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Enrichment mechanism of arsenic in fine ash deposits during co-combustion of rice husk and coal



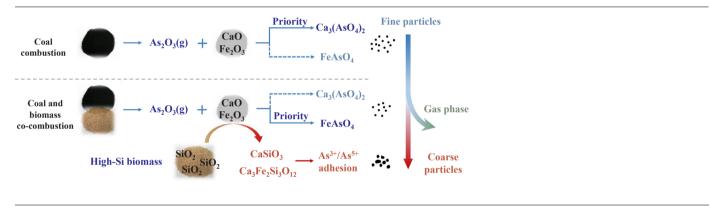
Huimin Liu^a, Yueming Wang^{b,c}, Hongyun Hu^{a,*}, Biao Fu^a, Hong Yao^{a,*}, Jost O.L. Wendt^c

^a State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, China

^b Southern Research, National Carbon Capture Center(NCCC), 31800, Highway 25 North, Wilsonville, AL 35186, United States¹

^c Department of Chemical Engineering and Institute for Clean and Secure Energy, University of Utah, Salt Lake City, UT 84124, United States

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ABSTRACT

Arsenic is a harmful trace element and its behavior under several combustion conditions is of interest. Though the mechanisms regarding arsenic capture and transformation in combustion systems are well known, it is still worth investigating the dominant factors for particular fuels and combustion conditions. Considering the widely application of biomass resources for power generation and the advantages of oxy fuel combustion, this work explored the partitioning behavior of arsenic in ash deposits during co-combustion of high-Si rice husk (RH) and coal at air and oxyfuel condition. Results showed that arsenic was enriched in the inside ash deposits with smaller particle sizes. A larger proportion of arsenic partitioned into the particle phase in oxygen-rich condition than in air. Fe was found to be the key mineral for arsenic enrichment in RH fine ash particles. Combined with thermodynamic calculation, it was concluded that RH doping would change the transformation mechanism of arsenic in size-segregated ash particles during coal combustion. Particularly, the role of Fe on arsenic capture was more remarkable than Ca with RH addition. The enrichment of arsenic in fine ash particles weakened due to the interactions of Si with Ca/Fe. As a result, more arsenic was assumed to be left in the flue gas, which might cause potential emission risk to the environment.

¹ Current affiliation.

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^{*} Corresponding authors at: State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, China.

E-mail address: hyao@hust.edu.cn (H. Yao).

1. Introduction

Biomass is a promising renewable green energy with great potential in reducing greenhouse gas emissions [1,2]. Among numerous thermal conversion technologies, co-combustion biomass with coal is one of the most direct, fastest, and cost-effective ways for energy recovery [3]. Meanwhile, due to the relatively high content of alkali and alkali-earth elements in biomass [4], the reduction of SO2 emissions under cocombustion conditions could be achieved. Rice husk (RH) is one of the typical high-yielding biomass resources, and therefore, has huge amounts from rice producing countries. Compared with other types of biomass, the extremely high concentrations of silicon in RH could improve the co-combustion performance and mitigate ash related issues that might be caused by biomass doping. While compared to coal, highvolatile matter in rice husk might have a promotion effect on the vaporization of inorganic matters in the fuels [5,6]. The enhanced interaction of Si and other minerals during co-combustion determined that the particle size distributions of ash aerosols could be very different from individual coal combustion. Fine ash particles are of special interest since they provide larger surface areas and more active sites for trapping heavy metals but are hard to be captured by traditional air pollution control devices (APCDs), bringing environment and people worse harms.

Among the volatilized heavy metals, arsenic has attracted increasing attention due to its toxicity, volatility, and potential carcinogenic properties [7]. During combustion, arsenic vaporizes into the gas phase first and then transfers into particulate phase probably through coagulation/condensation or chemical reactions. A large proportion of the particulate-bound arsenic is captured as fly ash particles by ash collectors [8], while the rest would emit directly into the air. Thus, the distribution of arsenic in fine ash particles is key to environmental emission of arsenic. The differences in biomass and coal compositions could cause variation in arsenic emissions, especially for rice husk in which the high amount of Si might affect the chemical reactions of arsenic and minerals. To reduce the emission of arsenic to the environment, it is necessary to understand the enrichment behavior of arsenic in fine ash particles during co-combustion of rice husk and coal.

