포스겐 및 염소혼합물을 이용한 비산재의 탄화염소화 반응

김재용 · 김광렬

충북대학교 환경공학과

Carbochlorination of Fly Ash with Phosgene and Chlorination Mixtures

Jae-Yong Kim · Kwang-Yul Kim

Department of Environmental Engineering, Chungbuk National University.

국문요약

포스겐과 CO 및 Cl_2의 혼합물을 사용하여 비산재의 탄화염소화 반응에 관하여 연구하였다. 순수 Cl_2와 염소화 혼합물 등으로 부터 얻은 결과를 나타내었다.

Abstract

Carbochlorination of fly ash with phosgene and mixture of CO, Cl_2 were investigated. The results obtained with pure chlorine, and/or chlorination mixtures were presented.

I. INTRODUCTION

There is a huge incentive to treat power plant fly ash as a useful by-product rather than a waste material. About 70% of the solid waste derived from the combustion of coal is fly ash and increased reliance on coal combustion will produce significant fly ash storage and disposal problems.[1]

Fly ash is currently used as a low-cost construction material and for landfill cover, but additional cost-effective uses for this inexpensive material are desired.

The use of polymetallic ores will become more important as the world's supply of primary ores is depleted. Aluminum, for example, is produced today from bauxite via the Bayer-Hall process but in the future will be derived from lower grade ores containing larger amounts of silica and other metal oxides.[2] Different recovry methods will be required, such as carbochlorination, which produce a mixture of volatile metal chlorides. When using phosgene, $COCl_2$, the following general reaction is applied:

$$M_xO_y + yCOCl_2 \longrightarrow x\ MCl_{(2y/x)} + yCO_2$$
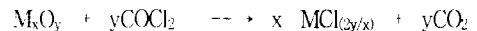
The volatile chlorides can be recovered from the effulent gas stream and separated to yield high-purity products.

To apply this method, carbochlorination reaction rate and product composition data are needed for reactor and product recovery system design.[3]

The carbochlorination of metal oxides in fly ash requires an oxygen sink and chlorine source such as carbon monoxide and chlorine, or phosgene.[4~20]

II. EXPERIMENTAL METHOD

Carbochlorination of fly ash was proceeded under following conditions: The sample was situated on the ceramic boat in limited amount to protect the mass transport limitation, usually sample weight is approximately 2g. Sample was heated in furnace to work temperature and kept at this temperature 20 min. in argon(Ar) atmosphere. Afterwards, the sample was exposed to chlorination gas for different period of time. After reaction time argon was introduced again, the sample was devolatilized at working temperature for 10 min. and cooled in argon to room temperature. Each samples were analyzed by DTA to determine the amount of inorganic matter and some of the samples were analyzed in Free-Col Laboratories in Pensylvania.

The fly ash used was from Kentucky power plants. Table 1 shows the chmical composition of fly ash used to experiment carbochlorination of this process.

A schematic flow diagram of the apparatus used to study the carbochlorination of fly ash is shown in Fig. 1.

Table 1. Chemical composition of fly ash

Constituents	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	TiO$_2$
Composition(%)	49.8	29.6	16.4	2.1

III. RESULTS AND DISCUSSION

1. Temperature influence on the conversion of inorganic compounds

A strong temperature dependence of effectiveness of chlorination was expected. The effect of temperature on inorganic material removal from fly ash is presented in Table 2 and Fig. 2 Samples were treated 10 minutes at various temperatures with phosgene.

