleftharpoons \text{FeCl}_2(\text{l}) + \text{Fe}_2\text{Cl}_6(\text{g}) + 2\text{O}_2(\text{g})$	$P_{\text{Fe}_2\text{Cl}_6}P_{\text{O}_2}^2/P_{\text{Cl}_2}^4$	$3.9 \times 10^{-4}/1273$
(6) $2/3\text{Fe}_2\text{O}_3(\text{s}) + 2\text{Cl}_2(\text{g}) \rightleftharpoons 2/3\text{Fe}_2\text{Cl}_6(\text{g}) + \text{O}_2(\text{g})$	$P_{\text{Fe}_2\text{Cl}_6}^{2/3}P_{\text{O}_2}/P_{\text{Cl}_2}^2$	$1.2 \times 10^{-2}/1273$
(7) $2\text{MgO}(\text{s}) + 2\text{Cl}_2(\text{g}) \rightleftharpoons 2\text{MgCl}_2(\text{l}) + \text{O}_2(\text{g})$	$P_{\text{O}_2}/P_{\text{Cl}_2}$	$1.7 \times 10^{-1}/1273$
(8) $2\text{CaO}(\text{s}) + 2\text{Cl}_2(\text{g}) \rightleftharpoons 2\text{CaCl}_2(\text{l}) + \text{O}_2(\text{g})$	$P_{\text{O}_2}^{1/2}/P_{\text{Cl}_2}$	$3.8 \times 10^9/1273$
(9) $2\text{CaCO}_3(\text{s}) + 2\text{Cl}_2(\text{g}) \rightleftharpoons 2\text{CaCl}_2(\text{l}) + 2\text{CO}_2(\text{g}) + \text{O}_2(\text{g})$	$P_{\text{CO}_2}^2P_{\text{O}_2}/P_{\text{Cl}_2}^2$	$1.6 \times 10^{10}/1123$
(10) $2\text{Na}_2\text{O}(\text{s,l}) + 2\text{Cl}_2(\text{g}) \rightleftharpoons 4\text{NaCl}(\text{l}) + \text{O}_2(\text{g})$	$P_{\text{O}_2}/P_{\text{Cl}_2}^2$	$1.6 \times 10^{29}/1273$
(11) $2\text{K}_2\text{O}(\text{l}) + 2\text{Cl}_2(\text{g}) \rightleftharpoons 4\text{KCl}(\text{l}) + \text{O}_2(\text{g})$	$P_{\text{O}_2}/P_{\text{Cl}_2}^2$	$1.0 \times 10^{37}/1273$

performed by heating the ashes mainly under atmospheric chlorine gas flow without any reducing agents in a thermobalance reactor at a rate of 10 K/min up to a holding temperature. The holding temperature was fixed at 1273 K. Analyses were conducted for elemental composition and some properties of the residual solids.

2. Experimental

2.1 Ash Samples and Model Compounds

Ash samples were obtained from three bituminous coals, a lignite and a brown coal. Analytical data of the parent coals are listed in Table 2. From individual coals except for Yallourn coal, two types of ashes were prepared by the following methods. One is a high-temperature ash (HTA) obtained by burning coal with air in a muffle furnace at 1088 K for an hour. The other is a low-temperature ash (LTA) which was produced

by decarbonizing coal in an oxygen plasma asher until no weight loss was observed under the following conditions; oxygen flow rate of 100 cm³/min-STP, radiofrequency power of 110 W, oxygen partial pressure of 65 to 95 Pa. The highest sample temperature in the asher was 470 K and the original chemical composition of minerals was preserved without oxidation and pyrolysis¹³⁾. An ash sample from Yallourn coal supplied from a company was further treated as obtained HTAs. All ash samples were pulverized and sieved to a size finer than 200 mesh.

Four metal oxides (CaO, MgO, Fe₂O₃ and Fe₃O₄) and a carbonate (CaCO₃) which are representative components in the ashes, were also employed as model compounds. These had purities of 99 to 99.99 wt% and were used without further purification.