Many researchers have studied the distribution of arsenic in coal fly ashes over a variety of combustion conditions [9-13], and reached conclusion is that arsenic is enriched in particles with smaller sizes. With regard to the enrichment mechanism of arsenic, Senior et al. [9] found that arsenic was concentrated in the high-density ash fractions where pyrite was enriched. Zhou et al. [10] indicated that arsenic was enriched in the fly ash mainly due to the interaction of arsenic and calcium. Through PM sampling of six coals in a 17 kW down-flow laboratory combustor, Seames and Wendt [11] inferred that arsenic preferred to associate with Ca and Fe, and SO₂ in flue gas might decrease the number of Ca and Fe surface sites for arsenic capture. These studies suggested the importance of Ca and Fe on arsenic enrichment in fine particles. Besides, an equilibrium thermodynamic model suggested by Bool and Helble [12] showed that for Si-rich fly ash, Fe₃(AsO₄)₂ was more likely to be formed rather than Ca₃(AsO₄)₂. The equilibrium calculations by Contreras et al. [14] on the behavior of arsenic during co-combustion of bio-waste materials and coal suggested that more arsenic would vaporize if Si was added as the system input. The thermodynamic result of Díaz-Somoano et al. [15] also indicated the promotion effect of Si on arsenic vaporization. However, there still lack of enough experimental work to evaluate the exact effect of Si on arsenic partitioning in ash particles in real high-temperature combustion process. Notably, popular particle size distribution (PSD) measurement techniques, such as low-pressure impactor seem to have difficulties in collecting sufficient amount of submicron particles for arsenic testing (usually ~ 0.1 g per set), making the key minerals that act on arsenic enrichment in fine particles still unclear in co-firing cases, along with the effect of Si on the interactions of arsenic and key minerals.

Furthermore, through the combination of oxy- and biomass

combustion, the negative carbon emissions was likely to be achieved [16]. In particular, the second generation oxy-fuel combustion which with minimum recycled flue gas was able to reduce the systematic energy penalty caused by air separation unit (ASU) and compression and purification unit (CPU) [17-19]. With this technology of large oxygen concentration in the inlet gas, higher flame temperature and enhanced combustion performance were assumed to be obtained. As a result, the vaporization of arsenic might be increased and cause arsenic emission problems. Thus attention should be paid to the effect of oxycombustion on the partitioning behavior of arsenic in fine ash particles during co-combustion of rice husk and coal. Despite some literature has reported arsenic partitioning during oxy-fuel combustion [20-22], almost all of their sampling work were done at low temperature conditions (~400 K), where the transformation of arsenic from gas phase onto ash particles was almost completed. According to Seames and Wendt [11], most of the arsenic partitioned to the solid phase prior to exiting the combustor for all the tested coal samples, indicating that the partitioning behavior of arsenic in the high-temperature environment is more important for understanding its final distribution in PM. The relevant work based on high temperature is, however, still rarely reported.

In our previous study, ash deposition experiments were conducted on simulated heat transfer surface (> 900 K) during coal combustion and the inner layer ash deposits were found to have similar compositions as the submicron ash aerosols while the outer layer ash deposits were closer to the supermicron ash aerosols [23]. Specifically, the deposition rate of the inner layer ash deposits could be correlated with PM_1 (particulate matters < 1 µm) for all tested coals. When the flame temperature was changed due to the variation of inlet oxygen concentration, the compositions of both the submicron ash and that of the inside deposit layer changed simultaneously. Based on the findings, this work gave insight into the partitioning behavior of arsenic in the hightemperature ash deposits during co-combustion of rice husk and coal. The partitioning of arsenic in the inner and outer layer ash deposits was studied, with subsequent investigation on the association regime of arsenic as input of high-Si. The effect of oxygen concentrations on arsenic enrichment in fine ash particles was also considered. The obtained partitioning mechanism of arsenic during co-combustion of coal and rice husk was expected to provide reference for arsenic emission control and broader biomass utilization in power plants.

2. Materials and methods

A typical biomass (rice husk, denoted by RH), a typical bituminous coal (Utah Sufco coal, denoted by Sufco) and their blends (mixed ratio 1:4, denoted by RH/Sufco) were chosen. Note that Sufco coal from Western US Power River basin is known for generating high CaO fly ash. All the feed samples were sieved to < 100 μ m. The ultimate and proximate analysis, ash composition, and arsenic content of the samples are shown in Table 1. Si was found to be the dominant component in the RH ash. For Sufco coal the content of Ca was relatively high.

A 100-kW-rated down-fired pilot-scale combustor was used to conduct the combustion experiment, as shown in Fig. 1. With a temperature-controlled ash deposition probe system, Ash deposits were sampled at Port 6 on the coupon surface of constant temperature 923 K and holding for 1 h. Detailed descriptions on the combustor and ash deposit sampling systems can be found elsewhere [24]. According to the adhesion strength, the collected ash deposits were divided into the tightly bound deposits next to the steel surface (denoted as inside deposits) and the loosely bound deposits that could be removed easily by air blowing (denoted as outside deposit). Further analyses on the deposition rate of the inside deposition rates and the compositions of the inside deposit, not only for single Sufco coal combustion but also for that of RH and RH/Sufco samples. It supported the correlation between inside deposits and submicron particles in a wider fuel adaption range.

