Promotion of Cotton Stalk on Bioavailability of Phosphorus in Municipal Sewage Sludge Incineration Ash

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Introduction

✦ Sewage sludge incineration

- Reduce the volume and mass of sludge by 90% and 70%, respectively
- Destroy pathogenic agents and generate thermal energy
- Alternative phosphorus resource
- Phosphorus recovery from the incineration fly ash

The fly ash from sludge incineration is contaminated by toxic trace metals and the phosphorus in the untreated fly ash shows low bioavailability, which cannot be applied directly in the farmland as phosphate fertilizer.

It is essential to reduce the toxicity of trace metals and increase the bioavailability of phosphorus in the fly ash.

Introduction

✓ Traditional treatment method

The additive of Ca, Al containing adsorbents

The thermal treatment of the fly ash in a reactor

✓ New research idea

Municipal sewage sludge | **Biomass**

Trace metals (As, Cd, Cr, Zn, etc.) + Mineral elements (Si, Ca, Mg, Al, etc.)

P **Co-firing**

The proposal to co-fire municipal sewage sludge (MSS) with biomass has been proposed to realize the synergistic conversion and chemical state stabilization of multiple trace metals and improve the bioavailability of phosphorus.

Experimental procedures

✓ Experimental material

Table 1 Proximate and ultimate analysis of MSS and biomass (wt.%, as dry basis)

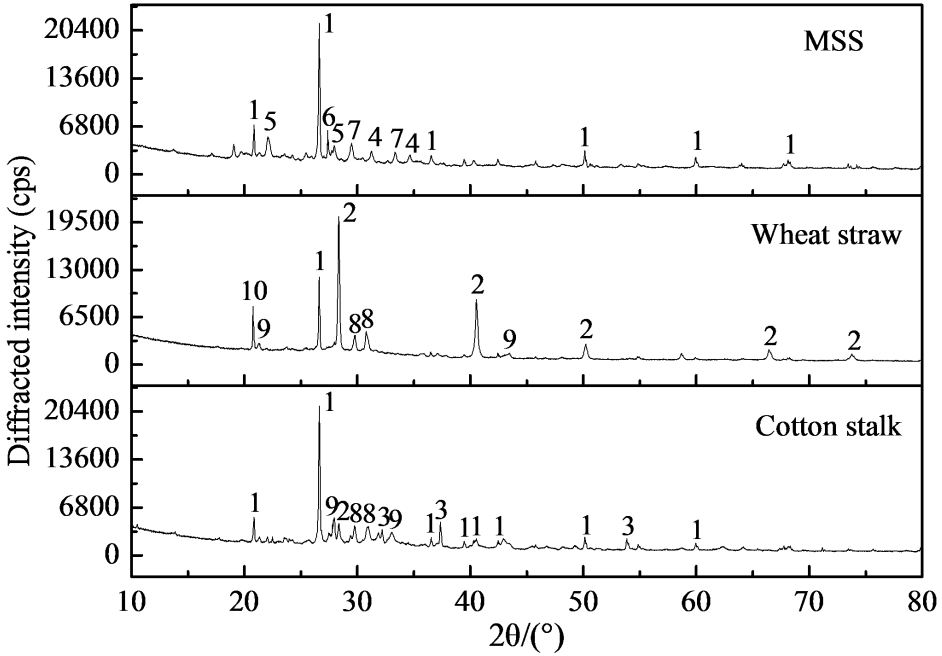
Fuel	Proximate Analysis			Ultimate Analysis					LHV (MJ/kg)
	ash	fixed carbon	volatile	C	H	O	N	S	
MSS	33.39	9.69	56.92	34.85	4.92	19.92	5.99	0.93	13.67
Wheat straw	6.97	19.73	73.30	45.10	5.60	41.56	0.57	0.20	16.46
Cotton stalk	11.79	20.02	68.19	43.22	5.13	38.79	0.92	0.15	16.02

Table 2 Main mineral elements of MSS and Biomass (wt.%, as dry basis)

Fuel	Al	Ca	Fe	K	Mg	P	Si	Na	Cl
MSS	1.76	1.77	1.58	1.06	0.95	1.06	5.27	0.33	0.03
Wheat straw	0.03	0.34	0.07	1.98	0.18	0.11	2.37	0.20	1.14
Cotton stalk	0.43	0.96	0.34	1.01	0.34	0.14	2.48	0.27	0.22

Experimental procedures

✓ Experimental material



1-SiO_2; 2-KCl; 3-CaO; 4-$Ca_9Fe(PO_4)_7$; 5-$NaAlSi_3O_8$; 6-$KAlSi_3O_8$;
7-$MgCa_2(PO_4)_2(H_2O)_2$; 8-K_2SO_4; 9-$CaAl_2Si_2O_8$; 10-$KAl_3Si_3O_{10}(OH)_2$.

Fig. 1. XRD patterns of MSS and biomass ash

- The forms of mineral elements in MSS and biomass samples are different. The interactions among the minerals with different forms and trace metals are different.

Experimental procedures

✓ Bubbling fluidized bed

- Thermal capacity: 5 kW;
- Bed material: quartz sand of 0.25-0.355 mm;
- Average aerodynamic diameter of granulated fuel: 1.6 mm;
- Excess air coefficient: 1.3-1.4;
- Fluidization velocity: 0.45-0.5 m/s.

