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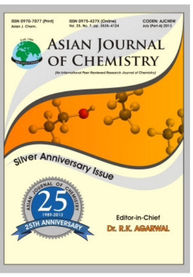

Computer-Controlled Scanning Electron Microscopy Investigation on Transformation of Minerals and $PM_{2.5}$ Emissions During Chinese Coal Combustion†

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The mineralogy of two coals and its combustion-generated particulate matter ($PM_{2.5}$) was characterized in detail by computer controlled scanning electron microscopy. The results show that the interactions among minerals plays an important role in the $PM_{2.5}$ formation. Transformations of fine Si-Al mineral grains provided by the minerals in coal HT into coarse particles are responsible for the reduction of $PM_{2.5}$ during the combustion of coal HT. The transformed fine Si-Al particles are captured by the coarse Ca-Mg-Al-Si provided by the minerals in coal HT to form larger Ca-Mg-Al-Si particles. Increasing Ca and Mg concentration in coal HT enhances the liquid concentration produced during combustion and hence affects the emissions of $PM_{2.5}$.

Key Words: Computer-controlled scanning electron microscopy, Coal combustionm, Mineral transformation, $PM_{2.5}$.

INTRODUCTION

Particulate matter ($PM_{2.5}$) emission from coal combustion is a major source contributing to air pollution in Huainan City. Computer-controlled scanning electron microscopy is a powerful tool for characterizing the size, chemical composition and morphology of large numbers of individual particles in a reasonable time. Typical applications of computer-controlled scanning electron microscopy to the study of coal minerals and fly ash can be found in Refs.[1,2]. Unfortunately, few studies have been conducted on the application of the computer-controlled scanning electron microscopy technique in the field of coal combustion in China. In this study, two representative types of coal used in coalfired power plants in Huainan of Anhui province were burnt in a laboratory-scale drop tube furnace. The transformation of inherent minerals in raw coals and their effect on the emissions of $PM_{2.5}$ is investigated.

EXPERIMENTAL

Coal properties: Two bituminous coals (XQ, HT) were supplied from power plant. Elemental compositions of the low-temperature ashes of two coals were determined by X-ray fluorescence spectrometry (XRF, RIX 2100 of Rigaku). Low-temperature ashess are obtained with an oxygen plasma reactor (Yamato PR 300). The analyses of the coals are presented in Table-1. Apparently, these two coals exhibit distinct properties. For the oxide compounds, SiO_2 and Al_2O_3 are the most prevalent in the ash of both coals. Besides of it, CaO and MgO are the next abundant compositions and their concentrations vary with coals.

Combustion, particle sampling and characterization: Combustion experiments were performed in a laboratory-scale drop tube furnace with 2000 mm length and having an inner diameter of 50 mm. The combustion temperature was set at 1723 K and the combustion was performed in air. LPI used here is composed of 13 stages having aerodynamic cut-off diameter ranging from 12.1 to 0.06 μm. Mineral particles in the raw coal and chemical speciation of PM were analyzed by JEOL JSM-6510 computer-controlled scanning electron microscopy coupled with an EDAX-EDX spectrometer. The analytical methods of particles have also been described elsewhere[2-4]. Around 1000 mineral particles in raw coal and 2000 mineral particles in PM were analyzed at each magnification, which is sufficient for statistical analyses.

RESULTS AND DISCUSSION

Mineralogical composition, association and particle size distribution of minerals in coals: The mineral composition and their association with organic materials in the raw

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TABLE-1
CHEMICAL ANALYSIS OF COALS USED (XQ AND HT)

	Proximate analysis/wt %, on air dried basis				Ultimate analysis/wt %, on dry free basis				
	Moisture	Ash	Volatile	Fixed carbon	C	H	N	S	O (diff.)
XQ	1.89	23.49	32.66	41.96	75.69	4.53	0.89	0.32	18.57
HT	11.87	11.78	29.27	47.08	68.54	4.22	0.31	0.52	26.41

	Ash composition/wt %, on ash basis										
	SiO_2	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	Na_2O	SO_3	P_2O_5	TiO_2	CuO	NiO
XQ	50.9	36.7	2.58	3.44	0.889	0.800	0.751	1.85	0.339	1.53	0.0134	0.014
HT	39.7	27.9	10.1	4.34	1.65	7.85	3.15	3.17	0.358	1.08	0.0182	0.015

coals are analyzed by computer-controlled scanning electron microscopy. Fig. 1 represents content of the minerals in two coals. The results show that the abundant elements of Si and Al in raw coal matrix are mainly present as Si-Al and Si-rich, especially exist as included association in coal HT. The element of Mg is found to associate with Ca-rich in HT matrix. The high content of calcium in coal HT must be present as Ca-rich,Ca-Mg and Ca-Al-Si. Moreover, elements of Na and K are mainly associated with Al-Si.