The dependence of conversion of inorganic compounds on temperature in temperature interval 400-1100°C is almost linear.
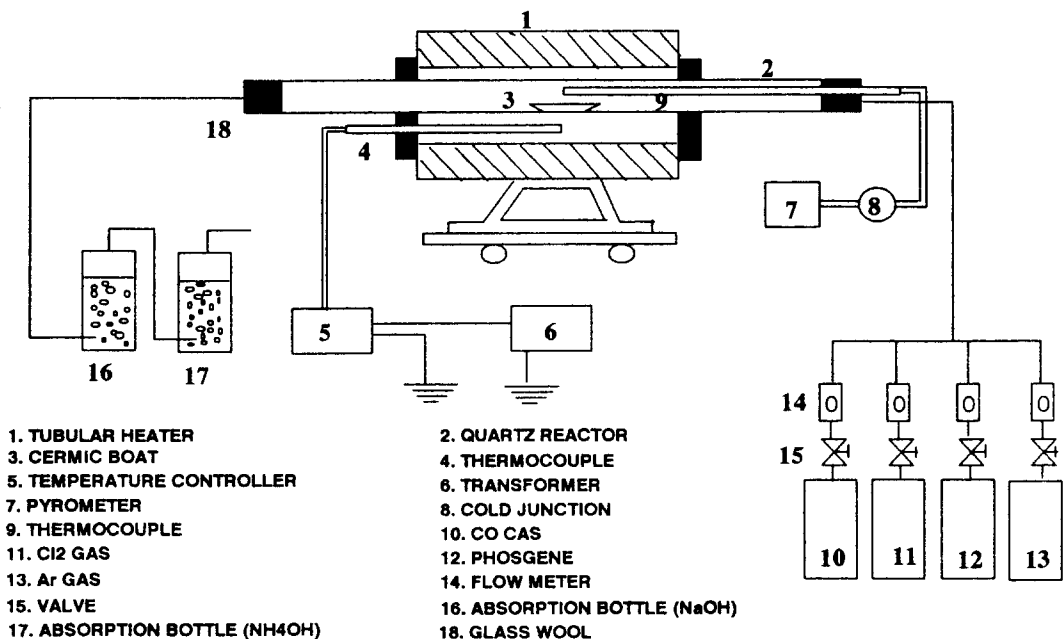

1. TUBULAR HEATER
3. CERMIC BOAT
5. TEMPERATURE CONTROLLER
7. PYROMETER
9. THERMOCOUPLE
11. Cl2 GAS
13. Ar GAS
15. VALVE
17. ABSORPTION BOTTLE (NH4OH)

2. QUARTZ REACTOR
4. THERMOCOUPLE
6. TRANSFORMER
8. COLD JUNCTION
10. CO CAS
12. PHOSGENE
14. FLOW METER
16. ABSORPTION BOTTLE (NaOH)
18. GLASS WOOL

Fig. 1. Schemetic flow diagram for carbochlorination of fly ash.

Table 2. Effect of temperature on conversion of inorganic material in chlorination of fly ash with phosgene.

	Temperature of chlorination [℃]	conversion of inorganic compounds
1	400	0.0554
2	600	0.2820
3	800	0.5540
4	1000	0.7162
5	1100	0.7374

Table 3. Conversion of inorganic components in fly ash.

	time of chlorination [min]	conversion of inorganic compounds	
		(CO:Cl₂ - 1:1)	(phosgene)
1	60	0.7289	0.7492
2	30	0.6912	0.7124
3	10	0.6835	0.7046
4	5	0.5545	0.5750
5	2	0.2402	0.2632
6	0	0.0000	0.0000

2. Chlorination mixture influence on the conversion of inorganic compounds

To compare effectiveness of chlorine sources between phosgene and CO+Cl₂ mixture, we reacted fly ash with two substances at 1000℃ as increasing the residence time from 5 to 60 minuites. Talele 3. and Fig. 3 are shown the fact that the effectiveness of phosgene on conversion of inorganic compouds of fly ash is more strong than the case of CO+Cl₂ mixture.

3. Chlorination with phosgene

Results obtained in experiments of chlorination at 1000℃ with phosgene are presented in Table 4 and Fig. 4.
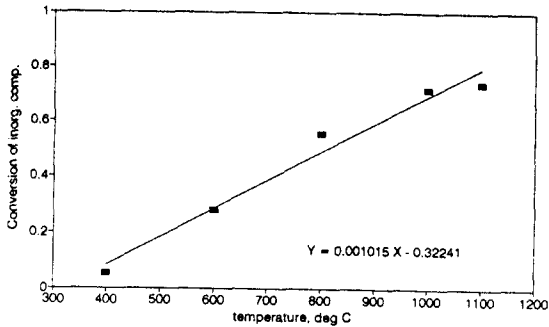
The effectiveness of individual compounds increases with time of chlorination and values reach higher than 80%. Effectiveness of removal of alumina. silica is more than 95%. High effectiveness of inorganic compounds removal is supposed to be due to the effects of intimate contact of carbon and inorganic species in fly ash and phosgene decomposition in situ in the chlorination reactor.