Table 2 Proximate and ultimate analyses of parent coals

Coal	Proximate analysis, wt%				Ultimate analysis, d. a. f. ¹ wt%				
	Mois.	Ash	V. M. ²	F. C. ³	C	H	O	N	S
Yallourn	-	-	-	-	-	-	-	-	-
Montana	8.4	11.8	37.3	42.5	72.9	5.1	23.6	0.7	0.9
Taiheiyo	5.0	13.8	42.7	38.5	74.7	6.1	17.7	0.7	0.4
Illinois	3.8	11.2	39.1	45.9	80.2	6.0	12.3	0.7	3.4
Datong	7.0	8.5	29.5	55.0	84.4	4.4	10.8	0.4	0.3

1; dry ash free

2; volatile matter

3; fixed carbon

2.2 Apparatus and Procedure

Fig.1 illustrates a schematic diagram of the experimental apparatus. The thermobalance reactor was made of a quartz glass tube with an inner diameter of 30 mm and a length of 1.2 m. At each run, 0.1 g of ash sample was loaded in a 10 mm i.d. and 10 mm deep quartz-glass basket, which

was hung in the reactor by fine quartz threads connected in series to a quartz-glass spring. The thermal expansion coefficient of the spring was determined prior to use. Displacement of a marker on one of the quartz threads from its initial position as a result of chlorination and volatilization was measured by a charge-coupled-device

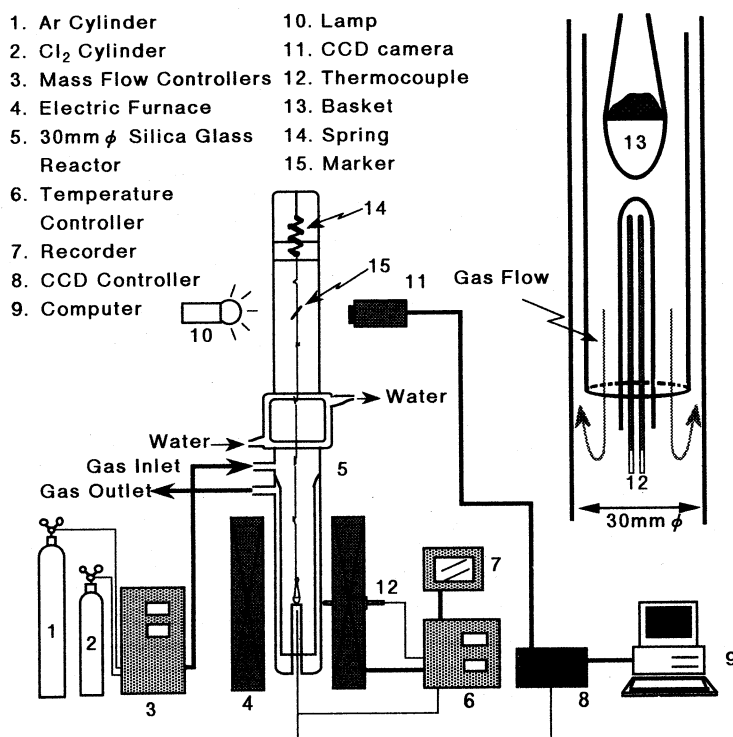


Fig.1 Schematic diagram of experimental apparatus

(CCD) camera every thirty seconds. The data were stored in a personal computer and then converted to the weight change.

Chlorination of ash was conducted in atmospheric flow of pure or diluted chlorine gas. After replacing air in the reactor by argon, chlorine gas was introduced through a mass flow controller at a prescribed flow rate. The partial pressure of chlorine gas was controlled by adjusting the argon flow rate. Preliminary experiments at different chlorine gas flow rates revealed that changes of the ash weight were not affected by the flow rate ranging from 30 to 100 cm³/min. Therefore, the experiments were carried out at a fixed flow rate of 30 cm³/min.

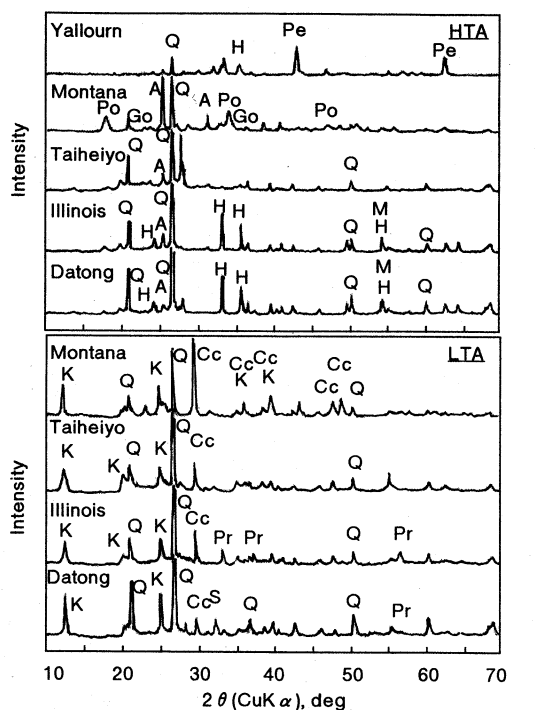
The reactor was heated in an electric furnace at a rate of 10 K/min to 1273 K where the temperature was kept for 60 min. The temperature was measured by a thermocouple introduced from the reactor bottom to a height a few millimeters below the basket bottom through a 4 mm o.d. quartz tube. Effluent chlorine gas was absorbed into aqueous NaOH solution in two trap bottles connected in series downstream the reactor.