 Table 1

 Composition analysis of raw samples

Sample	Ultimate a	analysis, w _{ad} ^a /9	%			As/ μ g g ⁻¹	Proximate analysis, $w_{\rm ad}/\%$				
	С	Н	Ν	S	Cl	O ^b		Moisture	Volatile	Ash	FC
RH	28.47	4.15	1.05	0.10	0.07	24.42	1.70	8.16	48.94	33.67	9.46
Sufco	67.87	5.45	1.09	0.36	_	16.87	1.77	6.11	38.49	8.36	47.04
Sample	Ash compositions, <i>w</i> /%										
	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	MnO_2	P_2O_5	K ₂ O	SiO ₂	Na ₂ O	SO_3	TiO ₂
RH	1.73	1.31	1.10	0.84	0.83	1.81	2.66	88.51	0.31	0.32	0.18
Sufco	8.34	18.21	5.25	2.84	0.05	0.01	0.33	48.85	3.09	5.96	0.64
Sufco	8.34	18.21	5.25	2.84	0.05	0.01	0.33	48.85	3.09	5.96	0.64

-: not detected.

^a: air-dried basis.

^b : by difference.

On the other hand, it provided the potential to investigate the enrichment mechanism of As in fine particles based on experimental results from the inside ash deposits.

Scanning electron microscopy equipped with energy-dispersive Xray spectroscopy (SEM-EDS) was applied to characterize the morphology and mineral compositions of the ash deposit samples. Though the SEM-EDS analysis was a semi-quantitative tool, the results were reliable for a concentration being higher than 0.1–0.5 wt% [25]. For the SEM-EDS analysis in this work, at least three sampling areas were analyzed with the size of each area about 1 mm × 1 mm, and the effect of heterogeneity within the samples was thought to be eliminated. In addition, the testing results were obtained in a short period of time based on the same instrument and could be reasonably repeated, eliminating the effect caused by the variation of background condition.

After each experimental set, all of the samples were digested with nitric acid and hydrofluoric acid, then an atomic fluorescence spectrometer (AFS) was used to determine the concentration of arsenic in the diluted solutions. Detailed analysis procedure can be referred to [26]. Procedure blanks and spiked samples were measured with each sample batch for quality control. Each sample was analysed in triplicate and the relative standard deviation for all results was within 5%.

The flue gas temperatures of all tested cases were measured through

Port 1 to Port 9 (Fig. 1). As a result of the low heating value and high ash content of RH, natural gas was co-fired during the individual RH combustion tests to reach adiabatic flame temperatures that comparable to coal combustion conditions. It is found that for all the tested fuels, OXY70 combustion tests showed a much higher flue gas temperature than AIR case. Nonetheless, the gas temperature at Port 6 was similar for the two atmospheres and thus the effect of local flue gas temperature on the formation of ash deposits was reasonably eliminated.

3. Results and discussion

3.1. Partitioning of arsenic in the ash deposits

The concentration of arsenic in the inside and outside deposits of rice husks during air and OXY70 combustion were tested and shown in Fig. 2. Compared to the outside deposits, the concentration of arsenic in the inside deposits was much higher in all cases. Based on the enrichment factor (*EF*) proposed by Ratafia-Brown [27], the *EF* values of arsenic in the ash deposits could be expressed by $[(C_{As}/C_{Fe})_{ash}]/[(C_{As}/C_{Fe})_{raw}]$, where C_{As} and C_{Fe} represent the concentration of arsenic and iron separately; the subscript ash and raw represents the ash residual of

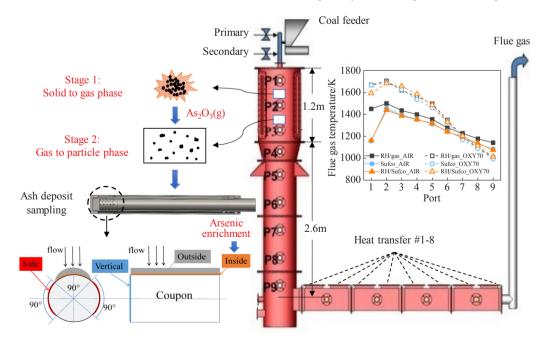


Fig. 1. Combustion and ash deposit sampling system of 100 kW down-fired combustor.

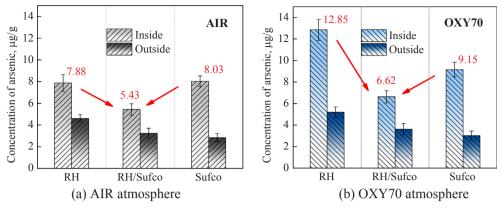


Fig. 2. Concentration of arsenic in the ash deposits of fuel samples.

 Table 2

 Enrichment factor (EF) of arsenic in the ash deposits of various samples.