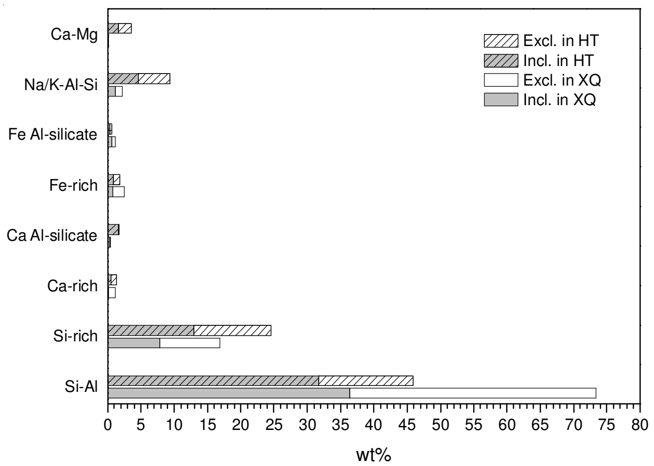


Fig. 1. Mineralogical composition and their association in raw coals

The cumulative particle size distribution of included minerals and excluded minerals (by computer-controlled scanning electron microscopy) is illustrated in Fig. 2a, b. Coals XQ are rich in the fine included minerals and excluded mineral grains. The amount of particles <10 μm within them is about 38 % and 17 % (wt %), respectively. In contrast, less of the fine particles are present in coals HT; The amount of the included minerals and excluded minerals <10 μm account for about 20 % and 10 % (wt %), respectively. It further indicates the different distributions of the minerals in two coals.

Emission of $PM_{2.5}$ generated from the combustion of coal: Fig. 3 shows the properties of $PM_{2.5}$ generated by the combustion of coal XQ and HT. According to the SEM images, shown in Fig. 3a and b, the $PM_{2.5}$ generated by the combustion of coal XQ and HT are different. $PM_{2.5}$ emitted from the combustion of coal XQ are almost fine particle size of single spheres with smooth surfaces, which implies that they are evolved from the liquid drops during combustion. Compared to PM emissions of coal XQ combustion, $PM_{2.5}$ emissions from coal HT combustion PM generated by the combustion of coal HT possess coarse particle size. This implies that the particle size of minerals in coal HT is larger than the size of the mineral in coal XQ. A part of the ash particles have sintered structure, which implies that they undergone melting and condensation.According to the elemental compositions of $PM_{2.5}$, shown in Fig. 3c, the morphological differences between the two kinds of $PM_{2.5}$ are attributed to Si, Al, Ca, Mg content. The differential particle size distributions of ash produced by coal XQ and HT are shown in Fig. 3d. The amount of $PM_{2.5}$ emitted from coal HT is much lower than that from coal XQ, which is consistent with observations from SEM.