4. Chlorination with phosgene and CO mixture

Effectiveness of inorganic compounds removal depends on the residence time of chlorination and the type of chlorination medium. The influence of carbon
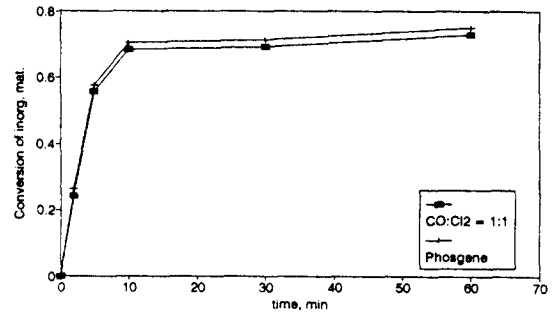

Fig. 2. Influence of temperature on conversion of inorganic material in chlorination of fly ash with phosgene at 10min.

Fig. 3. Conversion of inorganic components in fly ash Chlorination with CO:Cl₂ 1:1 and phosgene at 1000℃

Table 4. *Effectiveness of removal of individual inorganic compound by chlorination with phosgene at 1000°C*

effectiveness	η [%]				
time [min]	2	5	10	20	30
Al_2O_3	65.7	94.5	95.1	98.4	96.8
SiO_2	63.4	79.4	84.3	94.7	99.2
TiO_2	65.5	82.7	83.5	84.7	83.3
Fe_2O_3	56.5	83.7	87.2	97.1	89.1

Table 5. *Effectiveness of removal of individual inorganic compounds in chlorination with phosgene-CO mixture at 1000°C, 5 min.*

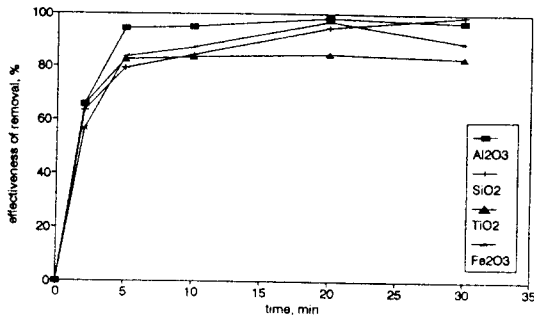| effectiveness	η [%]		
mol fraction of CO	0.0	0.5	0.89
Al_2O_3	94.5	92.9	88.3
SiO_2	79.4	85.0	79.7
TiO_2	82.8	76.6	81.1
Fe_2O_3	83.7	87.2	87.1

Fig. 4. *Influenec of time on effectiveness of individual inorganic compounds removal by chlorination with phosgene at 1000°C.*
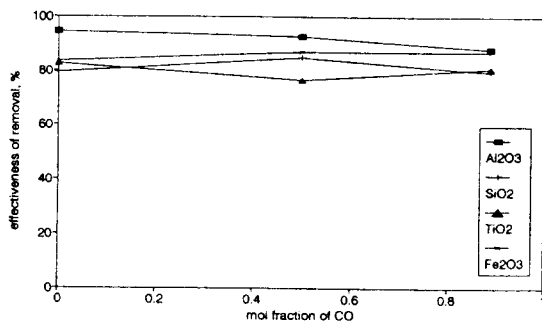

Fig. 5. *Influence of CO mole fraction on effectiveness of removal of individual inorganic compounds in chlorination with phosgene-CO mixture at 1000°C, 5 min.*

monoxide concentration on inorganic species removal for residence time 5 minutes is presented in Table 5 and Fig. 5.

It is well known that Al_2O_3, SiO_2, and TiO_2 cannot be reduced by CO to Al, Si, Ti, unlike Fe_2O_3. Therefore excess CO will supress the reduction of oxides by carbon (because the reduction is an equilibrium reaction).

