



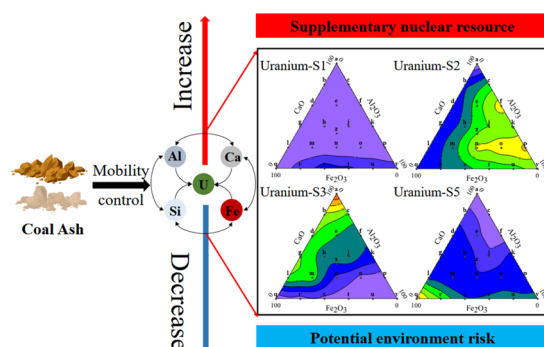
A quantitative evaluation of uranium mobility and potential environment risk in coal ash with $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-CaO}$ system

Zhe Yang^a, Changxiang Wang^a, Danqing Liu^{a,b}, Sen Yang^a, Yumei Li^{a,b}, Yu Ning^a, Yangyang Zhang^a, Ye Tang^a, Wei Zhang^a, Yilian Li^{a,*}

^a School of Environmental Studies, China University of Geosciences, Wuhan, 430074, China

^b State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan, 430074, China

GRAPHICAL ABSTRACT



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ABSTRACT

Uranium-enriched coal ash (CA) receives a significant attention as a supplementary nuclear resource also due to its potential environmental risk. Combining with CA, the changing trend of uranium occurrence in synthetic coal ash (SCA) was described at $\text{CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ ternary phase diagrams with a fixed SiO_2 (wt. %, 30%, 50% and 70%) and Na_2O (2%) content. This study reveals that the mode of uranium occurrence proposes a three-stage changing process during coal combustion including uranium oxidation, combination and encapsulation. Furthermore, a high frequency of encapsulated uranium resulted from the complicated interactions among major components with a medium SiO_2 content, whereas the degree was higher at a higher SiO_2 , resulting in the decrease of uranium mobility. Uranium was encapsulated by Si-Al matrix and Fe-Si depletion if provided the high Al_2O_3 and Fe_2O_3 but low CaO contents. However, with the development of calcium looping and biomass co-firing process, the change of element mobility should be considered in industry owing to the extra-added alkaline metals. As the activation of Ca^{2+} induces a significant susceptibility of acid attack, cautions must be paid in CA with a higher Ca/Si ratio to avoid its utilization as constructive materials for the potential environmental risk.

1. Introduction

Coal currently provides 37% of the world's electricity as a fossil fuel

due to the wide distribution and great abundance on earth (WCA, 2018), and about 2.712 billion tons of coals were consumed to dominantly generate electricity in China in 2017 (NBS, 2018). Based on

* Corresponding author.

E-mail address: yl.li@cug.edu.cn (Y. Li).

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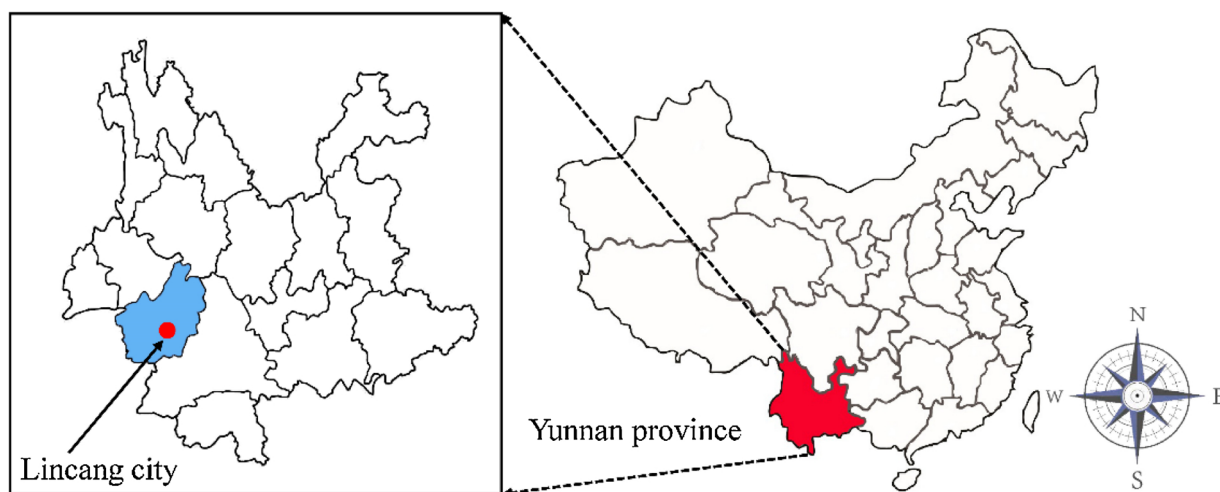


Fig. 1. Location of the Lincang city (Yunnan, southwestern China).

these statistic data, it is estimated that coal will still play a crucial role on China's energy supplement in the near future. Although coal ash (CA, coal combustion residue) can be reused to synthesize advanced microporous adsorbents and other construction materials (Kovler, 2012; Yoon and Bae, 2019; You et al., 2019), a large proportion of it is disposed directly as long-term surface impoundments and landfills (USEPA, 2015). The average content of uranium in Chinese and world coal is 2.43 and 2.40 $\mu\text{g/g}$, separately (Dai et al., 2012; Ketris and Yudovich, 2009), while its content can be as high as hundreds and thousands in certain coal deposits (7207 $\mu\text{g/g}$ of uranium in Yili basin) (Dai et al., 2015a; Lauer et al., 2017; Dai et al., 2015b; Dai et al., 2017a, 2015c). With the decreasing of U reserves in conventional deposits, the U-enriched coal has received a significant attention as a promising nuclear source and the cut-off grade is suggested to be 1000 $\mu\text{g/g}$ (ash basis) (Dai and Finkelman, 2018). However, it is necessary to be cautious on the utilization of such coal due to the anomalous elemental concentration as well as its potential environment risk (Hower et al., 2016). As not being a volatile element, uranium tends to enrich at CA during combustion, and its content in CA is at least 4 times higher than in coal (Yang et al., 2018, 2019a). This U-enriched CA is considered as a potential nuclear resource with the technology improved (Monnet et al., 2015; Dai et al., 2017b). Likewise, ashes containing valuable elements more or less may thus be a potential supplement of industrially demanded metals (Dai and Finkelman, 2018; Kermer et al., 2017), and a large number of researches were investigated to recovery them from CA including Si (Alam et al., 2019), Al (Doucet et al., 2016), Ga (Font et al., 2007), REE (King et al., 2018; Taggart et al., 2018), and etc.