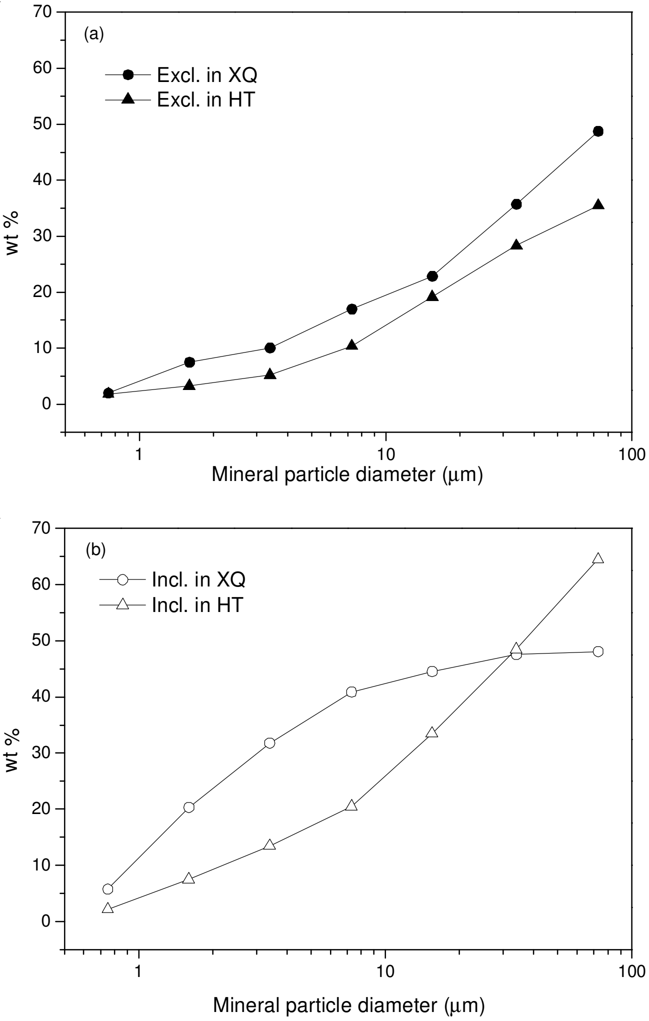


Fig. 2. Particle size distribution of included minerals and excluded minerals in parent coals.

Emission of $PM_{2.5}$ in coal combustion and influence of coal mineral properties: The transformation trends of Si and/or Al-Si bearing minerals, including Al-Si, Si-rich, Ca -and/or Mg-Al-Si in ash particles generated by the combustion of coal XQ

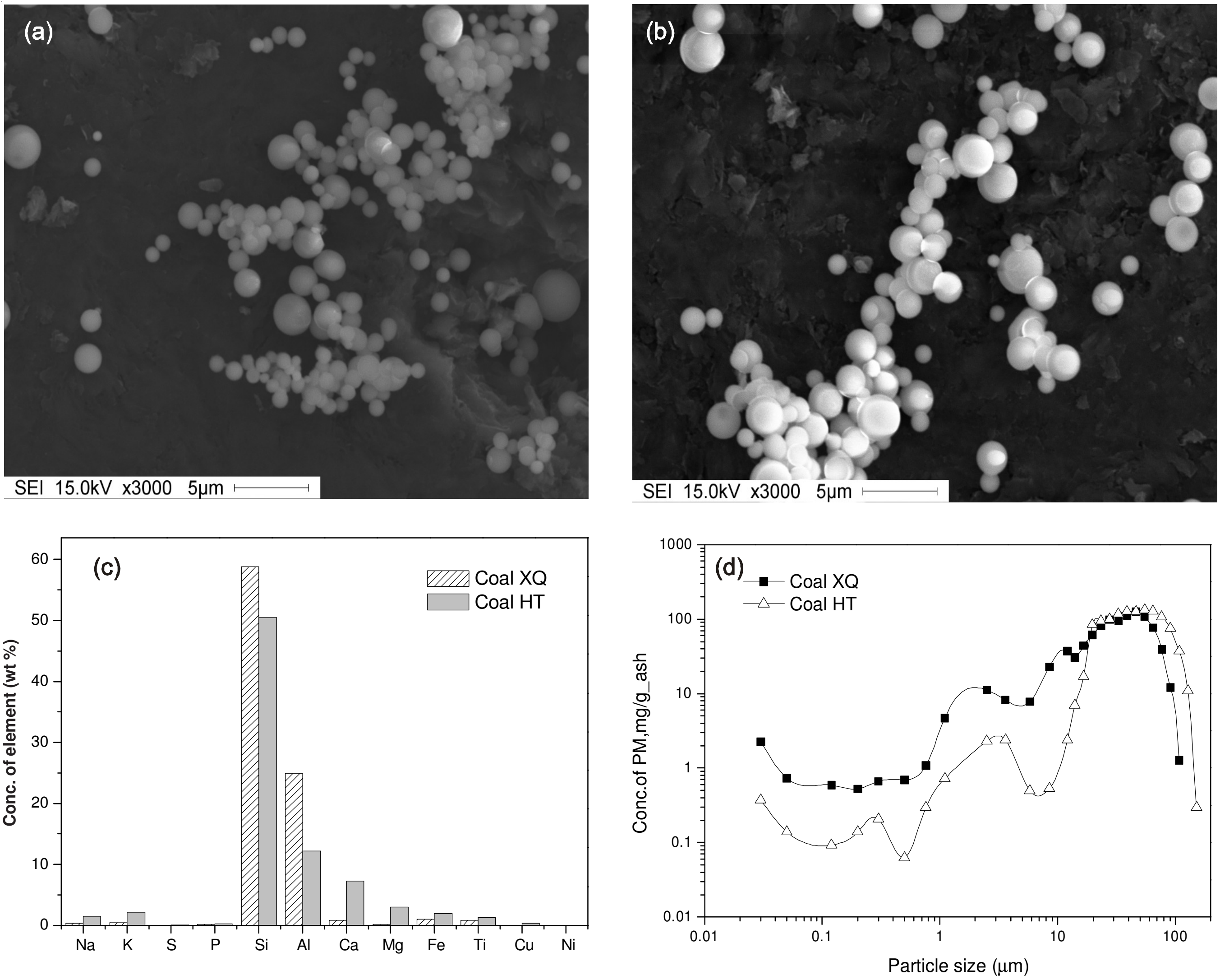
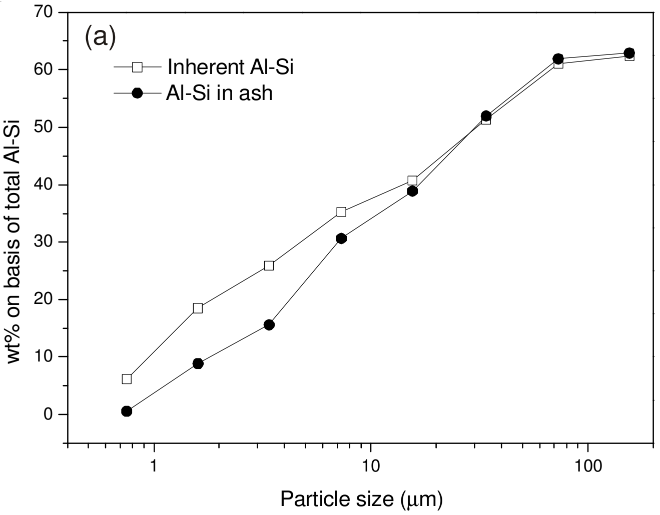