2.3 Analyses

Elemental compositions of the original and chlorine-treated ashes were determined by an atomic absorption spectroscopy. 50 mg of each sample was completely dissolved at 388 K in a mixed solution of 20 % HCl, 60 % HNO₃ and 48 % HF aqueous solutions with the respective volumes of 0.25, 0.75 and 1.0 cm³. Boric acid was then added to the solution to mask fluorine ions, which was finally diluted for analysis. Melting point temperatures of the original and chlorine-treated ashes were determined according to the Japan Industrial Standard (JIS-M8801). Two specimens were prepared for each ash, by shaping the ash powder into a triangular cone with edge lines of 6.4 mm of base regular triangle and a height of 19 mm. The specimens were settled on a support in an alumina tube which was heated in an electric furnace at a rate of 5 K/min up to 1770 K. The melting point temperature is defined as a mean of

the temperatures at which the cone melts into hemisphere shape. Difference in the measured temperatures for two specimens was within 20 K for all ashes.

Table 3 summarizes the elemental compositions, melting point temperatures, T_{mp} , and BET specific surface areas of HTA and LTA samples. Major differences in the elemental compositions of HTAs are as follows: 1) Si and Al contents are 30 to 40 wt% for Taiheiyō, Illinois and Datong coal HTAs while those for HTAs from the lower rank coals are much lower, 2) Fe is abundant in Yallourn, Illinois and Datong coal HTAs and 3) alkaline earth metals, i.e., Ca and Mg, are abundant particularly in Yallourn and Montana coal HTAs. Similar tendencies are found for LTAs, except for a large content of sulfur in Illinois coal LTA.



Q; Quartz	SiO ₂	K; Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄
M; Mullite	Al ₂ Si ₂ O ₇	H; Hematite	Fe ₂ O ₃
Go; Goethite	α-FeOOH	Po; Portlandite	Ca(OH) ₂
Pe; Periclase	MgO	Cc; Calcite	CaCO ₃
S; Siderite	FeCO ₃	P; Pyrite	FeS ₂
A; Anhydrite	CaSO ₄		

Fig.2 X-ray diffractograms of HTAs and LTAs

Table 3 Elemental composition, melting point temperature and specific surface area

Element [wt%]	Yallourn	Montana	Taiheiyō	Illinois	Datong
Si	1.5	11.4	25.2	21.9	32.0
	-	8.8	21.9	18.8	22.7
Al	1.1	7.9	13.9	9.8	7.4
	-	5.6	11.2	7.6	8.0
Fe	21.7	1.2	2.6	8.8	6.3
	-	1.6	2.3	8.7	7.8
Ca	11.9	22.2	4.4	3.1	1.3
	-	24.2	4.1	3.1	2.3
Mg	27.3	2.4	1.6	1.1	0.7
	-	2.0	1.4	0.8	0.7
K	0.2	0.2	1.2	1.4	0.8
	-	0.2	0.8	1.3	0.8
Na	4.5	1.0	0.9	0.6	0.1
	-	0.8	0.5	0.5	0.1
Ti	0.1	0.4	1.0	0.7	0.4
	-	0.6	0.8	0.7	0.4
S	6.2	4.5	0.7	1.1	0.6
	-	4.2	1.1	9.0	3.5
lg. loss	0	0	0	0	0
	-	22.4	14.5	15.3	13.0
T _{mp} [K]	>1770	1630	1710	1550	1760
	-	-	-	-	-
S. A. ¹ [m ² /g]	0.8	6.2	10.0	3.7	6.5
	-	6.2	11.3	6.1	5.8

upper and lower figures for each element indicate weight percents in HTA and LTA, respectively.