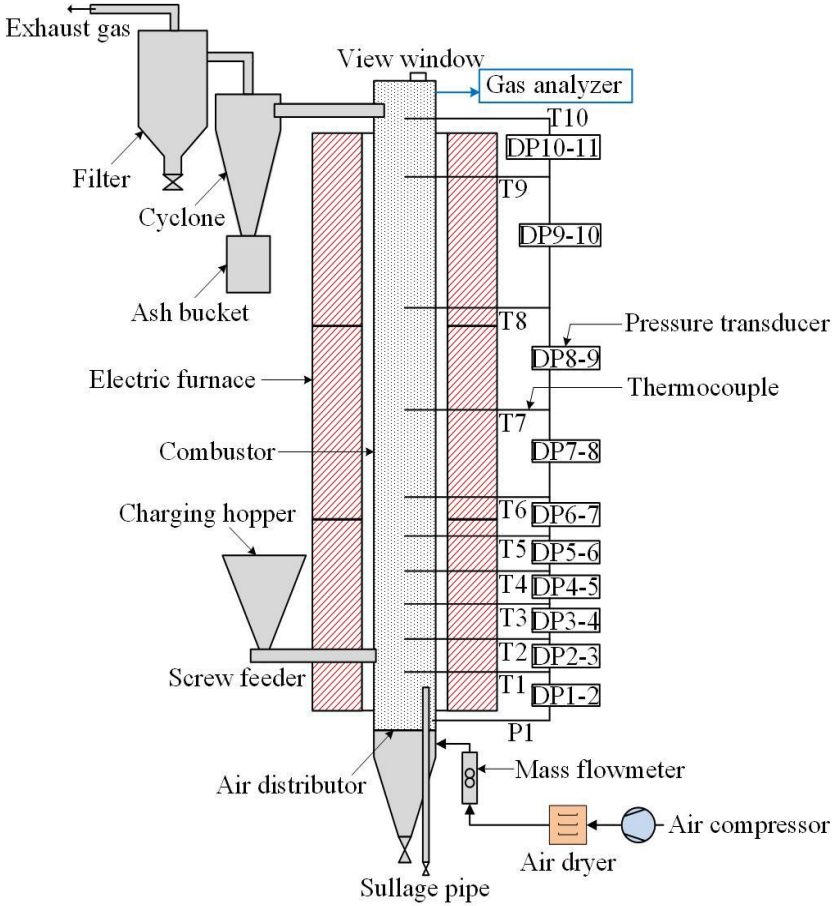


Fig. 2. Schematic diagram of the experimental system

Experimental procedures

✓ Analytical methods

- The concentrations of trace metals in the ash samples were analyzed by inductively coupled plasma mass spectrometry (ICP-MS, Thermo X Series);
- Cadmium (Cd), zinc (Zn) and Arsenic (As) were studied.
- The speciation of trace metals in the samples was analyzed using modified BCR sequential extraction procedures;
- The main chemical composition of the ash samples were determined by X-ray Fluorescence Spectrometer (XRF);
- The amount of free CaO (f-CaO) in the ash samples was measured by the glycol method;
- The concentrations of arsenate As(V) and arsenite (As(III)) were determined by ICP-MS coupled with ion chromatography (IC, Thermo ICS 2000). As(V) and As(III) were separated using an anion exchange column (Hamilton PRP-X100). The concentrations of the separated As(V) and As(III) were measured separately by ICP-MS.

Experimental procedures

✓ Analytical methods

- The crystalline structures of the samples were analyzed by X-ray powder diffraction (XRD, PANalytical, Netherlands);
- The pore structure of the fly ash samples was determined by a N_2 absorption apparatus (Demo 2020 V4.02), including the BET specific surface area and the pore volume;
- The speciation of phosphorus in the samples were separated using the Standards, Measurements, and Testing (SMT) protocol, and divided into five different chemical forms: total phosphorus (TP), organic phosphorus (OP), inorganic phosphorus (IP), apatite inorganic phosphorus (AP), and non-apatite inorganic phosphorus (NAIP). The concentrations of phosphorus in different forms were determined according to the molybdenum blue colorimetric method. The five phosphorus fractions can be represented by the equations TP = OP + IP and IP = AP + NAIP.

Results and discussion

✓ Cadmium (Cd) and zinc (Cd)