Fig. 3. Physical and chemical properties of $PM_{2.5}$ collected during single coal combustion. (a) SEM image of $PM_{2.5}$ formed from coal XQ; (b) SEM image of $PM_{2.5}$ formed from coal HT; (c) elemental composition of $PM_{2.5}$ produced from coals XQ and HT; (d) total size distribution of PM produced from coals XQ and HT

and coal HT are analyzed by computer-controlled scanning electron microscopy. It is plotted in Fig. 4. The results show that the particle size of Al-Si of ash generating from coal XQ combustion are comparable with its results of the inherent Al-Si in raw coal, while the particle size of Al-Si species of ash generating from in coal HT (mainly Ca/Mg-Al-Si) tends to increase during the combustion. For the coal HT, the contents of Al-Si bearing minerals in $PM_{2.5}$ fraction are reduced significantly.

The existence of Al-Si bearing minerals in $PM_{2.5+}$ of XQ and HT is shown in Fig. 5. The results show that Al and Si in $PM_{2.5+}$ from the combustion of coal HT are associated with Ca, Mg, *i.e.* present in Ca/Mg-Al-Si. In addition, for coal XQ, the total content of Ca, Fe and Mg accounts for around 7 wt. % and the contents of Al and Si are about 87 wt. %, is shown in Table-1. In the case of HT, the contents of Ca and Mg in $PM_{2.5+}$ are higher than those $PM_{2.5+}$ from the combustion of coal XQ. These results, combining with the results of Fig. 5, indicate that the fine Al-Si species in minerals in coal HT are captured by the particles of Ca/Mg-Al-Si provided by coal HT during combustion in order to form the large agglomerations of Ca/Mg-Al-Si in coarse ash. This is also shown by the SEM images of particles in Fig. 5. The fine particles of Al-Si or Si-rich of the cenosphere structures in Fig. 5a and b reacts with the coarse Ca/Mg-Al-Si particles. As a result, they change the irregular large agglomerations of Ca/Mg-Al-Si particles,shown as Fig. 5c and d.