1; specific surface area

An X-ray diffractometry was utilized to analyze mineral compositions. The diffractograms of HTA and LTA are shown in Fig. 2. It is seen that major structures of Fe, Ca, Mg in HTA are much different from those in LTAs. The Fe structures are hematite and goethite in HTAs whereas a carbonate (siderite) and sulfides in LTAs. Further, Ca and Mg in the latter are found as carbonates which are not detected in HTAs together with CaO or Ca(OH)₂, MgO and a few types of silicates.

3. Results and Discussion

3.1 Effect of Chlorine Partial Pressure on Ash Weight Change

Effect of the chlorine partial pressure on chlorination and volatilization was examined for Datong coal HTA. Fig. 3 shows the result where the residual solid weight fraction, w , based on the initial weight of ash is plotted against temperature for heating-up period and time for the succeeding period at the holding temperature. It is seen that a rapid decrease of w due to volatilization of minerals commences at about 900 K and terminates at 1150 to 1250 K and that no essential difference is brought about in the curves for the chlorine partial pressures from 0.01 to 0.10 MPa.

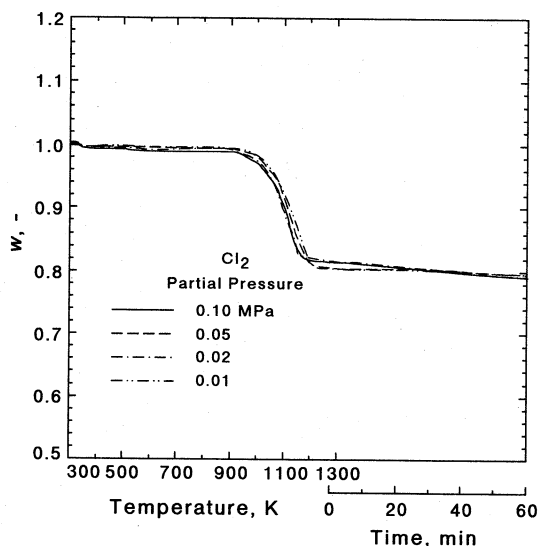


Fig. 3 Effect of chlorine gas partial pressure on change in weight fraction for Datong coal HTA
Heating rate; 10 K/min
holding temperature; 1273 K

This implies that in the above range of temperature the values of $(P_O^l P_X^m / P_{Cl}^n)$ in Eq. 1 are far less than K_{eq} for some of the chlorination reactions listed in Table 1.

3.2 Changes in Ash Compositions and Properties due to Chlorination and Volatilization

The elemental and mineral compositions varied by the chlorination treatment. Fig. 4 represents difference between the weight fractions before and after chlorination for elements in HTAs from all coals used. Here, the bars on the left- and right-hands for each HTA indicate the weight fractions for the initial HTA and those for the chlorine-treated HTA (C-HTA), respectively. The decrease of the total weight fraction by the chlorination treatment confirms that volatilization of some minerals occurs even without reducing agents. In particular, the weight fractions of Fe and Mg decrease dramatically by the treatment. Iron oxides are almost completely volatilized except for Yallourn coal HTA which exhibits an extent of volatilization of 80 wt%. A possible ex-

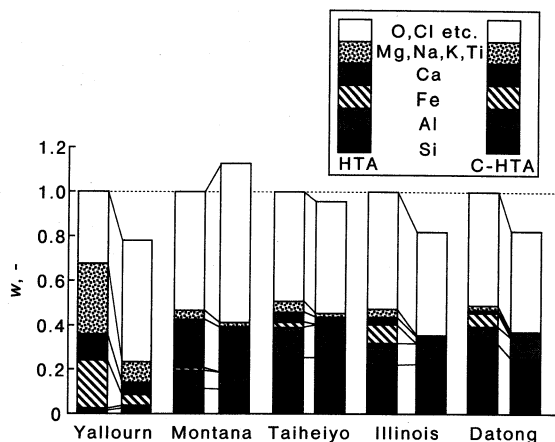


Fig. 4 Difference between weight fractions before and after chlorination for elements in HTAs

planation for the limited volatilization is that alkali and alkaline earth metal chlorides formed at lower temperatures become molten¹⁴⁾. The molten chlorides is supposed to act as a diffusion barrier against chlorine at higher temperatures and in turn to suppress the chlorination of iron oxides. A fairly extensive volatilization is also seen for Mg, Na, K and Ti. On the contrary, most of Al and Si components remains unchanged in spite of low vaporization temperatures of their chlorides (331 K for $AlCl_3$ and 456 K for $SiCl_4$), suggesting that oxides of Al and Si are not chlorinated under the present conditions. Except for Yallourn coal HTA, the extent of Ca volatilization is around 10 wt% at most. This may be attributed to slow vaporization of $CaCl_2$ formed from CaO, as is described below (Fig. 6).