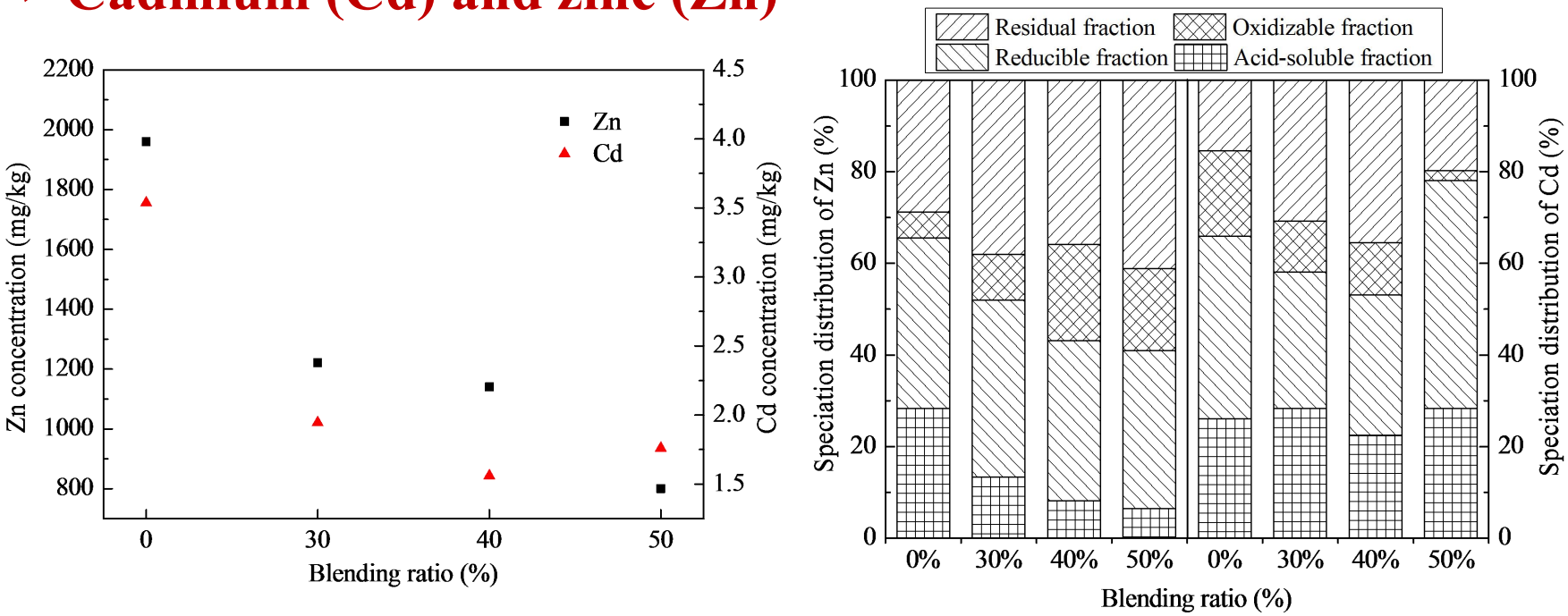


Fig. 3. Influence of blending ratio on the concentrations and speciation distribution of Zn and Cd in the fly ash from co-firing of MSS with cotton stalk (CS).

- Co-firing MSS with CS can promote the stabilization of Zn and Cd in the fly ash, reducing the toxicity of Zn and Cd in the fly ash.

Results and discussion

✓ Arsenic (As)

- The subsection water-cooling mode was adopted in the tail flue of the reactor to study the chemical state transformation of As.
- The bed temperature was 900 °C.
- Three fly ash sampling sites (sampling pipe 1 and 2, and ash bucket in the cyclone) were placed along the flue, and the corresponding fly ash samples were FA1, FA2, and FA3, respectively.
- The temperature for FA1, FA2, and FA3 were 610±5 °C, 460±5 °C, and 320±5 °C, respectively.

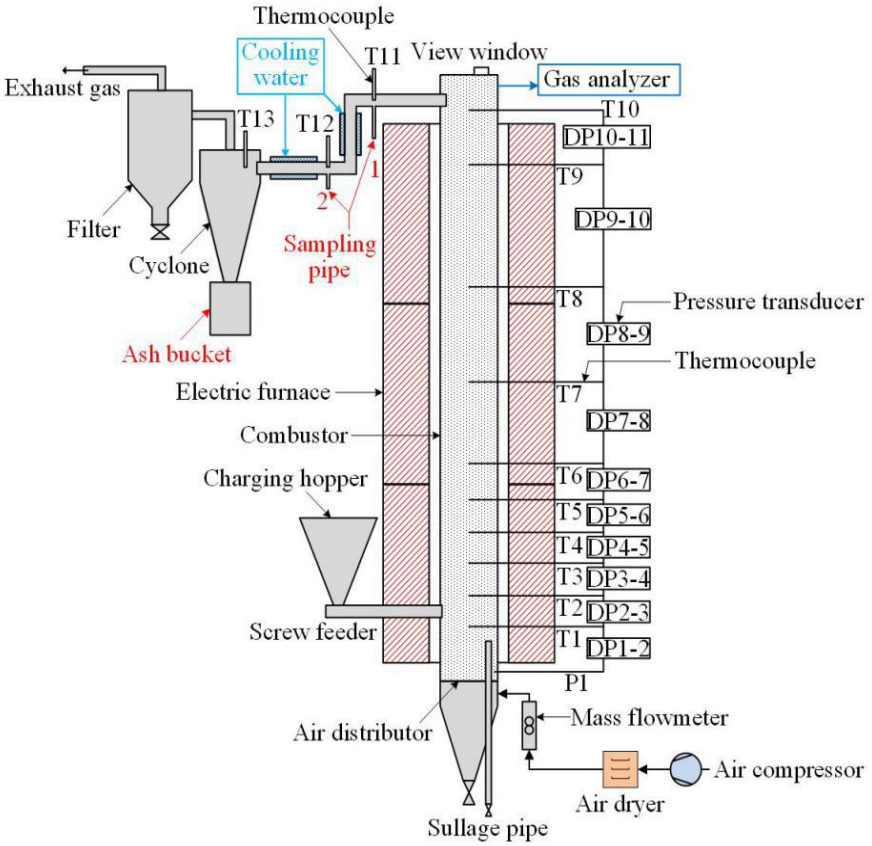


Fig. 4. Schematic diagram of the experimental system after the innovation.