During coal combustion process, exchangeable and organics-bound uranium are firstly oxidized to U-oxides, which further interact with alkaline/alkaline-earth metals to generate uranates at higher temperature (Yang et al., 2016). Sintering behavior of different CAs varies widely depending on the ash chemical composition and other factors including ash size, combustion temperature, atmosphere and pressure (Nel et al., 2015; Krishnamoorthy et al., 2017; Khadilkar et al., 2015; Jing et al., 2011). Thereinto, combustion temperature plays a critical role on determining the sintering and fusion behavior of CA and synthetic coal ash (SCA) (Hsieh, 2019; Yan et al., 2016; Li et al., 2017). As being evidenced that uranium can be encapsulated in silicates (Lei et al., 2014), amorphous phases (Yang et al., 2019a), Si-Al glass (Yang et al., 2019b) and Fe-oxides (Sun et al., 2018), it is difficult to leach uranium from CA especially prepared at a high temperature both in acid solution and aqueous alkaline (Yang et al., 2018, 2019a). Moreover, the agglomeration of some solid particles with large amounts of trace element results from the intensive behaviors of ash sintering and

slagging (Namkung et al., 2016; Hower et al., 2018; Dai et al., 2014). Due to the ubiquity of SiO_2 and Al_2O_3 in CA, the proportion between them also governs the formation of amorphous phases, degree of ash sintering and change of microstructure (Zhao et al., 2013; Hu et al., 2017). Furthermore, a higher proportion of alkaline-bearing fractions (e.g. Na, Ca, Fe, etc.) could interact with Si-Al compounds to form the low melting-point eutectic, recrystallization phase and intact Si-Al glass during combustion (Khadilkar et al., 2015; Pallarés et al., 2018; Niu et al., 2018).

Although the mode of uranium occurrence is dominated by residue in CA (Yang et al., 2019a, 2018), little research did contribute to investigating the effect of major components on uranium mobility and environment risk. Combining sequential extraction test and other analyses, CA and SCA, prepared by different proportions of Al_2O_3 - Fe_2O_3 -CaO and the fixed SiO_2 (wt. %, 30%, 50% and 70%) and Na_2O (2%), were employed to evaluate uranium mobility in CA/SCA. On this basis, interaction mechanisms among uranium and major components during combustion were systematically illustrated. Ultimately, a proper ratio of major components in coal itself was proposed to minimize the potential contamination to surface and groundwaters during ash stacking, or to maximize the uranium mobility once the CA is considered as potential nuclear resource in the future.

2. Materials and methods

2.1. Coal sample and reagents

Coal samples with the high uranium concentration were collected from four coal deposits, located at different villages (MW: Mengwang, DZ: Daizhai and ZT: Zhangtuo) of Lincang, Yunnan, Southwestern China. The location was shown in Fig. 1. The coal was firstly dried to constant weight at 105 $^{\circ}\text{C}$, crushed by a planetary ball mill (GSXX-4, Geological Experiment Institute of Hubei) to sieve through a 100-mesh sieve, and stored in a desiccator for future use. Major components and uranium contents of coals were listed in Table 1.

SiO_2 , Al_2O_3 , Fe_2O_3 , CaO as well as other chemical agents were supplied by Sinopharm Chemical Reagent Co., Ltd. Deionized (DI) water was prepared with the TKA GenPure system for the subsequent experiment and analysis.

2.2. Coal ash and synthetic coal ash

To evaluate the effect of ash chemical composition on uranium mobility and environment risk, the SCA was prepared with various amounts of SiO_2 , Al_2O_3 , Fe_2O_3 and CaO with fixed an amount of Na_2O

Table 1
Major composition of coal samples (wt. %, ash basis).

Sample	Element composition								
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	K ₂ O	TiO ₂	SO ₃	U ^a	LOI
MW1	40.4	19.0	17.0	6.35	2.40	0.829	10.5	101.22	88.90
MW2	56.7	23.0	6.22	2.35	2.53	0.19	7.15	112.56	78.39
DZ	58.4	13.4	6.97	7.85	2.25	0.46	ND	60.86	62.66
ZT	78.6	7.55	8.10	2.20	0.172	0.24	ND	14.23	74.73
China ^b	8.47	5.98	4.85	1.23	0.19	0.33	ND	2.43	ND

^a The uranium contents (μg/g) in four coals were determined according to the description in Section 2.5.

^b Average contents of elements in common Chinese coals (Dai et al., 2012).

(2%) to represent the natural CA. The chemical composition of SCA was supplied in supplementary materials (Table. 1 s, Table. 2 s and Table. 3 s). Every 0.5 g of aforementioned SCA was weighted and transferred into a 50 ml centrifuge tube. 2 ml of uranium standard solution (250 μg/g) was added to the tube and thoroughly mixed in a gas bath shaker without lids at the condition of 200 rpm, 12 h and 60 °C. The treated SCA was then completely dried to constant weight at 60 °C in a drying oven. Subsequently, 2 g of the coal sample and resulted SCA were transferred in quartz crucibles, and combusted in a muffle furnace at studied temperatures for 2 h. The 0.5 g of obtained CA and SCA were naturally cooled down to room temperature, and collected in a 50 ml centrifuge tube for following sequential extraction and other analyses.

2.3. Sequential extraction

The mode of uranium occurrence in CA and SCA was successively divided into 5 fractions (S1: ion exchangeable, S2: carbonates-bound, S3: Fe-Mn oxide-bound, S4: organic matter-bound and S5: remaining in residue) based on Tessier sequential extraction (TSE) method (Tessier et al., 1979; Sun et al., 2016). The digestion procedure of residue, which was fully described in previous work (Yang et al., 2019a), referred to the Chinese standard (Ministry of Land and Resources, 2016). The extraction process only involved S1, S2, S3 and S5 to investigate the mode of uranium occurrence in SCA. 0.5 g of sample was weighted and the experimental procedure was carried out as requested. Followed the every step of extraction, the sample was centrifuged at the speed of 4000 rpm for 5 min, and the supernatant was filtered through 0.45 μm and collected in the 10 ml of centrifuge tube for the following determination by ICP-MS. Subsequently, the proportion of uranium was projected into CaO-Al₂O₃-Fe₂O₃ ternary phase diagrams with the fixed SiO₂ (wt. %, 30%, 50% and 70%) and Na₂O (2%) contents, and its distribution was constructed by Kriging interpolation in software Surfer 12.

2.4. Analytical calculation on environmental implications

To investigate the uranium retention in various SCAs with different chemical compositions, individual contamination factors (C_f, calculated by Eq. 1) and risk assessment code (RAC, calculated by Eq. 2) were calculated. Thereinto, C_f is regarded as a ratio of the elemental concentration in active fractions (the sum of S1, S2 and S3 in this study) to its concentration in residue. A high C_f of studied element indicates a low retention time of studied element, resulting in a high risk to environment. On the other hand, RAC of studied element is also used to evaluate its risk, in which < 1%, 1–10%, 11–30%, 31–50%, and > 50% indicates the no risk, low risk, medium risk, high risk and very high risk, respectively (Hao et al., 2017; Nemati et al., 2011).

$$C_f = (C_{s1} + C_{s2} + C_{s3})/C_{s5} \quad (1)$$

$$RAC = \frac{C_{s1}}{C_{s1} + C_{s2} + C_{s3} + C_{s5}} * 100 \quad (2)$$

Where C_{s1}, C_{s2}, C_{s3}, and C_{s5} represent the contents of exchangeable, carbonates-bound, Fe-Mn oxide-bound and residual uranium, respectively.