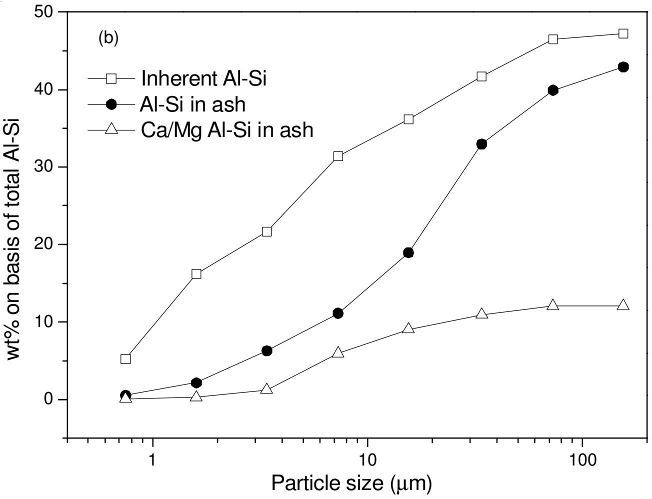


Fig. 4. Transformation of Al-silicate minerals ((a) for the inherent Al-Si in coal XQ and Al-Si in ash generating from coal XQ combustion and (b) for the inherent Al-Si in coal HT and Al-Si and Ca/Mg Al-Si in ash generating from coal combustion)

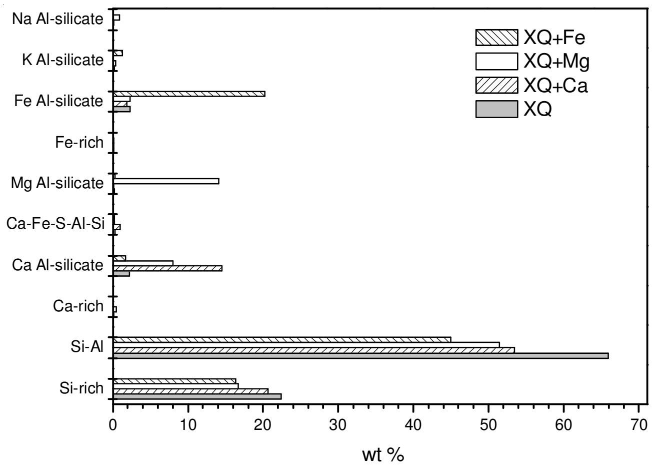


Fig. 6. A comparison of the mineral species in $PM_{2.5+}$ emited from the combustion of coal XQ and HT

For a further understanding of $PM_{2.5+}$ formation during coal combustion,the chemical species in the $PM_{2.5+}$ were quantified by computer-controlled scanning electron microscopy and the results are shown in Fig. 6. The results shown are consistent with the elemental composition as discussed above. That is, aluminosilicate dominates and its salts, including calcium, iron and alkali elements, are relatively prevalent too. For the XQ coal, Ca-Al-silicates and Mg-Al-silicates have minor contents. Both quartz and aluminosilicate should be formed by direct transformation of the inherent quartz and kaolinite in raw coals[5]. On the other hand, the existence of