Results and discussion

✓ Arsenic (As)

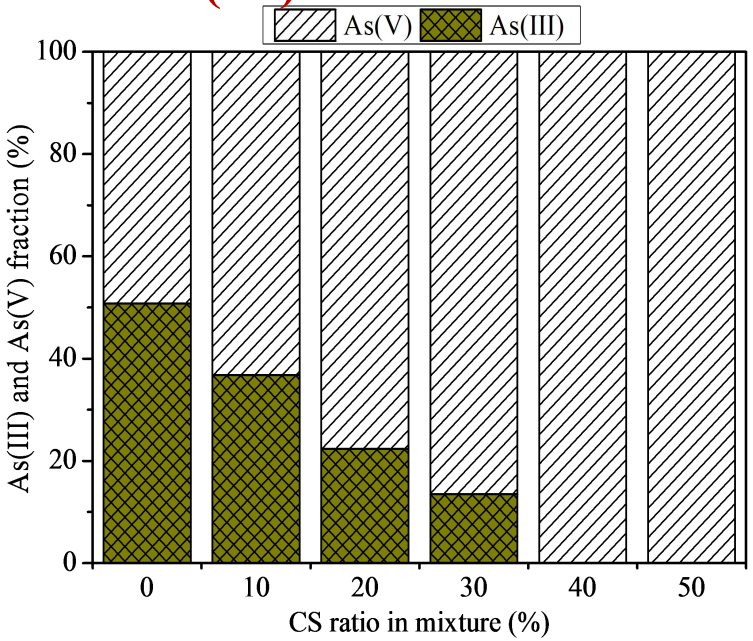


Fig. 5. Arsenic speciation in the fly ash (FA3) from co-firing of MSS and CS at 900 °C.

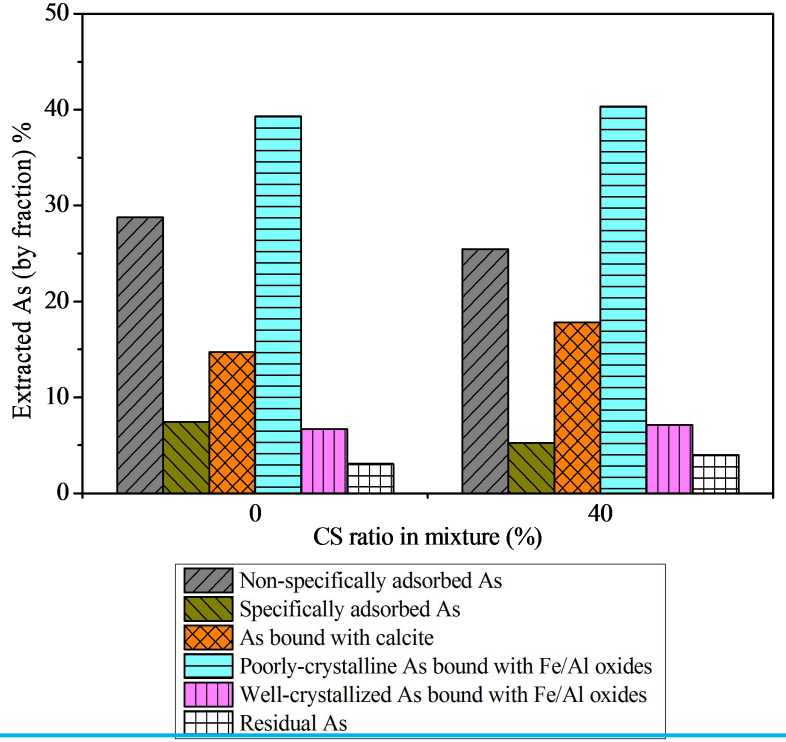


Fig. 6. Arsenic distribution in the six SEP fractions of MSS and CS incineration fly ash (FA3).

- The chemical oxidation of $As_2O_3(g)$ is greatly stimulated by the co-firing of MSS and CS.
- Mineral compounds such as Ca, Fe, and Al compounds in CS can provide additional chemical adsorption sites for arsenic to facilitate the chemical oxidation of arsenic by forming various arsenates (As(V)) .