2.5. Characterization measurement

X-ray diffraction (XRD, D8-FOCUS, Bruker Company, Germany) was employed to determine the mineralogy of samples by scanning at a 2θ interval of 5–70° with a step size of 0.01° based on Cu Kα radiation. Loss on ignition (LOI) of coal sample was calculated by combusting samples at 815 °C to constant weight. Major composition of coal samples was analyzed by X-ray fluorescence spectrometer (XRF, AXIOSmAX, PANalytical B.V. Company, Netherlands). Morphology and chemical composition of samples were characterized by field emission scanning electron microscope (FESEM, SU8010, Hitachi, Japan) in conjunction with energy dispersive X-ray spectroscopy (EDS). Experimental samples were firstly coated with gold, and images were captured via a back-scattered electron detector at a 10 kV accelerating voltage. Followed by the dilution of leaching and digestion samples with 2% nitric acid, uranium content was determined by inductively coupled plasma-mass spectrometry (ICP-MS, ELAN DRC-II, PerkinElmer Company, USA). The digestion procedure and uranium determination referred to the Chinese standard (Ministry of Land and Resources, 2016), and fully described in the previous study (Yang et al., 2019a). Simultaneously, the performance of ICP-MS was examined by inserting a bank and selected standard solution for every 20 samples. The value of standard solution was guaranteed at an acceptable range (80%–120%) during operation process.

3. Results and discussion

3.1. Mode of occurrence of uranium in CAs at different temperatures

According to Table 1, coal samples are mainly composed of SiO₂, Al₂O₃, Fe₂O₃, as well as CaO, along with a low content of K₂O and other minor elements. Except for K₂O, the content of major components is obviously higher than the average in Chinese coal, while the uranium contents in MW1, MW2, DZ and ZT are 41.7, 46.3, 25.0 and 5.86 times higher than the average, respectively (Dai et al., 2012). The SCA can nearly represent a large proportion of natural ashes in this study owing to the reasonable composition (Dai et al., 2015a). Due to a higher CaO content in MW1 and DZ, U-oxides tend to react with it to form uranates leading to a large amount of carbonates-bound uranium at 500 °C (shown in Fig. 2). However, carbonates especially CaCO₃ will be decomposed once the combustion temperature exceeds 700 °C (Zhou et al., 2019), and the CA begins to sinter at the temperature range of 700–900 °C (Li et al., 2017). Considering the different capacities of uranium integrating with major components, the mode of uranium occurrence in different CAs presents a distinguished change with rising the combustion temperature. Thereinto, the decrease of uranium in S2 contributes to its increases in S3 and S5 at 800 °C, as well as S1~S4 to S5 at 1100 °C. Compared with MW2, DZ and ZT at 800 °C, carbonates-bound uranium in MW1 nearly all transferred to Fe-Mn oxides rather than residue due to its highest content of Fe₂O₃. Although uranium can incorporate with Fe-oxides during combustion (Sun et al., 2018), it is eventually encapsulated in the compact aluminosilicate and Si-Al glass once the temperature rises to 1100 °C, leading to a prominent increase in the content of residual uranium (Yang et al., 2019b). As the sintering and fusion behaviors of CA can be limited by the sufficient SiO₂ (Yan et al., 2017), there is a small amount of Fe-Mn oxide-bound uranium in ZT without being totally depleted in Si-Al matrix even at 1100 °C.

Uranium mobility and environment risk of SCA combusted at 900 °C were investigated in this study, because the coal combustion temperature nearly concentrates at 900 °C for electricity generation in some power plants (Chen et al., 2019). Furthermore, interaction mechanisms among uranium and major components would be systematically

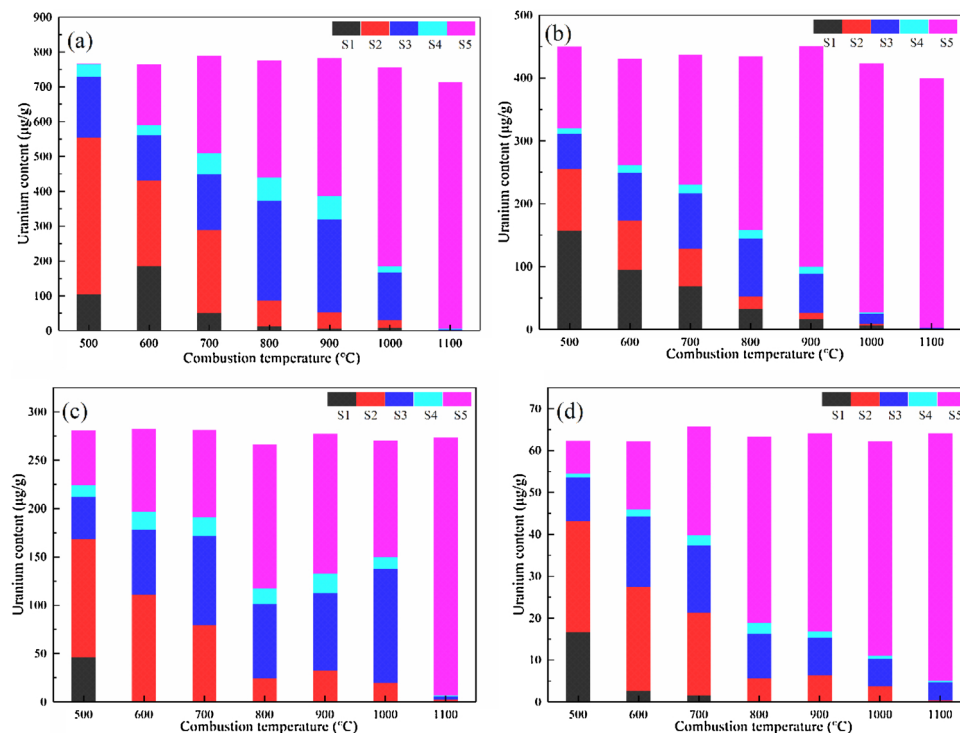


Fig. 2. The mode of uranium occurrence in CAs (a: WM1, b: WM2, c: DZ and d: ZT) prepared at different temperatures, where the data of WM2 from the previous study (Yang et al., 2019a).

discussed at following sections.

3.2. Mode of occurrence of uranium in SCA

3.2.1. Exchangeable uranium in SCAs prepared at 900 °C

The major composition of each spot was listed in supplementary materials, and color-filled contours represented various intervals of uranium proportion. Compared with the distinguishing distribution of other modes of uranium occurrences, the distribution of exchangeable uranium is homogeneous with a small proportion. Uranium can interact with some alkaline metals, alkaline earth metals as well as Fe-oxides during coal combustion, and is subsequently encapsulated in bulk minerals resulting in a stable chemical property. However, as shown in Fig. 3, the proportion of exchangeable uranium continuously decreased with rising CaO and Fe₂O₃ contents due to their combinations during combustion.

3.2.2. Carbonates-bound uranium in SCAs prepared at 900 °C

With increasing SiO₂ content, the proportion of carbonates-bound uranium involved a dynamic change trend. As shown in Fig. 4, there was a larger proportion of carbonates-bound uranium attributing to the

dissolutions of uranate and U-oxide at acid condition. Cautions must be paid in CA with a large amount of carbonates-bound element due to an adverse impact on human health as well as environment for a high chemical activity. Fixed the SiO₂ content, carbonates-bound uranium tends to accumulate at the certain area that is characterized by the relatively high Al₂O₃, medium CaO and low Fe₂O₃ contents (spots J, K, O and P in Fig. 4). However, increasing Ca/Si, Fe/Si and Al/Si ratio would contribute to the formations of alkaline eutectic, Fe-Si depletion and amorphous phase, respectively, leading to an increase in acid resistance of SCA (especially at spots A, Q and V). Therefore, compared with single mechanism, the proportion of carbonates-bound uranium is synthetically governed by the major components of SCA.