5. Chlorination with CO+ Cl_2

Effectiveness of chlorination of fly ash by CO + Cl_2 mixture (molar ratio 1:1) was investigated at the same experimetal conditions as chlorination with phosgene.

Experimental results are presented in Table 6 and Fig. 6.

The high effectiveness of inorganic compounds

Table 6. *Effectiveness of removal of individual inorganic compounds in chlorination with CO-Cl_2 mixture at temperature 1000°C.*

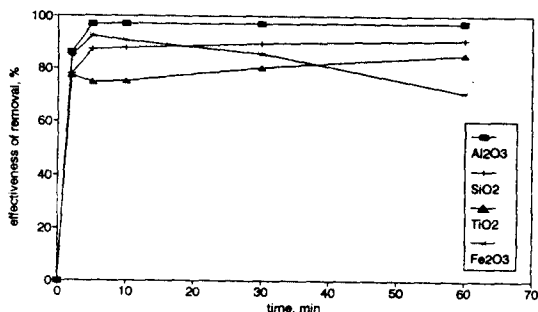| effectiveness	η [%]				
time [min]	2	5	10	30	60
Al_2O_3	86.0	96.8	96.9	97.0	97.2
SiO_2	77.9	87.2	87.6	89.3	90.8
TiO_2	77.3	74.9	75.2	80.3	85.1
Fe_2O_3	84.8	92.4	90.6	85.6	70.7

Fig. 6. Influence of time on effectiveness of removal of individual inorganic compounds in chlorination with CO-Cl₂ mixture (1:1) at 1000°C.
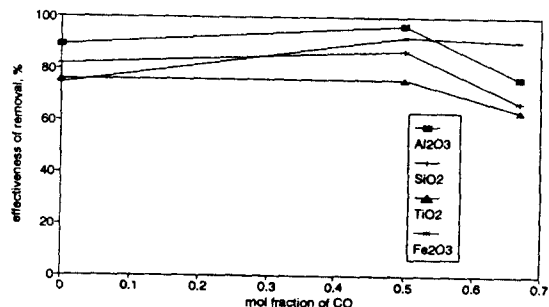

Fig. 7. Influence of CO mole fraction on effectiveness of removal of individual inorganic compounds in chlorination with CO-Cl₂ mixture at 1000°C, 5 min.

removal (approximately 80%) was obtained already at residence time 2 minutes and temperature 1000°C. The most high effectiveness of the process is achived in aluminum oxide. Conversion of silica, titanium and iron oxides respectively is lower than in chlorination with phosgene.

Dispite this the mixture of CO and Cl₂ in molar ratio 1:1 can be considered as highly effective in inorganic compounds removal from fly ash.

Influence of CO concentration on effectiveness of removal of inorganic compounds is presented in Table 7 and Fig. 7.

The maximum effectiveness of the process was observed at molar ratio CO and Cl₂. 1:1.

Table 7. Effectiveness of removal of individual inorganic compounds in chlorination with CO-Cl₂ mixture
(residence time 5 min, temperature 1000°C)

effectiveness	η [%]		
mol fraction of CO	0.0	0.5	0.67
Al₂O₃	89.3	96.8	76.3
SiO₂	81.9	87.2	66.9
TiO₂	75.9	75.9	63.6
Fe₂O₃	74.5	92.4	90.7

The interesting result is the lower effectiveness of chlorination of inorganic compounds at CO mol fraction 0.667 as pure chlorine.

This phenomenon can be explained by the lower partial pressure of chlorine in the reactor.

IV. CONCLUSION

1) Experimental results indicate that to achive high conversion of inorganic material in the fly ash require residence time approximately 5-10 minutes and temperature 1000°C.

2) The rate of removal of inorganic material from concentrated fly ash for phosgene and CO/Cl₂ mixture is comparable.

3) The many problems and difficulties envisaged for the carbochlorination of low-aluminum and non-bauxite ores requires much basic and applied research with usful reference to the established processes for titanium and other metal oxide.

4) The actual development of a carbochlorination process for non-bauxite materials should be foreseen in a wider technological scenario in which the traditional view of separate monometallurgies would turn to a chloride-metallurgy of general use for processing polymetallic oxide ores.

ACKNOWLEDGEMENT

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