Fig. 5 shows XRD diffractograms of C-HTA and C-LTA. Variation in the mineral compositions by the treatment is evident if compared with those of the original ashes shown in Fig. 2. The peaks arising from anhydrite and portlandite, prominent in the diffractograms of the original HTAs, are not found in those of C-HTAs. Instead, clear peaks attributed to calcium and magnesium chlorides appear for Yallourn and Montana coal C-HTAs. Especially, peaks arising from calcium chloride clearly appear for Montana coal C-LTA. These indicate accumulation of calcium

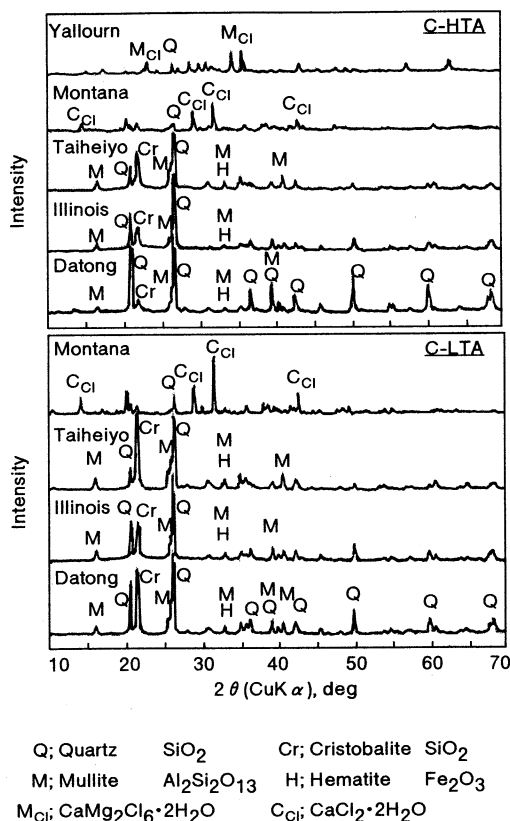


Fig. 5 X-ray diffractograms of C-HTAs and C-LTAs

chloride due to its vaporization much slower than formation. No peaks ascribed to other metal chlorides are detected for all C-HTAs and C-LTAs, indicating that elements other than Ca remain as their oxides. It should also be noted that C-HTAs and C-LTAs from the three bituminous coals give similar diffractograms. This similarity well corresponds to that in the elemental compositions of C-HTAs shown in Fig. 4 and is expected to result in reduction of the difference among the properties such as the melting point temperature, T_{mp} , and the acid-base index, I_{ab} , of the original HTAs because the mineral composition is a dominant factor that determines them¹³⁾. Here, I_{ab} is a parameter empirically used to correlate T_{mp} to the mineral composition of ash and is defined as

$$I_{\text{ab}} = \frac{[\text{total mass of } \text{Fe}_2\text{O}_3, \text{CaO, MgO, Na}_2\text{O and K}_2\text{O}]}{[\text{total mass of } \text{SiO}_2, \text{Al}_2\text{O}_3 \text{ and } \text{TiO}_2]} \quad (2)$$

Table 4 Melting point temperatures and acid-base indices of HTAs and C-HTAs

Coal	T_{mp}, K		I_{ab}	
	HTA	C-HTA	HTA	C-HTA
Yallourn	>1770	-	18.01	3.96
Montana	1630	-	0.96	0.84
Taiheiyō	1710	1660	0.19	0.08
Illinois	1550	1630	0.32	0.08
Datong	1760	1690	0.16	0.05

As shown in Table 4, for all HTAs, the chlorination treatment lowers I_{ab} . The decrease of I_{ab} results in an increase of T_{mp} for Illinois coal HTA while a decrease for Taiheiyō and Datong coal HTAs. This coincides with the result indicated by Unuma *et al.*¹³⁾ that one of the definite factors for T_{mp} is not generally I_{ab} but the mineral composition. The deviations in T_{mp} and I_{ab} among the C-HTAs from the three bituminous coals were respectively 60 K and 0.03 and were much smaller than those among HTAs, i.e., 210 K and 0.16. This is attributed to selective volatilization of base components other than CaO by the treatment.

