Migration of Cr-containing Ti-nanominerals from coal to coal fly ash Zhao Yueyuan¹, Takahashi Fumitake^{1*}

1: Tokyo Institute of Technology, Suzukake, 4259, Nagatsuta, Midori-ku, Yokohama, 226-8503 Japan *corresponding author: takahashi.f.af@m.titech.ac.jp

Keywords: Cr; Ti-nanominerals, coal fly ash, migration pathway

INTRODUCTION

Cr was classified by the US National Research Council (1980) as an element of moderate environmental concern in coal utilization activities. As described by Zhao et al. (2017), high resolution transmission electron microscopes (HR-TEM) coupled with energy dispersive spectrometers (EDS) have been used to identify the largest proportions of Cr in association with Ti-nanominerals in a coal sample. Ti-nanominerals incorporating Cr exert dangerous impacts on human health and environment because they are ultra-fine fragments that are difficult to control during coal utilization, especially in the coal fly ash (Silva et al. (2012)). Thus, it is necessary to investigate the migration of Cr-containing Ti-nanominerals from coal to coal fly ash.

MATERIALS AND METHODS

Density separation of coal fly ash

Through four times of distilled water separation, coal fly ash (Fig.1A) has been separated into dark floating particles (mainly unburned carbon: see Fig. 1B), white floating particles (Fig. 1C), light deposition particles (Fig. 1D), and heavy deposition particles (Fig. 1E)).

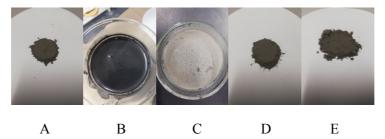


Figure 1 Macro morphology of separated coal fly ash samples: A: unseparated coal fly ash; B: unburned carbon-based floating particles; C: white floating particles; D: light deposition particles; E: heavy deposition particles

Element analysis

The contents of Ti and Cr in coal fly ash were determined by X-ray fluorescence spectrometry (XRF, PW2404) with 0.001% detection limit as listed in Table 1.

Tuble I Contents of IT and of in cour and couring ash samples (Cinter (C/O)							
Elements	Coal	Coal fly ash	Floating particles		Deposition particles		
			Unburned carbon	White particles	Light particles	Heavy particles	
Ti	1.18*	2.0715	2.459	0.315	2.04	2.345	
Cr	0.03038*	0.03015	0.0442	0.021	0.0329	0.0469	
-							

Table 1 Contents of Ti and Cr in coal and coa	al fly ash samples (Unit: wt%)
---	--------------------------------

*: revised from Zhao et al (2017)

Nano-scale mineralogical analysis

The nanominerals in coal fly ash samples were analyzed by HR-TEM (JEM-2010, JEOL). Elemental contents of nanominerals were measured by energy dispersive spectrometers (EDS).

RESULTS AND DISCUSSION

Element contents

As shown in Table 1, compared with the coal sample (Zhao et al (2017)), the content of Ti in coal fly ash is higher than coal. On the other hand, Cr content of coal fly ash are basically similar with that of coal. In the separated coal fly ash samples, Ti and Cr are concentrated in unburned carbon-based floating particles and heavy deposition particles. Therefore, these two samples were selected for further anlaysis using HR-TEM.

TEM-EDS analysis results

In coal fly ash samples, the most of spherical Ti-Fe-Si-Al-nanominerals (Fig. 2B) were detected in unburned carbon-based floating particles. Only one spherical Ti-Fe-nanomineral (Fig. 2C) was found in heavy deposition particles. However, Cr was not detected in these observed nanominerals. Compared with Cr-containing Ti-nanominerals in Fig. 2A, the shape of Ti-nanominerals in coal fly ash are close to the sphere with clear boundary. They are partially clustered and the elemental compositions are complex. If Ti-nanominerals in coal are melted and transformed to aluminosilicate minerals during coal combustion, the analysis results suggest that some of Cr, originally associated with Ti-nanominerals in coal, might have migrated to other unknown parts of coal fly ash. It might imply missed risk of heavy metal emission from coal combustion.

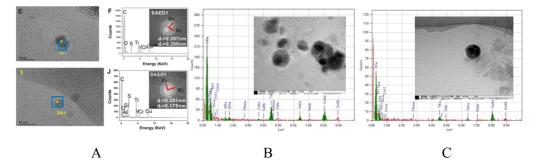


Figure 2. Spherical Ti-nanominerals through TEM-EDS: A: Cr-containing Ti-nanominerals in coal (revised from Zhao et al (2017)); B: Spherical Ti-Fe-Al-Si-nanominerals in unburned carbonbased floating particles; C: Spherical Ti-Fe-nanominerals in heavy deposition particles

CONCLUSION

Through the TEM-EDS anlysis, the most of spherical Ti-Fe-Si-Al-nanominerals were detected in unburned carbon-based floating particles of coal fly ash. Cr was not detected in observed nanominerals. It might suggest that some of Cr, originally associated with Ti-nanominerals in coal, might have migrated to other unknown parts of coal fly ash. Further researches are necessary to investigate Cr migration in coal combustion.

ACKNOWLEDGEMENT

This research was supported financially by JSPS KAKENHI Grant numbers 18H01567. The authors appreciate them greatly.

REFERENCES

- Silva et al (2012) The occurrence of hazardous volatile elements and nanoparticles in Bulgarian coal fly ashes and the effect on human health exposure, *Science of the Total Environment*, 416, 513-526.
- US National Research Council (1980) Trace element geochemistry of coal resource development related to environmental quality and health. Washington, DC, USA: National Academy Press
- Zhao et al. (2017) Chromium and vanadium bearing nanominerals and ultra-fine particles in a super-highorganic-sulfur coal from Ganhe coalmine, Yanshan Coalfield, Yunnan. China, *Fuel*, 203, 832-842.