Results and discussion

✓ Arsenic (As)

Effect of fly ash sampling site on arsenic speciation

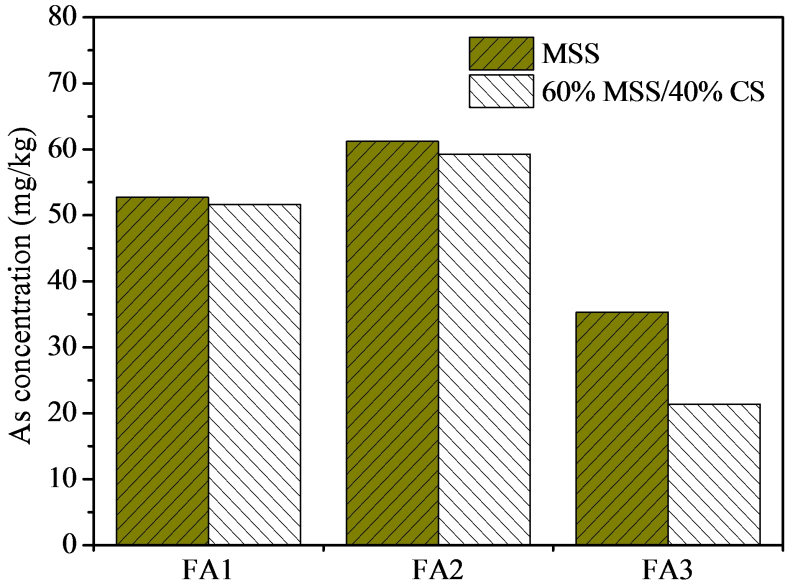


Fig. 7. Arsenic concentration in the fly ash from different sampling sites during co-firing of MSS and CS.

- Arsenic is more easily captured in the fly ash at about 460 °C than 610 °C or 320 °C.
- Low temperature could be adverse for the capture of arsenic in the fly ash.

Results and discussion

✓ Arsenic (As)

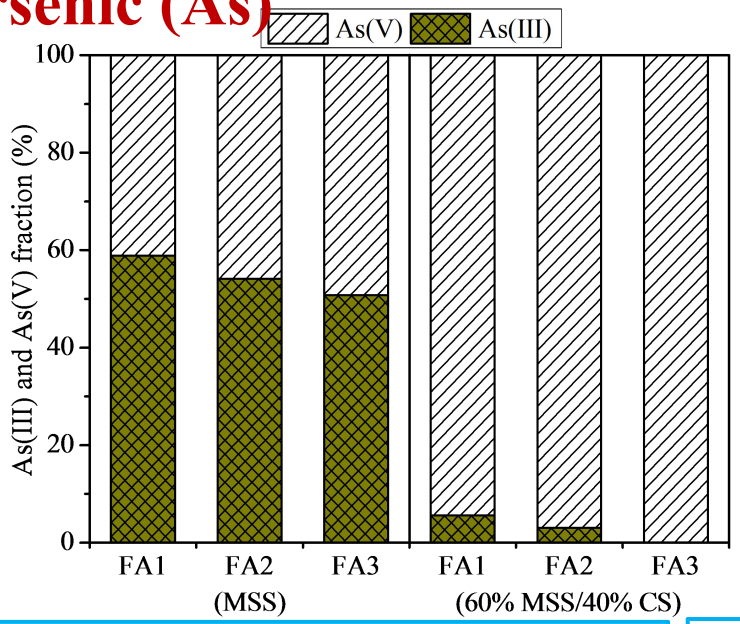


Fig. 8. Arsenic speciation in the fly ash from different sampling sites during co-firing of MSS and CS.

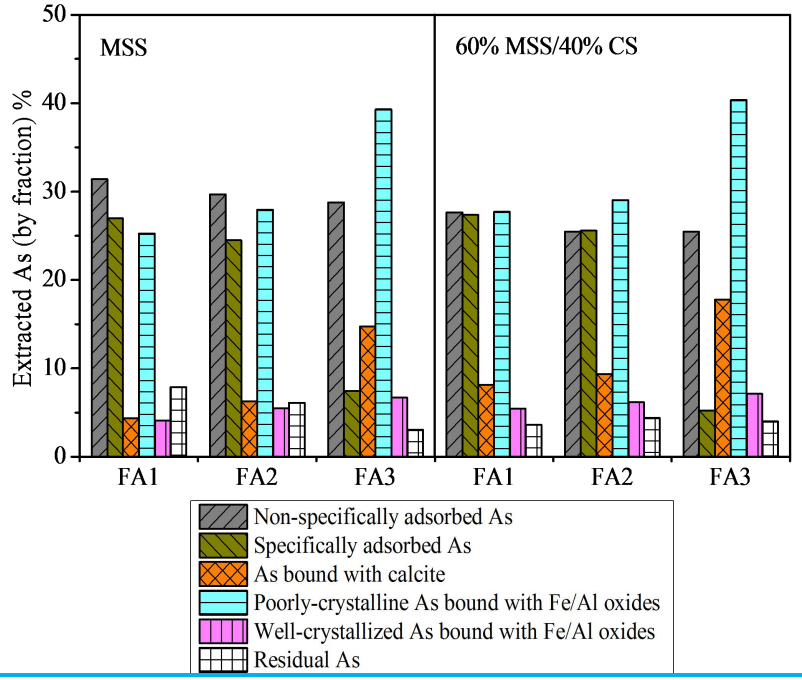


Fig. 9. Arsenic distribution in the six SEP fractions of the fly ash from different sampling sites during co-firing of MSS and CS.

- The chemical oxidation of $As_2O_3(g)$ is continuously conducted during the flue gas cooling process, at 320-610 ^oC.
- The oxidation of $As_2O_3(g)$ in the flue gas cooling process occurs through the interactions of arsenic vapors and Ca, Fe, and Al compounds.