Sample name	Inside deposi	its	Outside de	Outside deposits		
	AIR	OXY70	AIR	OXY70		
RH RH/Sufco Sufco	0.90 0.82 1.72	1.02 1.48 2.04	0.60 0.64 0.66	0.51 0.73 0.88		

RH or raw rice husk sample, respectively. If the *EF* value of one trace element in ash is above 0.7, the element is regarded to be enriched [27].

According to the calculation results in Table 2, the *EF* value of arsenic in the inside deposits was above 0.7 in each case, indicating that arsenic tended to be enriched in the inside ash deposits. In contrast, almost all of the *EF* values of arsenic in the outside deposits were below 0.7 and no significant enrichment of arsenic was observed. Through the morphology analyses of the inside and outside ash deposits by SEM, it was found that the inside ash deposits contained a larger proportion of particles with smaller sizes. Besides, only submicron particles participated in the formation of deposit at early stages since their velocity was low enough [28]. From this perspective, the results confirmed the enrichment of arsenic in fine particles.

Besides, Fig. 2 showed that compared to AIR condition, the arsenic concentration in the ash deposits at OXY70 condition was higher for all the fuels, either in the inside or outside deposit parts. It indicated that a larger proportion of arsenic was transferred into the particle phase under oxy-fuel combustion. The possible explanation was that at the

OXY70 case, higher adiabatic flame temperature was obtained (e.g. 3036 K vs. 2238 K for RH combustion), followed by the enhanced vaporization of inorganic matters. The vaporized particles usually own larger specific surface area and more active cation sites for arsenic adsorption [13], contributing to the partitioning of arsenic from gas phase to solid phase. Meanwhile, arsenic in the included and excluded mineral matters was assumed to vaporize easier at OXY70 condition, which also led to the increased arsenic concentration in the inside/ outside ash deposits.

In addition, an interesting phenomenon found in Fig. 2 is that the concentration of arsenic in the inside RH/Sufco ash deposits is significantly lower than that of RH or Sufco ash deposits, while it does not exist for the outside deposits. Previous study [29] had confirmed that the major contributor to arsenic enrichment in the inside Sufco ash deposits was the interaction between Ca and arsenic, it was thus hypothesized that a larger amount of Si in the ash from high-Si input of RH might reduce the capability of Ca on arsenic capture. However, the key minerals acting on arsenic enrichment in the ash deposits of RH combustion have not been confirmed yet. The overall effect of Si on the association between arsenic and the key minerals for RH/Sufco blends will be discussed in detail below.

3.2. Key minerals for arsenic enrichment in rice husk ash deposits

The mass fractions of major compositions in the RH ash deposits were measured with SEM-EDS and shown in Fig. 3. Since EDS analysis is semi-quantitative, the results focus more on the difference between inside and outside particles of RH. The components were divided into two groups: group A including Fe, K, Al, S, and P (see Fig. 3(a)) and

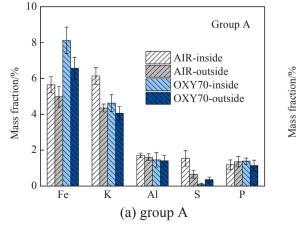
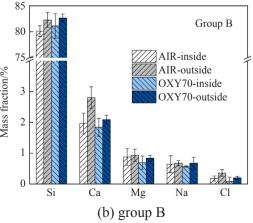


Fig. 3. Mass fractions of major compositions in inside and outside RH ash deposits, adapted from [24]



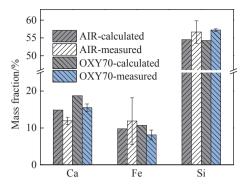


Fig. 4. Measured and calculated mass fractions of Ca/Fe/Si in the inside ash deposits of RH and Sufco blends.

group B including Si, Ca, Mg, Na, and Cl (see Fig. 3(b)). For the elements in group A, their concentrations in the inside deposits were almost larger than the outside part. For elements in group B on the contrary, their concentrations in the outside deposits were larger.

Compared to the inside part, more Si was contained in the outside part. It was probably due to that silicon usually occurred in the forms of silicates in rice husk, which were refractory and tended to form larger ash particles. At the same time, the relatively high fraction of Si in ash aerosols enhanced the combination of alkaline earth metals (typically Ca and Mg) and Si to form high-temperature alkali silicates melts [30], thus Ca and Mg were also observed in group B. Though Al might be more inert than Si in high temperature combustion, the mass fraction of Al in the inside deposits was slightly higher than the outside part in both atmospheres. The possible explanation to this phenomenon was that aluminosilicate in the deposits tended to be coated by Fe to form sticky Fe-rich aluminosilicate particles [31], enriching Fe and Al in the inside deposits.