Furthermore, uranium could be extracted only under a stronger acid condition if provided excess the CaO, Fe₂O₃ and Al₂O₃, and the potential interaction mechanisms would be discussed in following sections.

3.2.3. Fe-Mn oxide-bound uranium in SCAs prepared at 900 °C

Compared with it in S2, the proportion of uranium in S3 is mainly governed by the contents of CaO and Al₂O₃. Furthermore, without or with the composition of Fe-Mn oxide, a large amount of uranium could

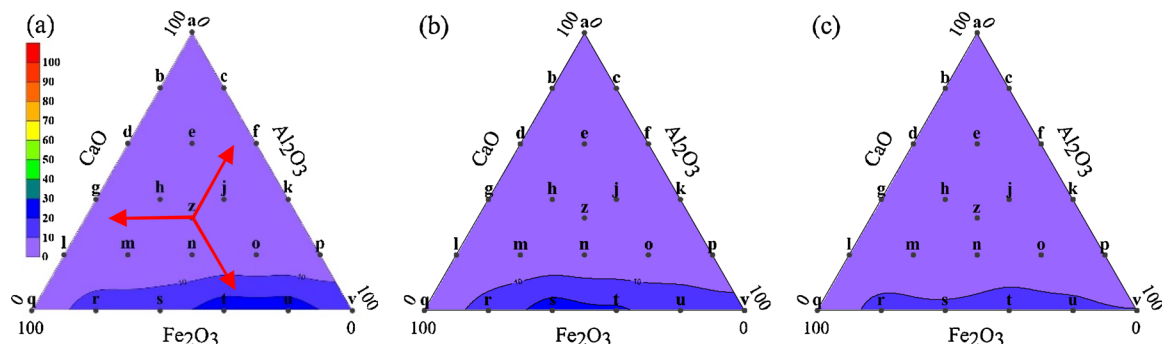


Fig. 3. The distribution of ion exchangeable uranium in SCAs (a: 30% SiO₂, b: 50% SiO₂ and c: 70% SiO₂ content) prepared at SiO₂-Al₂O₃-Fe₂O₃-CaO system.

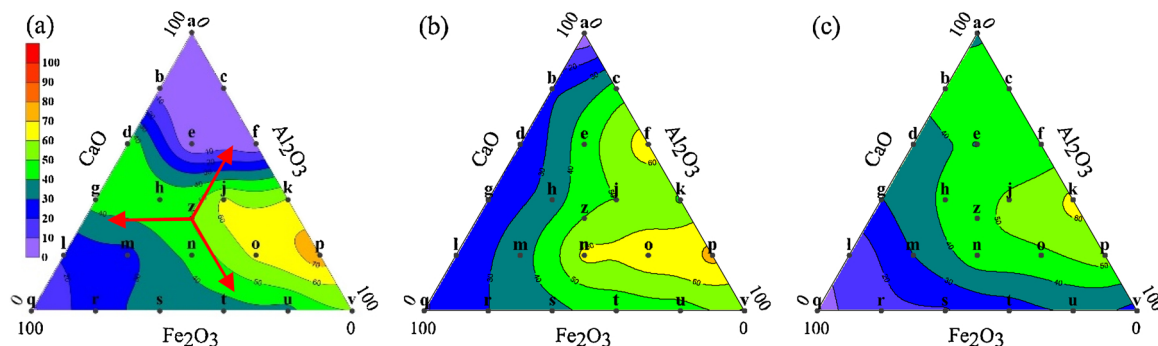


Fig. 4. The distribution of carbonates-bound uranium in SCAs (a: 30% SiO₂, b: 50% SiO₂ and c: 70% SiO₂ content) prepared at SiO₂-Al₂O₃-Fe₂O₃-CaO system.

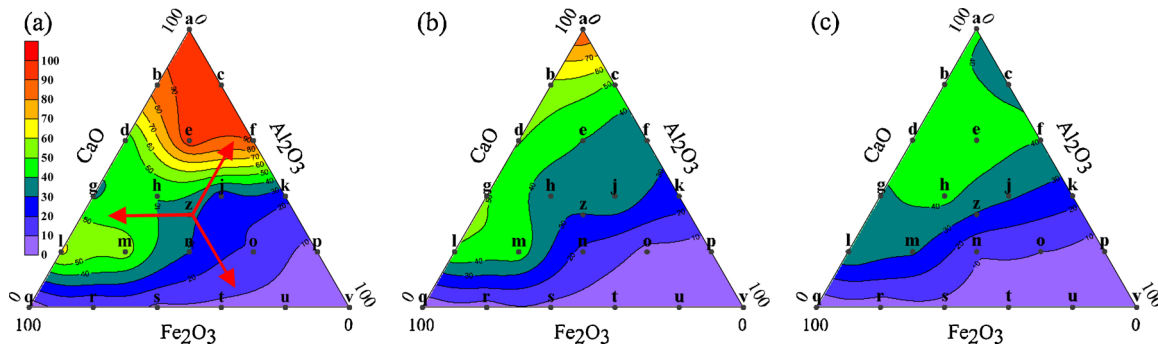


Fig. 5. The distribution of Fe-Mn oxide-bound uranium in SCAs (a: 30% SiO₂, b: 50% SiO₂ and c: 70% SiO₂ content) prepared at SiO₂-Al₂O₃-Fe₂O₃-CaO system.

be both extracted from certain SCAs (spots A and L in Fig. 5). Therefore, it is necessary to illustrate that the sequential extraction of uranium not only depends on the composition but also the solubility of major minerals in SCA. According to Fig. 2, since carbonates-bearing compounds would decompose and interact with other acid components especially at the higher temperature, there was a trend of carbonates-bound uranium transferring to Fe-Mn oxide or residue during coal combustion. Furthermore, uranium can be extracted due to a higher acidity of 25% CH₃COOH solution without regard to the uranium that was largely extracted within previous extraction processes or still encapsulated in bulk minerals (spots Q–V in Fig. 5). The leaching of active uranium (the sum of uranium in S1, S2 and S3) during ash stacking can lead to the contamination of environment and the adverse impact on human health.

3.2.4. Residual uranium in SCAs prepared at 900 °C

Considering the different treatments of CA, e.g. recycling valuable elements to synthesize the new advanced materials or stabilizing toxic elements to decrease their environmental risks, it is necessary to control the element occurrence and mobility in CA. Residual uranium is relatively inert than other modes of occurrence. Fig. 6 showed that the

proportion of residual uranium is mainly governed by CaO and Fe₂O₃ contents. As the mode of uranium occurrence is dominated by residue once the CaO content below a limited value, the extraction efficiency of uranium was significantly improved by activating CA with molten CaCl₂ (Lei et al., 2014). Considering the encapsulated uranium in silicate (Lei et al., 2014), Si-Al matrix (Yang et al., 2019b), amorphous phase (Yang et al., 2019a) as well as Fe oxide (Sun et al., 2018) in CA, the encapsulated behaviors might be strengthened and contributed to a higher proportion of residual uranium with rising SiO₂, Al₂O₃ and Fe₂O₃ contents. Furthermore, the increasing occurrence and degree of ash sintering ascribed to the inhomogeneous components of SCA. The proportion of residual uranium is higher with continuously rising SiO₂ content, different from the largest distribution at the 50% of SiO₂ content (as shown in Fig. 6). Hence, it is conjectured that the occurrence of encapsulated uranium is easier at a medium SiO₂ content, while the degree is higher with rising SiO₂ content. The potential mechanism of element encapsulation would be discussed in detail at following sections.