Results and discussion

✓ Arsenic (As)

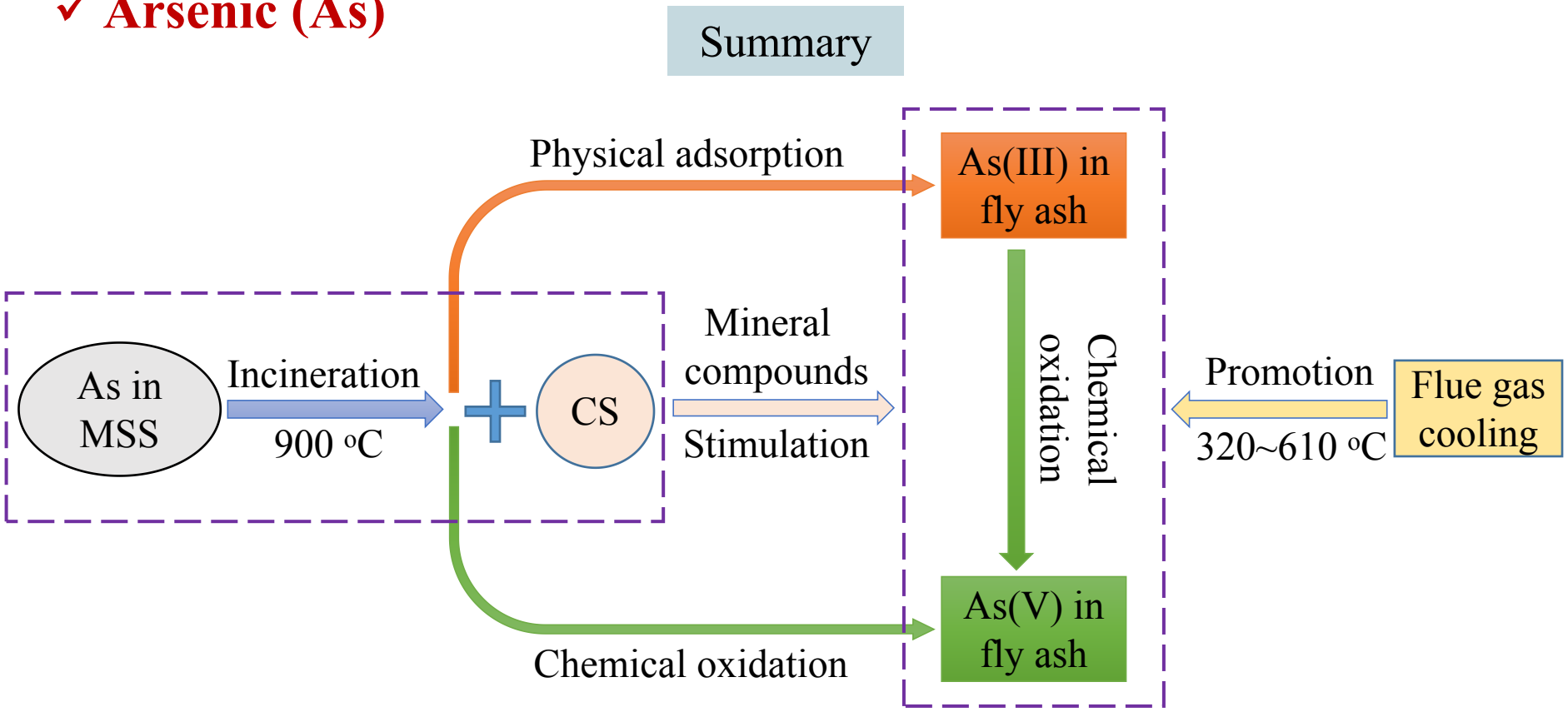


Fig. 10. The mechanism of arsenic speciation transformation during municipal sewage sludge (MSS) incineration with cotton stalk (CS).

Results and discussion

✓ Phosphorus (P)