3.3 Changes of Ash Weight Fraction with Temperature and Time

As is known, coal ash is a complicated mixture of metal oxides, sulfates and carbonates. Hence, a quantitative evaluation of ash chlorination and volatilization characteristics would require knowledge of those for the individual constituents. In Fig. 6 the weight fractions, w , for some model compounds are plotted in the same manner as in Fig. 3. The horizontal lines drawn in the figure indicate the stoichiometric weight fraction for each compound at its complete conversion to the chloride without volatilization. For Fe_2O_3 and Fe_3O_4 , w never increases in the whole ranges of temperature and time. It rapidly decreases in a temperature range from 900 to 1250 K, suggesting that from stoichiometric calculations the rate of FeCl_3 volatilization is higher than a half of the rate of chlorination. On the other hand, for CaO and CaCO_3 the volatilization occurs after their complete conversion to CaCl_2 . It is clearly shown in

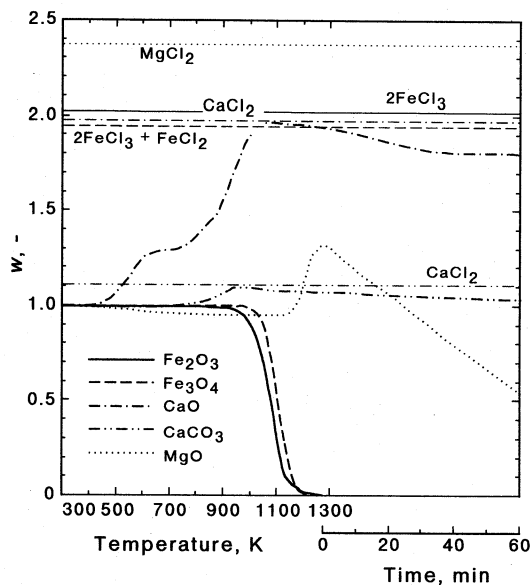


Fig. 6 Changes in ash weight fractions with chlorination and volatilization for model compounds
Heating rate ; 10 K/min
holding temperature ; 1273 K

the figure that the weight fractions of CaO and CaCO_3 increase gradually from about 300 and 650 K, respectively, until attaining stoichiometric weight fractions at their complete conversion. Then, they decrease very slowly along with the chloride vaporization which is not completed at the present experimental condition. For MgO, w is seen to increase in a temperature range between 1130 and 1270 K and to decrease moderately with time at the holding temperature. Though not shown in the figure, the volatilization was completed at a holding time of 120 min.

Changes of w for all HTAs occurred reflecting the above-described characteristics of the model compounds. The result is shown in Fig. 7. For Illinois and Datong coal HTAs, w decreases rapidly at temperatures from 900 to 1100 K and gradually at higher temperatures without exhibiting any increase. As shown in Table 3, these coals have a fairly high iron content than the others and hence the changes of w become similar to those for the iron oxides shown in Fig. 6. Taiheiyō coal HTA gives a similar change.

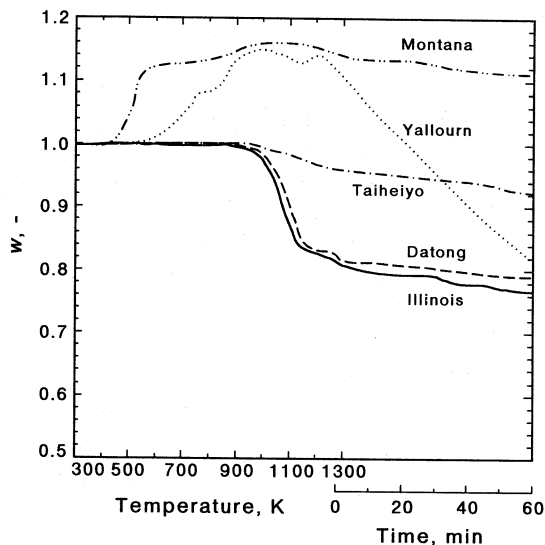


Fig. 7 Changes in ash weight fractions with chlorination and volatilization for HTAs
Heating rate ; 10 K/min
holding temperature ; 1273 K

However, w decreases much more slowly than the above two HTAs due to its lower Fe content. The changes for Montana and Yallourn coal HTAs are much different from those for the others. These coal HTAs have considerably high contents of Ca and/or Mg, the chlorides of which have slow vaporization rates (Fig. 6). Hence, w of these HTAs increases from 300 K, reaches a maximum at 1100 K and then decreases slowly at higher temperatures. The decrease is more rapid for Yallourn than for Montana coal HTA. This is because the former has a Mg content higher than the latter. On the other hand, w for Yallourn coal HTA, which has high contents of Fe, Ca and Mg (Table 3), exhibits a complicated change. It increases from 500 up to 1000 K in the same manner for CaO and CaCO_3 shown in Fig. 6. Further increase in temperature results in a maximum at ca. 1000 K due to the occurrence of the rapid volatilization of iron oxides which contributes to the decrease in w . Then, another maximum of w appears at about 1200 K which is caused by the dominant chlorination and volatilization of MgO. The linear decrease of w with time at the holding temperature also suggests that the decrease is

mainly due to volatilization of MgO.