As for the alkali metals, it is known that biomass is famous for the high concentration of K and the volatilization of K during combustion is directly related to the formation of intransigent surface deposits [32]. The possible speciation of K in the ash aerosols are chloride and sulfate. Kinetic model results of Glarborg and Marshall [33] indicated that SO₃ would react with KCl or KOH to form KHSO₄ or KSO₃Cl, which may then be converted to K₂SO₄. As a consequence, the enrichment of both K and S was observed in the inside RH ash deposits, as seen in Fig. 3(a). The result was consistent with Reichelt et al. [34] who reported that K₂SO₄ mainly accumulated on high-temperature heating surfaces. Besides, it is found that when air combustion was transferred to OXY70 combustion, the contents of K and S in the inside deposits decreased remarkably and S was even higher in the outside part. This is probably due to that higher flame temperature in the OXY70 case accelerated the sticky coating of K₂SO₄ on the surface of inert particles, such as silicate to form clusters with larger sizes [35]. In addition, the high amount of P in rice husk may lead to the formation of partially molten alkali-rich phosphate, such as K₃PO₄ that adhered to the fine particles [36] and thus maintained in the inside deposits. Compared with K, the content of Na was much lower in the rice husk sample, making the impact of Na less significant. More importantly, it was reported that the diffusion coefficient of Na was only about one fourth of that of K [37]. The competitive sulfation of KCl to NaCl might inhibit the generation of sticky Na₂SO₄, so Na and Cl tended to be more concentrated in the outside RH ash deposits. Considering the lower limit of the quantitative analysis of EDS (0.1-0.5%) [25], the partitioning behavior of Na and Cl in the RH ash deposits could not be quantified yet.

Overall, Fe, Al, K, S and P showed the enrichment tendency in the inside RH ash deposits. However, as presented in Fig. 3, one exceptional case is the simultaneous increase of Fe in the inside and outside deposits of rice husk either in the AIR or OXY70 atmosphere. Combined with the arsenic partitioning trend in the inside/outside RH ash deposits (see Fig. 2), it was not surprising to find that arsenic behaved in the same

way as mineral Fe, indicating effective capture of Fe on arsenic vapor. Therefore, it was reasonably concluded that the key mineral for arsenic enrichment in the RH fine particles was Fe [11,38,39].

3.3. Partitioning mechanism of arsenic during co-combustion of coal and rice husk

Considering that the variation in fuel properties would lead to different enrichment mechanism of arsenic, the effects of minerals on arsenic enrichment in the inside ash deposits during mono Sufco combustion were also conducted experimentally in our previous study [29]. Unlike the RH combustion case, Ca rather than Fe was found to be the major contributor for arsenic enrichment in the inside Sufco ash deposits, mainly due to the inherent high Ca content in Sufco that resulting in the remarkable increase of Ca in submicron particles. With the discussions above, it suggested that the evolution of minerals Ca, Fe and Si should be of concern regarding arsenic partitioning behavior during co-combustion. By comparison, the calculated and measured concentrations of these elements in the inside ash deposits of RH/Sufco blends are shown in Fig. 4. Note the calculated values were obtained by weighting two fuels according to the blending ratio.

Results in Fig. 4 presented that regardless of the atmosphere, the measured mass fractions of Ca and Fe in the inside ash deposits tended to be lower than the calculated results, while the mass fraction of Si was higher. Previous study of Han et al. [40] on fine ash formation during Si-rich biomass and coal co-combustion pointed out that interactions between biomass and coal inhibited the vaporization of Ca and Fe from coal. This was expected to explain the less amount of Ca and Fe in the inside deposits. Based on the close relationship of arsenic and Ca/Fe to form stable arsenates (R1 and R2) [41], a smaller amount of arsenic vapor was assumed to be captured in the fine particles during cocombustion conditions, thus arsenic enrichment in the inside RH/Sufco ash deposits was weakened to some extent (see Fig. 2). In addition, when high-Si biomass was blended, the interaction between Si and Ca was expected to be improved (R3). Accordingly, the transformation of Ca from fine particles to coarse particles contributed to the less significant partitioning of arsenic onto fine particles [40].

$$CaO + 1/3As_2O_3(g) + 1/3O_2 \rightarrow 1/3Ca_3(AsO_4)_2$$
 (R1)

$$Fe_2O_3 + As_2O_3(g) + O_2 \rightarrow 2FeAsO_4$$
 (R2)

$$CaO + SiO_2 \rightarrow CaO \cdot SiO_2$$
 (R3)

$$3\text{CaO} + \text{Fe}_2\text{O}_3 + 3\text{SiO}_2 \rightarrow \text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$$
(R4)

To further study the inhibition effect of Si on the association of As and Ca/Fe, thermodynamic equilibriums of the As-M-O system (M referred to Ca and/or Fe) and As-Si-M-O system were calculated by HSC chemistry 6.0. The considered arsenic species included $As_2O_3(g)$, $As_4O_6(g)$, $As_4O_{10}(g)$, $Ca_3(AsO_4)_2$, $Ca(AsO_2)_2$, FeAsO₄, Fe₃(AsO₄)₂. The input minerals were simplified as CaO, Fe₂O₃ and SiO₂, with excess O₂ in the atmosphere and N₂ as the balance gas. The input mole ratio of CaO:Fe₂O₃:SiO₂ was set to 10:1:63 according to their amounts in the RH/Sufco fuel mixtures. The results were shown in Fig. 5.