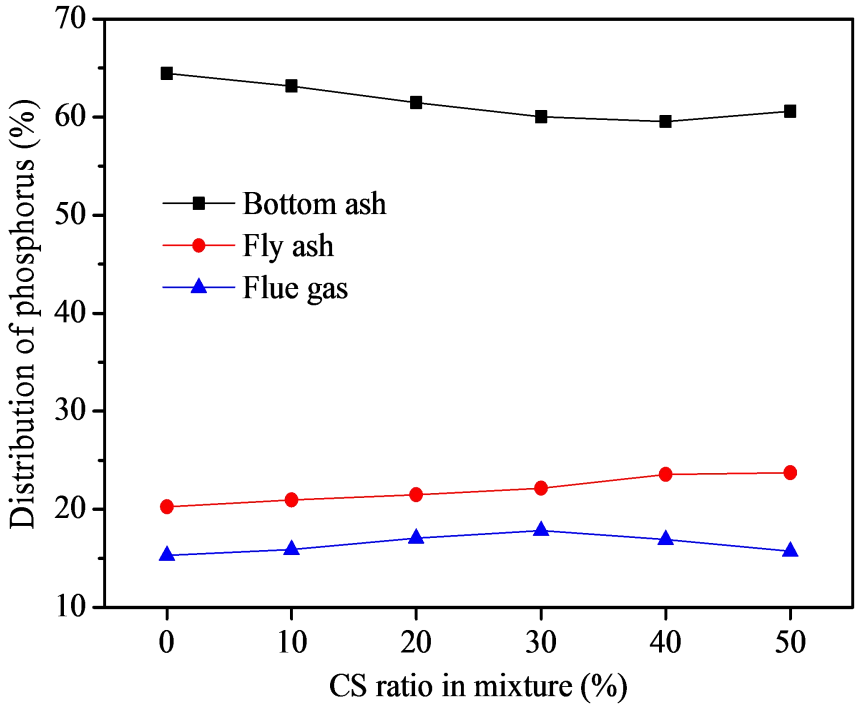


Fig. 11. Phosphorus distribution in bottom ash, fly ash, and flue gas at different CS ratios in mixture.

- Most of P was detected in the bottom ash (64.44%) and fly ash (20.26) during MSS incineration at 900 °C.
- The content of total P in fly ash tends to increase with increasing the CS ratio in the mixture.

Results and discussion

✓ Phosphorus (P)

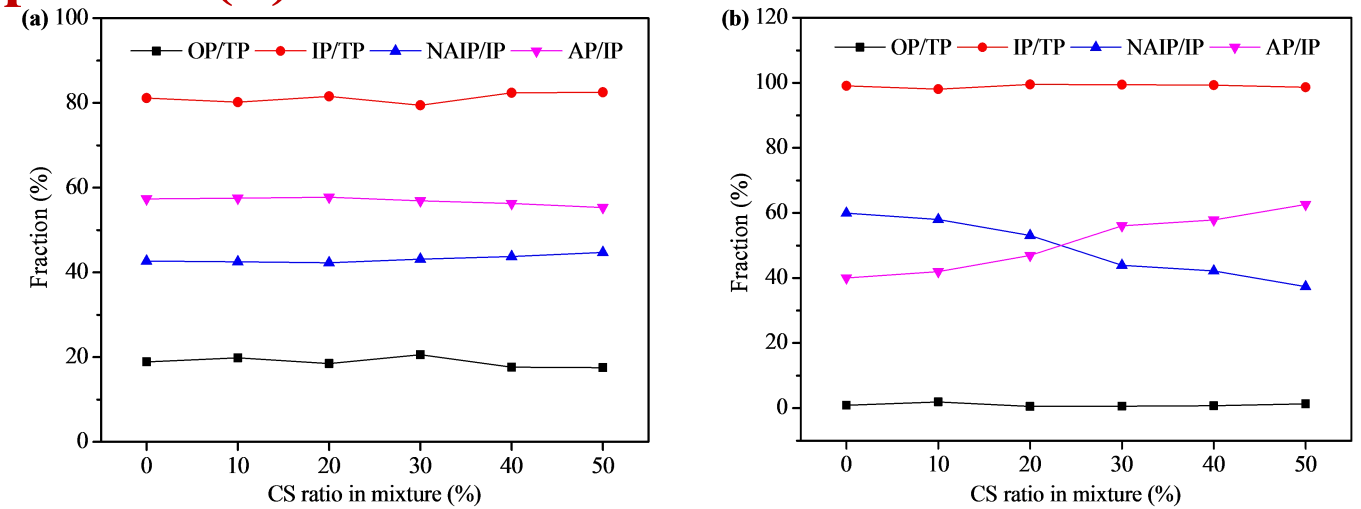


Fig. 12. Fraction of OP/TP, IP/TP, NAIP/IP, and AP/IP in the samples from co-firing of MSS and CS: (a) bottom ash, (b) fly ash.

- The addition of CS exhibits no effects on the fraction of P in different forms in the bottom ash during MSS incineration.
- Adding CS into MSS can stimulate NAIP transformed to AP in the fly ash during incineration, which promotes the formation of Ca/Mg-P compounds, thus improving the bioavailability of phosphorus in the fly ash.

Results and discussion

✓ Phosphorus (P)

Table 3 Main constituents of the fly ash samples collected from co-firing of MSS and CS