The above results for HTAs can qualitatively be explained on the basis of those for the model compounds shown in Fig. 6. However, it was at present impossible to predict the results from the elemental composition of HTAs and the stoichiometric change of the model compounds for all HTAs. As an example, Table 5 compares w observed after chlorination of HTAs at 1273 K for an hour, $w_{\text{obs.}}$, with that calculated, $w_{\text{calc.}}$, for Fe, Ca, Mg, K, Na, Ti and S elements, assuming that these elements exist as Fe_2O_3 , CaO , MgO , K_2O , Na_2O , TiO_2 and SO_2 , respectively, and that from Fig. 6 the weight gains are +80 % for CaO , -50 % for MgO and -100 % for the other oxides based on the initial weight. For Yallourn coal HTA, 80 % decrease was further assumed for Fe_2O_3 from the result in Fig. 4. It is seen that $w_{\text{calc.}}$ approximately agrees with $w_{\text{obs.}}$ for Montana, Taiheiyō and Illinois coal HTAs while the agreements are poor for Yallourn and Datong coal HTAs, suggesting that a further knowledge is needed for complicated structures and stoichiometric equations of the minerals.

Changes in the weight fraction for LTAs differed considerably from those of HTAs as shown in Fig. 8. The weight fraction keeps decreasing with increasing temperature without any appreciable increase. This is probably due to chlorination of carbonates of Fe, Ca and Mg typically contained in LTAs since chlorination of the carbonates gives much smaller weight gains than those of the oxides on mass basis. The curves of w also indicate that chlorination of iron carbonates occurs at temperatures much lower than that of the oxides.

Table 5 Comparison of $w_{\text{obs.}}$ and $w_{\text{calc.}}$ for HTAs

Coal	$w_{\text{obs.}}$	$w_{\text{calc.}}$
Yallourn	0.185	0.529
Montana	-0.110	-0.099
Taiheiyō	0.078	0.059
Illinois	0.232	0.242
Datong	0.208	0.111

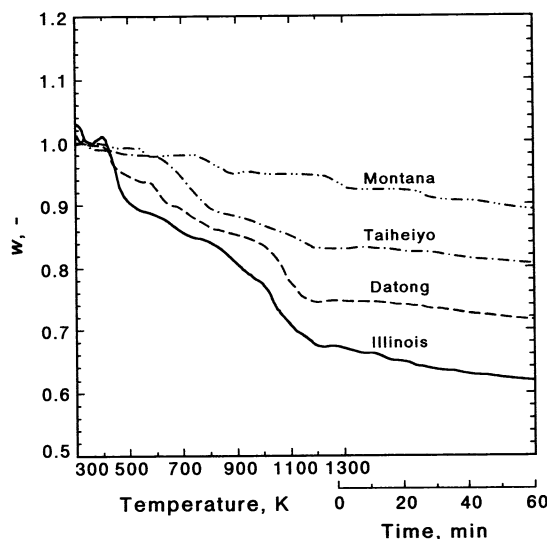


Fig. 8 Changes in ash weight fractions with chlorination and volatilization for LTAs
Heating rate ; 10 K/min
holding temperature ; 1273 K

3.4 Application of Chlorination Treatment to Coal Char

The chlorination treatment was also tested for chars prepared by carbonization of Taiheiyō and Datong coals at 1173 K in a fluidized bed. Fig. 9 represents changes of the weight fraction of ash based on initial weight fraction in char assuming the carbonaceous portion of char being inert with temperature and time, W_{ash} , i.e.,

$$W_{\text{ash}} = \frac{W_{\text{char}} - W_{\text{char},0}}{W_{\text{ash},0}} \quad (3)$$

where W_{char} , $W_{\text{char},0}$ and $W_{\text{ash},0}$ are the weight of sample at temperature T and time t , the initial weight of carbonaceous portion in char and the initial weight of ash in char, respectively. Also, the horizontal lines in the figure indicate the weight fraction of residual solid which was obtained by burning char chlorine-treated at 1273 K for 60 min. It is seen that chlorination and volatilization proceed as quickly as those for the ashes and, moreover, the extents of decrease of the weight fraction exceed the above-described weight fraction possibly due to carbon consumption during the treatment. Therefore, the present