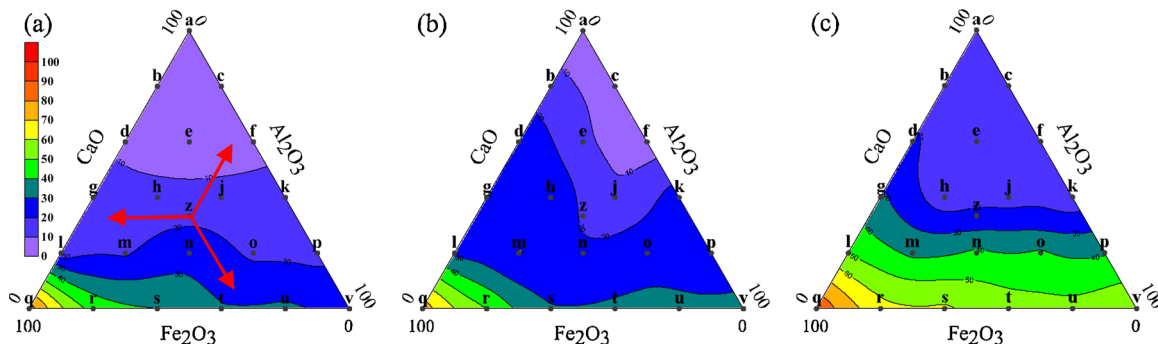


Fig. 6. The distribution of residual uranium in SCAs (a: 30% SiO₂, b: 50% SiO₂ and c: 70% SiO₂ content) prepared at SiO₂-Al₂O₃-Fe₂O₃-CaO system.

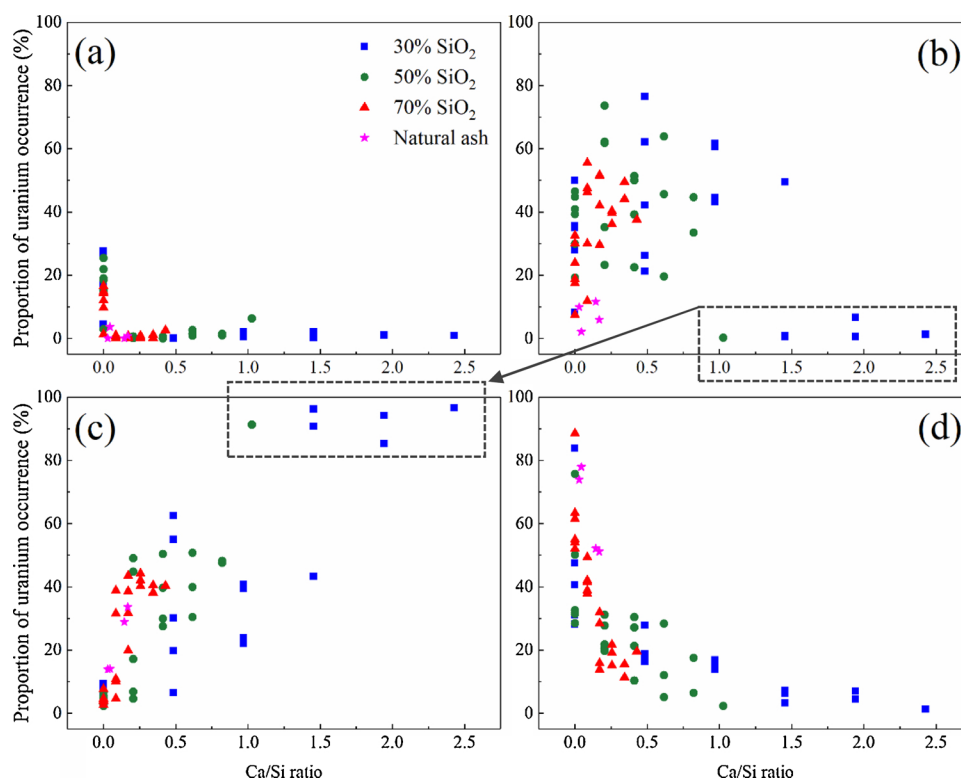


Fig. 7. Changing characteristic of uranium occurrence (a: exchangeable uranium, b: carbonates-bound uranium, c: Fe-Mn oxide-bound uranium, d: residual uranium) in SCAs at different Ca/Si mole ratios.

3.3. Interaction mechanisms among uranium and major components

Combing the distribution of uranium occurrences at $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-CaO}$ system, XRD and FESEM-EDS analyses were employed to unveil the potential mechanism of uranium mobility in different fractions. XRD patterns of SCAs prepared with 30%, 50% and 70% SiO_2 contents were supplied in supplementary materials and shown in Fig. 1s (a), Fig. 1s (b) and Fig. 1s (c), respectively. Based on the determination by FESEM-EDS analysis, the morphology and mineral composition of SCAs at a fixed SiO_2 content (50%) were also attached in supplementary materials (from Fig. 2s to Fig. 8s). Considering that SiO_2 is the most common component in CA, the proportion of different modes of uranium occurrences was collected and projected into a coordinate system with an abscissa of Ca/Si, Al/Si and Fe/Si mole ratio.

3.3.1. Effect of CaO on uranium mobility in SCA

(1) Exchangeable uranium:

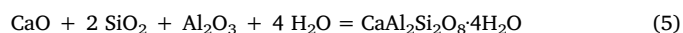
It is well suggested that there is an immobilizing effect of Ca^{2+} on uranium during combustion (Yang et al., 2016). As shown in Fig. 7(a), the proportion of exchangeable uranium significantly dropped down with the existence of CaO in SCA, resulting from the reaction between uranium and alkaline earth metals.

(2) Carbonates-bound uranium:

According to the calculated result by FactSage, the proportion of quartz and hematite decreased with rising content of CaO, and contributed to the increasing formation of andradite (Zhao et al., 2013). The mineral transformation was responsible for a significant change of uranium mobility. Based on XRD patterns in Fig. 1s (SCA-A/E in supplementary materials), Ca^{2+} can interact other intact components to form Ca-enriched fractions including larnite (Eq. 3), mayenite (Eq. 4),

gishmondine (Eq. 5), srebrodolskite (Eq. 6) and amorphous phases. Hence, an improvement in acid solubility of SCA might lead to a higher proportion of carbonates-bound uranium. Furthermore, the excess CaO promotes the generation of lime as well as portlandite with a higher acid resistance of SCA. As shown in Fig. 2s and Fig. 3s (in supplementary materials), lime, larnite, mayenite and alkaline eutectic were generated as the forms of flake aggregation, bulk, cube and flocculent cluster, respectively. Those newly generated minerals might incorporate with U-enriched particles owing to their close associations. On these bases, uranium tends to be extracted at the process of S3 rather than S2 by comparing Fig. 4 with Fig. 5.

Overall, the decreasing proportion of silicates and Fe-oxides and the subsequent generation of excess alkaline minerals were responsible for the firstly increased and then decreased proportion of carbonates-bound uranium with rising Ca/Si ratio. Compared with SCA, the proportion of carbonates-bound uranium in natural CA is lower under the same temperature, mainly because the heat release by organic oxidation can promote the carbonates decomposition and mineral transformation completely.