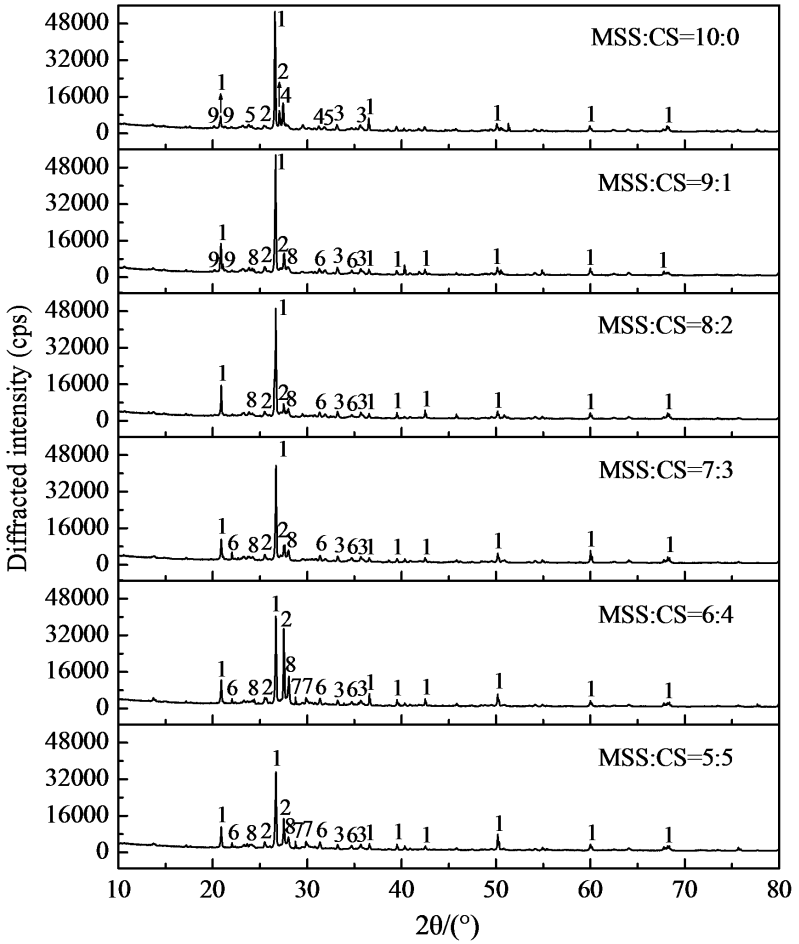
Constituents (%)	MSS	90%MSS/ 10% CS	80%MSS/ 20% CS	70%MSS/ 30% CS	60%MSS/ 40% CS	50%MSS/ 50% CS
Si	18.35	18.07	18.02	19.08	19.18	19.73
P	9.36	9.18	9.02	8.09	7.74	7.04
Ca	5.79	6.20	6.34	6.58	6.66	6.96
Al	5.74	5.61	5.64	5.51	5.49	5.34
Fe	4.00	3.96	3.85	3.50	3.42	3.34
Mg	3.52	3.61	3.68	3.58	3.66	3.65
K	3.92	3.98	4.10	4.46	4.51	4.68
S	0.75	0.85	0.78	1.00	0.99	1.05
Na	0.72	0.92	0.96	1.05	1.18	1.18
free CaO	0.028	0.059	0.084	0.098	0.108	0.101

- The fly ash samples contained high contents of Si, P, Ca, Mg, Al, Fe, and K.
- The Ca and f-CaO fractions in fly ash increased with increasing the CS ratio in mixture.

Results and discussion

✓ Phosphorus (P)

- The XRD results demonstrate that adding CS can stimulate the transformation of NAIP (such as $AlPO_4$) to AP (including $Ca_{18}Mg_2H_2(PO_4)_{14}$ and $Ca_2P_2O_7$) in the fly ash.



1-SiO_2; 2-$KAlSi_3O_8$; 3-Fe_2O_3; 4-$Ca_9(Fe, Al)(PO_4)_7$; 5-$Ca_4(Fe, Mg)_5(PO_4)_6$
6-$Ca_{18}Mg_2H_2(PO_4)_{14}$; 7-$Ca_2P_2O_7$; 8-$KH_5(PO_4)_2$; 9-$AlPO_4$

Fig. 13. XRD patterns of the fly ash from co-firing of MSS and CS.

Results and discussion

✓ Phosphorus (P)

Table 4 Pore structures of the fly ash samples derived from co-firing of MSS and CS

Samples	MSS	90%MSS/ 10% CS	80%MSS/ 20% CS	70%MSS/ 30% CS	60%MSS/ 40% CS	50%MSS/ 50% CS
BET surface area (m^2/g)	1.451	1.455	1.549	1.609	1.615	1.663
Pore volume (cm^3/g)	0.0052	0.0056	0.0066	0.0069	0.0074	0.0089

- The bigger specific surface area and pore volume offer a larger reaction contact area for the conversion of NAIP to AP.
- The Ca and Mg compounds in CS can provide chemical reactive sites for phosphorus to form $Ca_{18}Mg_2H_2(PO_4)_{14}$ and $Ca_2P_2O_7$ during MSS incineration.

Conclusions

- Co-firing MSS with biomass can promote the stabilization of some trace metals (Cd, Zn, and others) in the fly ash, reducing the toxicity of Zn and Cd in the fly ash;
- Mineral compounds such as Ca, Fe, and Al compounds in CS can provide chemical adsorption sites for arsenic to facilitate the chemical oxidation of arsenic by forming various arsenates (As(V)) during MSS incineration, significantly reducing the toxicity of arsenic in the fly ash;
- The chemical oxidation of arsenic is continuously conducted during flue gas cooling at 320-610 ^{o}C;
- Addition of CS into MSS is advantageous for the conversion of non-apatite inorganic phosphorus (NAIP) to apatite inorganic phosphorus (AP) in the fly ash;
- The Ca and Mg compounds in CS can provide chemical reactive sites for phosphorus to form $Ca_{18}Mg_2H_2(PO_4)_{14}$ and $Ca_2P_2O_7$;
- The bioavailability of phosphorus in fly ash is greatly improved by MSS incineration with CS additive.

Acknowledgements

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Thank you!