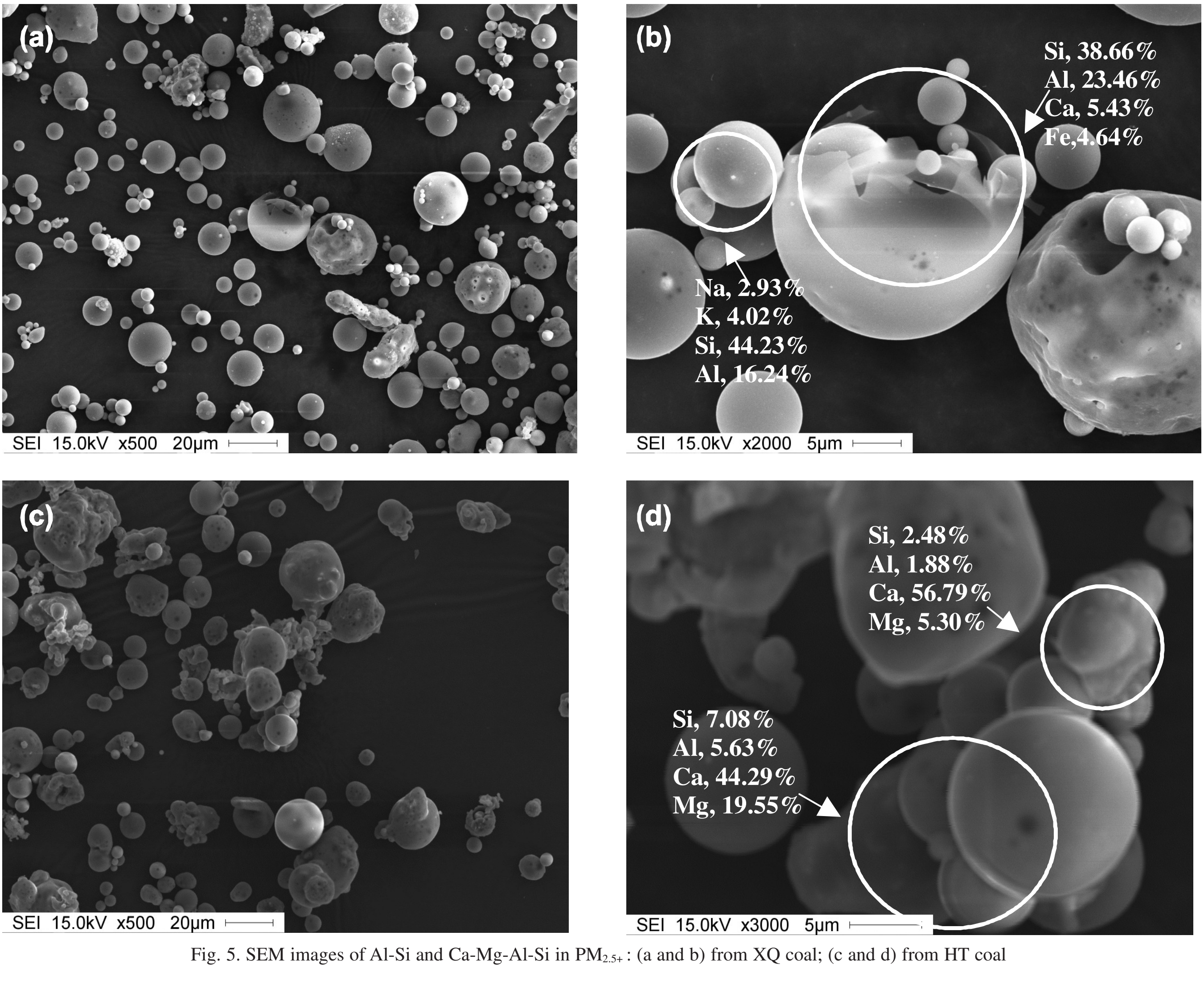


Fig. 5. SEM images of Al-Si and Ca-Mg-Al-Si in $PM_{2.5+}$: (a and b) from XQ coal; (c and d) from HT coal

Ca-Al-silicates and Mg-Al-silicates indicates that the chemical reactions between different elements also play an important role in the transformation of excluded minerals during coal HT combustion. It indicate that the fine Al-Si species in minerals in coal HT are captured by the particles of Ca/Mg-Al-Si provided by coal HT during combustion in order to form the large agglomerations of Ca/Mg-Al-Si in coarse ash. Increasing Ca and Mg concentration in coal HT enhances the liquid concentration produced during combustion and hence affects the emissions of $PM_{2.5.}$

Conclusion

The study show that the interactions among minerals plays an important role in the $PM_{2.5}$ formation. Transformations of fine Si-Al mineral grains provided by the minerals in coal HT into coarse particles are responsible for the reduction of $PM_{2.5}$ during the combustion of coal HT.The transformed fine Si-Al particles are captured by the coarse Ca/Mg-Al-Si provided by the minerals in coal HT to form larger Ca/Mg-Al-Si particles. Increasing Ca and Mg concentration in coal HT enhances the liquid concentration produced during combustion and hence affects the emissions of $PM_{2.5}$.

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