(3) Fe-Mn oxide-bound uranium:

There was a continuous increasing content of Fe-Mn oxide-bound uranium with rising Ca/Si ratio. Carbonates-bound uranium could transfer to Fe-Mn oxide with a stabilized proportion of residual uranium once the Ca/Si ratio was over 1.0 (auxiliary line in Fig. 7). This phenomenon was also verified by other heavy metals (Zhou et al., 2017), and the potential reason was discussed above.

(4) Residual uranium

It was evidenced that uranium is incorporated into silicate (Lei et al., 2014), Si-Al matrix (Yang et al., 2019b), Fe-oxide (Sun et al., 2018) and amorphous phase (Yang et al., 2019a). According to XRD results in Fig. 1s, Ca^{2+} can integrate with these refractory substances to form different minerals with a greater acid solubility, including larnite, mayenite, srebrodolskite as well as multi-element eutectic. Hence, the proportion of residual uranium continuously decreased with rising Ca/Si ratio owing to the activations of Si-O bond and Si-Al bond. Furthermore, instead of Fe-Si depletion, the proper amount of Ca^{2+} may also promote the integration of CaO with Fe_2O_3 and bulk minerals to form srebrodolskite and other Fe-bearing eutectics. Nowadays, with the development of calcium looping and biomass co-firing process, the extra-added CaO might increase the element mobility and potential environment risk in combustion by-products. On the other side, increasing Ca/Si ratio to 1.0 is effective enough to improve the extraction efficiency of uranium if the CA is served as a potential nuclear resource in the future.

3.3.2. Effect of Al_2O_3 on uranium mobility in SCA

(1) Exchangeable uranium:

As shown in Fig. 8 (a), little effect of Al_2O_3 on exchangeable uranium could be found when compared with CaO and Fe_2O_3 . There was still 20% of uranium adsorbing at the surface of ash particles once the SCA was prepared without CaO. It indicates that the biased combination of uranium especially with CaO is prior to the passive encapsulation by Si-Al matrix during coal combustion.

(2) Carbonates-bound uranium and Fe-Mn oxide bound uranium

Except for the spot of SCA-V, a large amount of uranium in S2 tended to be extracted at a higher Al/Si ratio, while it was opposite in

S3. Since the proportion of uranium in S2 ranges from 0% to 60% with a same Al/Si ratio of 0.5 (as shown in Fig. 8(b)), it is reasonable to conjecture a synergetic rather than determining effect of Al_2O_3 on uranium occurrence. There were massive compounds, regarded as Ca-Al and Ca-Si-Al eutectics, generated in SCA-O (as shown in Fig. 5s). Despite few diffraction peaks of other minerals but quartz (as shown in Fig. 1s), the mineral composition of SCA-V was constituted by amorphous aluminum oxide, aluminosilicate (as shown in Fig. 7s). Because rising Al/Si ratio was beneficial for the increasing proportion of uranium in S2 and the decreasing in S5, the encapsulated behavior of uranium by Si-Al matrix might be weakened if provided the excess Al_2O_3 . Moreover, it was also evidenced that the mineral composition is mainly consisted of independent SiO_2 , lowering melting eutectics and large agglomeration in SCA when the Al/Si ratio is 0.22, 0.29-0.67 and 2, respectively (Hu et al., 2017). The difference in acid solubility among them leads to the change of element mobility, where uranium might be easier to extract from the latter than independent SiO_2 , resulting in a firstly increasing and then stabilizing trend of uranium in S2. As being little uranium encapsulated in quartz (Zhang, 1987), the proportion of uranium in S3 significantly decreases with rising Al/Si ratio, indicating an encapsulated uranium in amorphous aluminosilicates and aluminum oxides.

(3) Residual uranium

Considering that uranium can be separately activated and encapsulated with a higher amount of CaO and Fe_2O_3 , the SCA without Al_2O_3 could be reasonably eliminated to propose a proper analysis. On this basis, the proportion of residual uranium was gradually stabilized with rising Al/Si ratio at a fixed SiO_2 content (shown in Fig. 8(d)). As uranium is encapsulated with amorphous Al and Si-Al matrix in CA (Yang et al., 2019a, b), increasing Al/Si ratio can promote the competition of uranium occurrence in amorphous phases instead of silicates and Fe-oxides in SCA combusted at 900 °C. The decreasing proportion of residual uranium in SCA-V as SiO_2 content increased indicates that

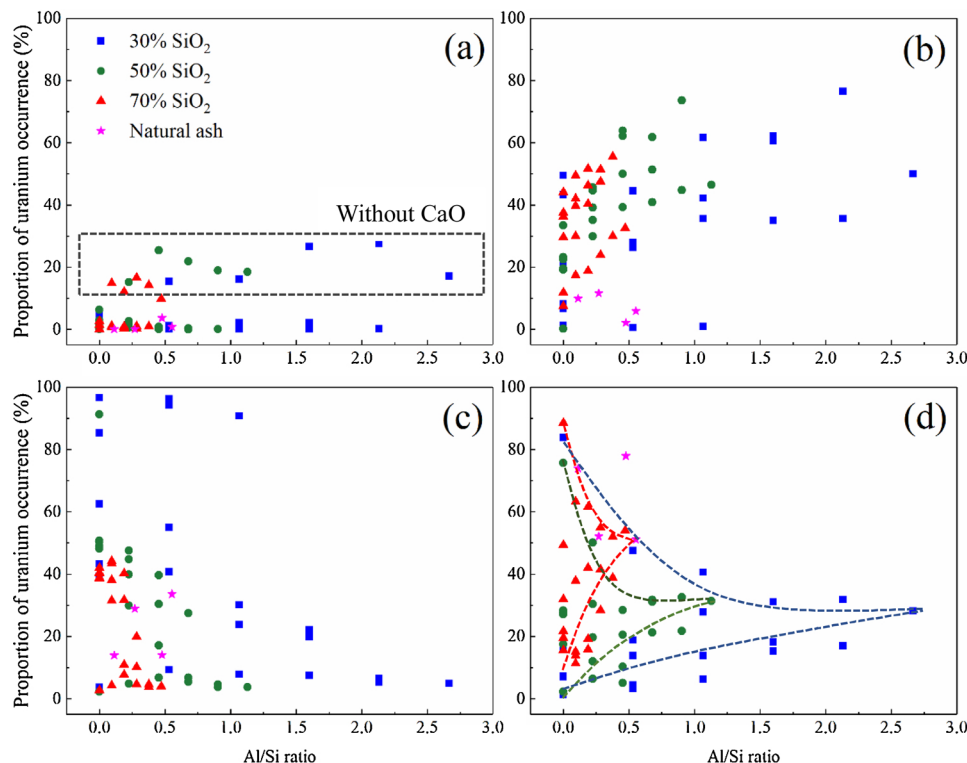


Fig. 8. Changing characteristic of uranium occurrence (a: exchangeable uranium, b: carbonates-bound uranium, c: Fe-Mn oxide-bound uranium, d: residual uranium) in SCAs at different Al/Si mole ratios.