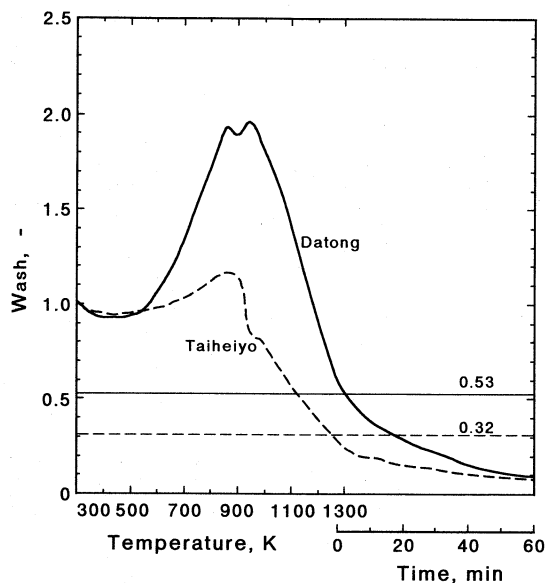


Fig.9 Changes in ash weight fractions with chlorination and volatilization for Taiheiyō and Datong coal chars
Heating rate ; 10 K/min
holding temperature ; 1273 K

chlorination treatment is applicable not only for chemical modification of ash composition and properties but also for direct demineralization of coal char.

4. Conclusions

Chlorination and volatilization characteristics were investigated for HTAs and LTAs prepared from five different coals. The ashes were heated to 1273 K in a thermobalance reactor and exposed to atmospheric flow of chlorine gas.

Elemental and XRD analyses of the original ashes and chlorine-treated ashes after the chlorination treatment revealed that volatilization of mineral components other than oxides of Si and Al occurs even in the absence of oxygen sink. Especially, volatilization of Fe and Mg as well as K and Na nearly completed at the present experimental conditions. Chlorination and volatilization characteristics of HTAs with different mineral compositions were well explained on the basis of those of model compounds such as metal

oxides and carbonates. The volatilization resulted in mineral compositions of C-HTAs similar for some HTAs which in turn gave similarities in their XRD spectra, melting point temperatures and acid-base indices. In addition, the chlorination treatment of LTAs gave the same results as above.

[Acknowledgments]

The authors wish to thank the Research Institute of Innovative Technology for the Earth (RITE) who financially supported the research in part.

References

- 1) Nagataki, S., *Proceedings of International Clean Coal Tech. Sym. on Coal Ash Utilization*, Japan (1996)
- 2) Okutani, T. and Y. Nakata, *High Tech Ceramics*, Edited by Vincenzini P., Elsevier Publishing Co., Amsterdam, 511 (1987)
- 3) Landsberg, A., *Metallurgical Transactions B*, 6 B, 207 (1975)
- 4) idem, *ibid.*, 8 B, 435 (1977)
- 5) Landsberg, A. and R. D. Wilson, *ibid.*, 15 B, 695 (1984)
- 6) Landsberg, A., R. D. Wilson and W. Burns, *ibid.*, 19 B, 477 (1988)
- 7) Mehrotra, A. K., P. R. Bishnoi and W. Y. Svrcek, *Can. J. Chem. Eng.*, 57, 225 (1979)
- 8) Mehrotra, A. K., L. A. Behie, P. R. Bishnoi and W. Y. Svrcek, *IEC Proc. Des. Dev.*, 21, 37 (1982)
- 9) idem, *ibid.*, 21, 44 (1982)
- 10) Bishnoi, P. R., W. Y. Svrcek and A. K. Mehrotra, *Can. J. Chem. Eng.*, 58, 273 (1980)
- 11) Adelman, D. J. and G. Burnet, *AIChE J.*, 33, 64 (1987)
- 12) Kubaschewski, O. and C. B. Alcock, *Metallurgical Thermochemistry* 5th Edition, vol.24, p. 340 (1979)
- 13) Unuma, H., S. Takeda, T. Tsurue, S. Ito and S. Sayama, *Fuel*, 65, 1505 (1986)
- 14) Jeong, J. and K. Y. Park, *J. Chem. Eng. Japan*, 25, 160 (1992)