When Ca and Fe were co-existing, the calculation results of As-Ca-Fe-O system showed that arsenic tended to react with CaO rather than Fe_2O_3 and $Ca_3(AsO_4)_2$ was the main product (R1). It well explained that in the high-Ca Sufco coal combustion case, Ca was observed as the key mineral for arsenic enrichment in fine particles. When Si was added into the system, $Ca_3(AsO_4)_2$ decomposed at about 900 K followed by the generation of FeAsO₄ in a wide temperature range of 800–2200 K (R2), which supported the important role of Fe for arsenic retention in rice husk. From the equilibrium compositions for Si, Ca, and Fe (not displayed here), it was found that CaO preferred to combine with SiO₂ to form CaSiO₃ throughout the process (R3). Moreover, a small amount of Ca₃Fe₂Si₃O₁₂ was observed at < 1000 K zone in the As-Ca-Fe-Si-O system (R4). These interactions between Si and Ca/Fe largely inhibited

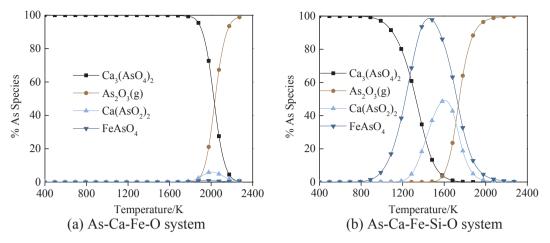


Fig. 5. Equilibrium compositions for As with and without Si in the combustion system.

the adsorption of gaseous arsenic by key minerals, thus the enrichment phenomenon of arsenic in the inside RH/Sufco ash deposits was less remarkable.

In summary, our experimental observations and theory calculations propose a schematic partitioning pathway of arsenic during co-combustion of high-Ca coal (i.e. Sufco coal) and high-Si biomass (i.e. rice husk) (Fig. 6). Arsenic in gas phase tended to react with Ca/Fe to form arsenates and the role of Ca was more important for high-Ca coal. When high-Si biomass was blended with coal, the interaction of Si with Ca and Fe converted more of key minerals Ca/Fe into coarse particles, which had an inhibition effect on the enrichment of arsenic in fine particles. Due to the less efficient capture of gaseous arsenic by Ca/Fe, the proportion of arsenic that left in the flue gas was assumed to be larger, which might cause a higher emission risk to the environment. Meanwhile, there might be some amount of arsenic transferring into the coarse phase, mainly caused by the adhesion of As^{3+}/As^{5+} on Ca/Fe-Si compounds with larger particle sizes. However, it was hard to quantify the mass quota of arsenic in the gas phase, fine particle phase and coarse particle phase at present, since the amount of arsenic in hightemperature flue gas was failed to be measured due to the limitation of experimental conditions. More validation work is thought to be carried out in the near future, expecting to get a deeper understanding on the partitioning behavior of arsenic under various combustion conditions.

4. Conclusions

Co-combustion experiments of Rice husk (RH) and a typical bituminous coal (Sufco) were carried out in a 100kw down-fired oxy fuel combustor. The sticky-bound inside and loosely-bound outside ash deposits were sampled with a coupon fixed at 923 K to study the enrichment of arsenic in fine ash particles of high temperature background. The key minerals acting on arsenic enrichment were analyzed and the effect of Si was discussed. Main conclusions are drawn below.

- (1) Arsenic tended to be enriched in the inside ash deposits rather than the outside parts, confirming the enrichment fact of arsenic in fine particles. Compared with air combustion, a larger proportion of arsenic was transformed into the particle phase under oxy-fuel combustion mainly due to the higher flame temperature.
- (2) For individual RH combustion, Fe, Al, K, and S were observed with a higher mass fraction in the inside ash deposits, while only Fe behaved in the same way as arsenic regardless of the variation in atmosphere. Fe was claimed as the key mineral for arsenic enrichment in RH fine ash particles.
- (3) When high-Si biomass was blended with coal, the interaction of Si with Ca and Fe converted more of key minerals Ca/Fe into coarse particles, which had an inhibition effect on the enrichment of arsenic in fine particles. More arsenic was assumed to be left in the flue gas, while some might be adhered by Ca/Fe-Si compounds with larger particle sizes.