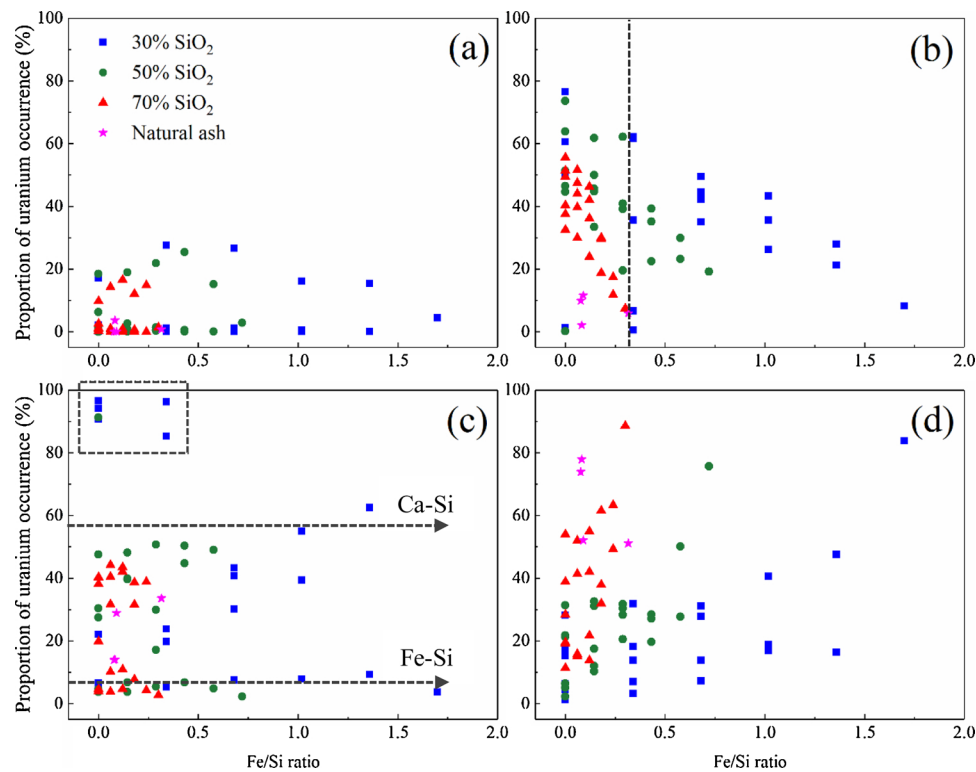


Fig. 9. Changing characteristic of uranium occurrence (a: exchangeable uranium, b: carbonates-bound uranium, c: Fe-Mn oxide-bound uranium, d: residual uranium) in SCAs at different Fe/Si mole ratios.

the composition of Si-Al amorphous phase with a higher Al/Si ratio might contribute to the integration with uranium. Furthermore, it is found that the uranium occurring in amorphous Al is relatively more active than in Fe-Si depletion by comparing SCA-Q with SCA-V in Fig. 6.

3.3.3. Effect of Fe₂O₃ on uranium mobility in SCA

(1) Exchangeable uranium:

As shown in Fig. 9(a), the proportion of exchangeable uranium gradually decreased with rising Fe₂O₃ content due to its affinity with uranium (McBriarty et al., 2018), while it suddenly decreased if only provided a small amount of CaO. It indicates that the combination capacity of uranium with Fe₂O₃ is lower than the interaction between uranium and CaO during combustion.

(2) Carbonates-bound uranium and Fe-Mn oxide-bound uranium

Although U-oxides and uranates are the major compositions of uranium in CA, they can integrate with Fe-oxides during coal combustion (Sun et al., 2018). According to XRD analysis in Fig. 1s (supplementary materials), SCA-M/Q is mainly consisted of quartz and hematite, while Fe₂O₃ can react with lime, quartz and aluminumsilicate to form large-sized eutectics with dense amorphous structures (as shown in Fig. 5s) (Khadilkar et al., 2015; Rivera et al., 2015). As shown in Fig. 8(b), increasing Fe/Si ratio can result in the decreasing proportion of carbonates-bound uranium with a fixed SiO₂ content, whereas Fe-Mn oxide-bound uranium showed a scattered distribution at different SiO₂ contents.

The abnormally high proportion of uranium in S3 ascribed to the increasing alkalinity of SCA and a higher acid resistance, which were systematically discussed at Section 3.3.1. On this basis, although increasing Fe/Si ratio seldom contribute to the change of Fe-Mn oxide-bound uranium especially at a lower SiO₂ content, the distribution of uranium in S3 was divided into three parts due to the entirely different

effects of major oxides on uranium. Thereinto, there was a stabilized proportion of uranium in S3 once the SCAs were constituted by CaO-SiO₂ or Fe₂O₃-SiO₂. Despite of the higher Fe/Si ratio in SCA-M/Q, uranium was extracted as the form of S5 rather than S3. It indicates that the investigation of the mode of element occurrence in CA based on TSE method not only depends on the binding priority of elements to minerals but also on the dissolution of element-enriched fractions at different extraction solutions. The reason for that phenomenon was discussed as following.

(3) Residual uranium

Due to few reactions between U-oxides and quartz, the proportion of residual uranium was higher if provided a larger amount of Fe₂O₃. The formations of iron silicates and iron aluminum silicates may melt at low temperatures (900 °C–1000 °C) (Wang et al., 2012), resulting in the encapsulated behavior of uranium. It was verified that rare earth element as well as uranium were hosted in Fe-oxides and partly depleted in SiO₂ particles (Sun et al., 2018; Kolker et al., 2017), and led to an obvious increase in residual uranium with rising Fe/Si ratio. This phenomenon was similarly evidenced and shown in Fig. 4s and Fig. 6s, where Fe₂O₃ particles could integrated with independent SiO₂ and silicate to form large-sized eutectics. Furthermore, the decrease in the apparent density of Fe-oxides followed the combustion also leads to a low uranium mobility (Zhang, 1987). The existence of alkaline metals in SCA could weaken the encapsulated behaviors of uranium in silicate and Fe-Si depletion for the generation of alkaline eutectics and the increase of acid solubility. Hence, although the Fe/Si ratios are different in SCA-Q, they are all characterized by the low uranium mobility without the activations of Ca²⁺.

3.3.4. Effect of SiO₂ on uranium mobility in SCA

As shown in Fig. 7–9, the change trend of uranium occurrence remained unchanged under different SiO₂ contents. The content of SiO₂ in CA also plays a significant role on ash sintering and slagging. Despite

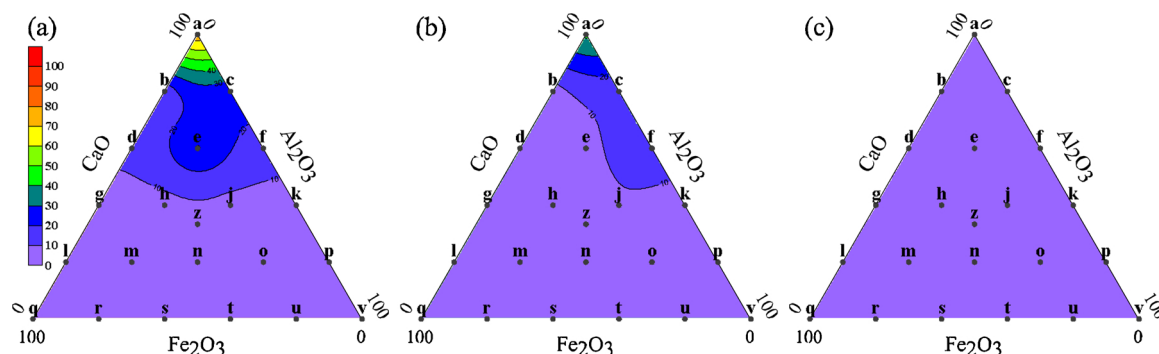


Fig. 10. The distribution of contamination factor in SCAs (a: 30% SiO₂, b: 50% SiO₂ and c: 70% SiO₂ content) prepared at SiO₂-Al₂O₃-Fe₂O₃-CaO system.

little encapsulated uranium in quartz at 900 °C (Zhang, 1987), the mode of uranium occurrence is governed by the complicated interactions among SiO₂ and other major components, which were discussed in detail at previous sections. Overall, the incorporation of SiO₂ with Fe₂O₃ and Al₂O₃ particles could result in the decreasing of uranium mobility in SCA, while an opposite trend was observed in the incorporation with CaO. Since SiO₂ itself is a refractory mineral with a high melting point, the excess SiO₂ obstructs the formation of low melting eutectics, prevents the ash sintering, and results in the decreasing of the acid solubility in CA (Hu et al., 2017). It is a fact that the proportion of residual uranium increases with rising SiO₂ content (as shown in Fig. 6) mainly due to the strengthened encapsulations by Fe-Si depletion and Si-Al matrix. On the other hand, the lower SiO₂ content could promote the formation of alkaline eutectics, leading to the increase of uranium mobility.

3.4. Environmental implications of SCA with different chemical components

RAC and C_f of uranium were both calculated to evaluate its retention in SCA. The distribution of RAC at different SCAs was depicted at Fig. 3. Uranium poses a greater risk to environment with a higher proportion of exchangeable uranium because of its weak binding with the solid phase. RAC of uranium ranged from 11% to 30% especially in some SCAs mainly consisted of SiO₂ and Al₂O₃ but seldom CaO (spots S–V) with a medium risk, whereas it significantly decreased to < 5% if provided a small amount of CaO as a result of a low risk.

Due to a high mobility of carbonates-bound uranium in CA, it is also important to evaluate the ratio of the uranium concentration in active phase to it in residue. As shown in Fig. 10, owing to the significant decrease of C_f with rising SiO₂ content, the CA mainly constituted by SiO₂ (> 70 wt. %) could be selectively used to synthesize some construction materials due to little risk to environment. Furthermore, increasing proportion of CaO contributes to a higher C_f and leads to a potential environmental risk (shown in Fig. 10). The SCAs located at the coordinate axis should be firstly excluded because of their few existences in natural, and then it is necessary to caution the use of CA

with the proportion of chemical component like SCA-E/H/J due to an extraordinarily high risk. Moreover, Fig. 11 showed that the C_f of uranium in SCA gradually increased with decreasing Al/Si and Fe/Si ratio and increasing Ca/Si ratio. Relating to the disposal of CA in long-term retention ponds, there were 113 potential contamination cases in the United States since 1955 (USEPA, 2016). Moreover, with the development of calcium carbonate looping and biomass co-firing process (Criado et al., 2017; Verma et al., 2017), the extra-added CaO may significantly increase the element mobility and induce a potential environment risk, where the uranium and other heavy metals might leach out during ash stacking and resulted in a contamination of soil and underground water (Ramsey et al., 2019). Hence, cautions must be paid in the CA especially with a high Ca/Si ratio.

On these bases, increasing SiO₂ content and regulating Ca/Si, Al/Si and Fe/Si mole ratio < 0.5, > 1.25 or > 0.75 before coal combustion is effective enough to decrease the environment risk of uranium in CA.

4. Conclusion

As the CAs with different components show a diversity in physico-chemical properties, it is necessary to investigate the uranium mobility considering the various utilizations and treatments of ash. In this study, the mode of uranium occurrence in CA and SCA were systematically investigated based on the SiO₂-Al₂O₃-Fe₂O₃-CaO system, and a reasonable ratio of major component of coal itself was proposed to regulate the uranium mobility followed the coal combustion. The results lead to conclusions as follows:

- (1) Mode of uranium occurrence involves a three-stage changing process during coal combustion. Exchangeable and organics-bound uranium in coal are firstly oxidized to U-oxides, which tend to interact with Ca²⁺ to form stable uranates. However, U-oxides and uranates transfer to integrate with Fe-oxides and aluminosilicates due to the decomposition of carbonate minerals and the formation of low melting-point eutectic once the temperature exceeds 700 °C. Finally, the compact Si-Al matrix generated at 1100 °C can

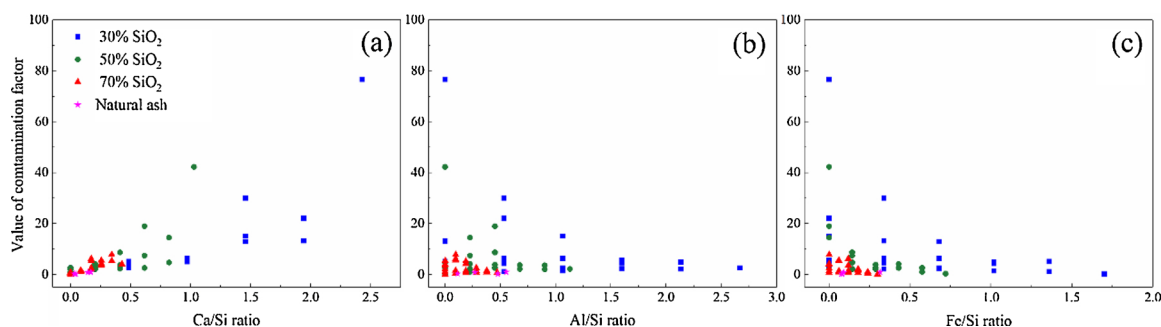


Fig. 11. Changing characteristic of contamination factor in SCA at different Ca/Si (a), Al/Si (b) and Fe/Si (c) mole ratios.

- encapsulate U-bearing fractions, leading to a low chemical activity.
- (2) Although uranium mobility in SCA can be significantly improved with increasing CaO content, uranium, incorporated by low melting point eutectics, tends to be extracted as the form of S3 rather than S2 if provided excess CaO.
 - (3) Without the activation of Ca^{2+} on bed minerals, the sufficient amounts of Fe_2O_3 contributes to the formation of Fe-Si depletion and promotes the encapsulated behavior of uranium, resulting in a larger proportion of residual uranium in SCA.
 - (4) The effect of Al_2O_3 on uranium mobility is between CaO and Fe_2O_3 , while the competition of uranium occurrence in Si-Al amorphous phase cannot be ignored due to its largest distribution in ash.
 - (5) SiO_2 content plays a critical role on ash sintering as well as uranium mobility. A high frequency of encapsulated uranium ascribes to the inhomogeneous composition at a medium SiO_2 content, whereas the degree of encapsulated behaviour is continuously strengthened with rising SiO_2 content leading to the decrease of uranium mobility.
 - (6) Increasing SiO_2 content and regulating Ca/Si, Al/Si and Fe/Si mole ratio <0.5 , >1.25 or >0.75 before coal combustion can benefit from decreasing the environment risk of uranium in CA. On the other hand, it is effective enough to improve the extraction efficiency of uranium when the Ca/Si ratio is 1.0 once the U-enriched CA is served as the potential nuclear resource in the future.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jhazmat.2019.120977>.

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