CRediT authorship contribution statement

Huimin Liu: Conceptualization, Methodology, Investigation, Writing - original draft, Writing - review & editing. Yueming Wang: Resources, Data curation, Investigation. Hongyun Hu: Conceptualization, Methodology, Supervision, Writing - review & editing. Biao Fu: Methodology. Hong Yao: Supervision, Funding acquisition. Jost O.L. Wendt: Resources, Supervision.

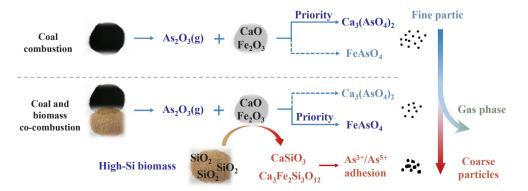


Fig. 6. Partitioning pathway of arsenic during co-combustion of high-Ca coal and high-Si biomass.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- Demirbas A. Potential applications of renewable energy sources, biomass combustion problems in boiler power systems and combustion related environmental issues. Prog Energy Combust Sci 2005;31(2):171–92.
- [2] Zou H, Li W, Liu J, Buyukada M, Evrendilek F. Catalytic combustion performances, kinetics, reaction mechanisms and gas emissions of Lentinus edodes. Bioresour Technol 2020;300:122630.
- [3] Raclavska H, Juchelkova D, Roubicek V, Matysek D. Energy utilisation of biowaste—Sunflower-seed hulls for co-firing with coal. Fuel Process Technol 2011;92(1):13–20.
- [4] Sandberg J, Karlsson C, Fdhila RB. A 7 year long measurement period investigating the correlation of corrosion, deposit and fuel in a biomass fired circulated fluidized bed boiler. Appl Energy 2011;88(1):99–110.
- [5] Wang T, Yang Q, Wang Y, Wang J, Zhang Y, Pan W-P. Arsenic release and transformation in co-combustion of biomass and coal: effect of mineral elements and volatile matter in biomass. Bioresour Technol 2020;297:122388.
- [6] Liu H, Wang C, Zhang Y, Huang X, Guo Y, Wang J. Experimental and modeling study on the volatilization of arsenic during co-combustion of high arsenic lignite blends. Appl Therm Eng 2016;108:1336–43.
- [7] Wang C, Liu H, Zhang Y, Zou C, Anthony E. Review of arsenic behavior during coal combustion: volatilization, transformation, emission and removal technologies. Prog Energy Combust Sci 2018;68:1–28.
- [8] Tang Q, Liu G, Yan Z, Sun R. Distribution and fate of environmentally sensitive elements (arsenic, mercury, stibium and selenium) in coal-fired power plants at Huainan, Anhui, China. Fuel 2012;95:334–9.
- [9] Senior CL, Zeng T, Che J, Ames MR, Sarofim AF, Olmez I, et al. Distribution of trace elements in selected pulverized coals as a function of particle size and density. Fuel Process Technol 2000;63(2–3):215–41.
- [10] Zhou C, Liu G, Wang X, Qi C, Hu Y. Combustion characteristics and arsenic retention during co-combustion of agricultural biomass and bituminous coal. Bioresour Technol 2016;214:218–24.
- [11] Seames WS, Wendt JOL. Regimes of association of arsenic and selenium during pulverized coal combustion. Proc Combust Inst 2007;31(2):2839–46.
- [12] Bool LEI, Helble JJ. A laboratory study of the partitioning of trace elements during pulverized coal combustion. Energy Fuels 1995;9(5):880–7.
- [13] Tian C, Gupta R, Zhao Y, Zhang J. Release behaviors of arsenic in Fine particles generated from a typical high-arsenic coal at a high temperature. Energy Fuels 2016;30(8):6201–9.
- [14] Contreras ML, Arostegui JM, Armesto L. Arsenic interactions during co-combustion processes based on thermodynamic equilibrium calculations. Fuel 2009;88(3):539–46.
- [15] Díaz-Somoano M, Unterberger S, Hein KRG. Prediction of trace element volatility during co-combustion processes. Fuel 2006;85(7):1087–93.
- [16] Lim JS, Manan ZA, Alwi SRW, Hashim H. A review on utilisation of biomass from rice industry as a source of renewable energy. Renew Sustain Energy Rev 2012;16(5):3084–94.

- [17] Escudero AI, Espatolero S, Romeo LM, Lara Y, Paufique C, Lesort A-L, et al. Minimization of CO₂ capture energy penalty in second generation oxy-fuel power plants. Appl Therm Eng 2016;103:274–81.
- [18] Liszka M, Ziębik A. Coal-fired oxy-fuel power unit process and system analysis. Energy 2010;35(2):943–51.
- [19] Ochs T, Oryshchyn D, Woodside R, Summers C, Patrick B, Gross D, et al. Results of initial operation of the Jupiter Oxygen Corporation oxy- fuel 15 MWth burner test facility. Energy Procedia 2009;1(1):511–8.
- [20] Low F, Zhang L. Arsenic emissions and speciation in the oxy-fuel fly ash collected from lab-scale drop-tube furnace. Proc Combust Inst 2013;34(2):2877–84.
- [21] Oboirien B, Thulari V, North B. Major and trace elements in coal bottom ash at different oxy coal combustion conditions. Appl Energy 2014;129:207–16.
- [22] Zhuang Y, Pavlish JH. Fate of hazardous air pollutants in oxygen-fired coal combustion with different flue gas recycling. Environ Sci Technol 2012;46(8):4657–65.
 [23] Zhan Z, Fry AR, Wendt JOL. Relationship between submicron ash aerosol char-
- acteristics and ash deposit compositions and formation rates during air- and oxycoal combustion. Fuel 2016;181:1214–23.
- [24] Wang Y. Ash aerosol and ash deposit formation during high temperature oxycombustion of various solid fuels. Department of Chemical Engineering. Ph.D. The University of Utah; 2019.
- [25] Newbury DE, Ritchie NW. Is scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDS) quantitative? Scanning 2013;35(3):141–68.
- [26] Zou C, Wang C, Liu H, Wang H, Zhang Y. Effect of volatile and ash contents in coal on the volatilization of arsenic during isothermal coal combustion. Energy Fuels 2017;31(11):12831–8.
- [27] Ratafia-Brown JA. Overview of trace element partitioning in flames and furnaces of utility coal-fired boilers. Fuel Process Technol 1994;39(1):139–57.
- [28] Kleinhans U, Wieland C, Frandsen FJ, Spliethoff H. Ash formation and deposition in coal and biomass fired combustion systems: progress and challenges in the field of ash particle sticking and rebound behavior. Prog Energy Combust Sci 2018;68:65–168.
- [29] Liu H, Sun X, Wang Y, Zou C, Wang C, Wendt JO. Arsenic partitioning in hightemperature ash deposits during oxy-fuel combustion. Energy Fuels 2019;34(1):863–70.
- [30] Lindström E, Sandström M, Boström D, Öhman M. Slagging characteristics during combustion of cereal grains rich in phosphorus. Energy Fuels 2007;21(2):710–7.
- [31] Wang Y, Wu J, Li X, Yu D, Xu M, Wendt JOL. Ash aerosol partitioning and ash deposition during the combustion of petroleum coke/natural gas mixtures. Fuel 2019;256:115982.
- [32] Niu YQ, Tan HZ, Hui SE. Ash-related issues during biomass combustion: alkaliinduced slagging, silicate melt-induced slagging (ash fusion), agglomeration, corrosion, ash utilization, and related countermeasures. Prog Energy Combust Sci 2016;52:1–61.
- [33] Glarborg P, Marshall P. Mechanism and modeling of the formation of gaseous alkali sulfates. Combust Flame 2005;141(1):22–39.
- [34] Reichelt J, Pfrang-Stotz G, Bergfeldt B, Seifert H, Knapp P. Formation of deposits on the surfaces of superheaters and economisers of MSW incinerator plants. Waste Manage 2013;33(1):43–51.
- [35] Gallagher NB, Peterson TW, Wendt JOL. Sodium partitioning in a pulverzed coal combustion environment. Symp (Int) Combust 1996;26(2):3197–204.
- [36] Grimm A, Skoglund N, Boström D, Ohman M. Bed agglomeration characteristics in fluidized quartz bed combustion of phosphorus-rich biomass fuels. Energy Fuels 2011;25(3):937–47.
- [37] Thy P, Lesher CE, Jenkins BM. Experimental determination of high-temperature elemental losses from biomass slag. Fuel 2000;79(6):693–700.
- [38] Zhang Y, Wang C, Liu H. Experiment and mechanism research on gas-phase As2O3 adsorption of Fe₂O₃/γ-Al₂O₃. Fuel 2016;181:1034–40.
 [39] Liu Z, Yang S, Li Z, Xie X, Li Y, Sun Z, et al. Three-layer core-shell magnetic Fe₃O₄@
- [39] Liu Z, Yang S, Li Z, Xie X, Li Y, Sun Z, et al. Three-layer core-shell magnetic Fe₃O₄@ C@ Fe₂O₃ microparticles as a high-performance sorbent for the capture of gaseous arsenic from SO₂-containing flue gas. Chem Eng J 2019;378:122075.
- [40] Han J, Yu D, Wu J, Yu X, Liu F, Wang J, et al. Fine ash formation and slagging deposition during combustion of silicon-rich biomasses and their blends with a lowrank coal. Energy Fuels 2019;33(7):5875–82.
- [41] Zhang Y, Wang C, Li W, Liu H, Zhang Y, Hack P, et al. Removal of gas-phase As₂O₃ by metal oxide adsorbents: effects of experimental conditions and evaluation of adsorption mechanism. Energy Fuels 2015;29(10):6578–85.