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# Effect of modified Ca-Al adsorbents on heavy metal fixation during co-combustion of coal and coconut shells: Experiments and simulations \*

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#### ABSTRACT

As an alternative fuel, bio-waste coconut shells have shown promise in reducing pollution during the cocombustion process. In this study, a novel metal-mineral adsorbent, Ca-Al (Ca<sub>5</sub>Al<sub>6</sub>O<sub>14</sub>), was prepared and physically (ultrasonic) and chemically (ethylene glycol) modified to enhance its adsorption properties. Thermal adsorption experiments investigated the effect of the adsorbents on the fixation of six heavy metals (HMs): Cr, Cu, Mn, Ni, Pb, and Zn. XRD, SEM, BET, and XPS were used to analyze the adsorbents and the adsorption mechanism was investigated by combining lattice oxygen concentration and Factsage simulation calculations. The ecological risk assessment of heavy metals was used to comprehensively evaluate the fixation effects of the three Ca-Al adsorbents at different additive levels. The results showed that the modification significantly changed the morphological characteristics and oxygen activity of the Ca-Al adsorbents, increased the lattice oxygen and chemisorbed oxygen concentration, and laid the foundation for promoting the chemisorption process in the fixation of heavy metals. In combination with the Er (environmental risk factors), adding all three adsorbents reduced Ri (Risk index). Among them, Ca-Al (EG) at 3% had the best effect on Ri. 3% Ca-Al (EG) reduced the Er value of Ni by 49.02%. 5% Ca–Al (EG) reduced the  $E_r$  value of Cr by 86.01%. 5% Ca–Al (UM) had the best effect on Mn, with a reduction of 46.13%. The addition of 10% Ca-Al (UM) reduced Er of Ni by 50.43%. Considering the practical application in coal-fired power plants, Ca-Al(EG), which exhibits a higher fixation rate at small additions, is more suitable.

# 1. Introduction

Co-combustion of coal and biomass is a much-anticipated fossil energy-utilizing method and has been applied in many power plants (WASIELEWSKI et al., 2021; MUNAWER, 2018; LUO et al., 2020). Among the advantages, biomass is renewable, widely distributed, highly productive, and inexpensive, making it well suited as a partial replacement for coal combustion. As a bio-waste with large reserves and long-term availability, coconut shells are well suited as a co-combustion material for coal, and co-combustion of the two effectively reduces greenhouse gas emissions. On the other hand, it is also effective in disposing of hoarded coconut shells (SAIKAEW et al., 2012; CHAN et al., 2022).

However, coal and biomass combustion still produce large amounts of pollutants, including heavy metals (HMs). Currently, the most common strategies for controlling heavy metals in flue gas are adsorption, condensation, and combustion. The adsorption method is productive, easy to use, environmentally friendly (KE et al., 2019), and commonly used to control heavy metal pollutants. HMs are controlled by adsorbents through physical and chemical adsorption to capture HMs. In the current research, attention is generally focused on Ca-, Al-, and Si-based adsorbents, including kaolin, montmorillonite, limestone, zeolite, dolomite, and seafoam, among others (YAO and NARUSE, 2009; XUE et al., 2021; WANG et al., 2007). Zhang investigated the effects of CaO and montmorillonite (MMT) on the adsorption of HMs during sludge combustion and environmental risks. It was found that the addition of

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Abbreviations: XRD, X-ray diffractometer; BET, Brunner-Emmet-Teller; HMs, Heavy metals; SEM, Scanning electron microscopy; XPS, X-ray Photoelectron Spectroscopy; CE, Capture efficiency.

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CaO could effectively inhibit the volatilization of Cr, Cu, and Zn, although it would increase the release of As to some extent. The novel ore adsorbent MMT could inhibit the volatilization of As, Cr, Zn, and Cu, but "adsorption failure" would occur at high temperatures (ZHANG et al., 2022). Cheng's results showed that Si/Al mixtures of kaolin and montmorillonite were more effective than single SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. This is attributed to the binding of Pb/Cd atoms to surface-exposed O in the adsorption reaction and the strong interaction between Cl and unsaturated Al atoms (CHENG et al., 2023). In addition, it has been shown that to improve the adsorption effect, the physical or chemical adsorption capacity can be increased by modification (KE et al., 2019). Physical modification includes heat treatment, ultrasonication, and surface coating. During ultrasonication, intense mechanical agitation can have various effects, including emulsification, dispersion, and even reactions like sonochemistry (SARAVANAN et al., 2023). Chemical modification can alter the pH, generate specific structures, or introduce new functional groups, providing more adsorption sites and improving reactivity (MEDFAI et al., 2022). Zheng demonstrated that limestone modified with K<sub>2</sub>CO<sub>3</sub> improved the capture performance for Cr and Cu, whereas limestone modified with Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> showed an enhanced capture performance for Cr, Cu, Pb, and Zn (ZHENG et al., 2018). Xue demonstrated that the intercalating agent's cetyltrimethylammonium bromide (CTAB) and sodium dodecylbenzene sulphonate (SDBS) could be successfully stripped (XUE et al., 2021). The process resulted in the montmorillonite being transformed into fine flakes, thereby exposing more active centers, which enhanced the chemisorption of HMs.

Ca-Al adsorbent (Ca<sub>5</sub>Al<sub>6</sub>O<sub>14</sub>) is a novel type of heavy metal adsorbent in the form of calcium-aluminium oxides. It is primarily employed in hydrogen production from reformed methane, photocatalysis, and carbon capture (XU et al., 2016; LIANG et al., 2023a; SUN et al., 2023), with limited applications in heavy metal control. To reduce the emission of heavy metals (HMs), it is helpful to investigate the application of a Ca-Al adsorbent (Ca<sub>5</sub>Al<sub>6</sub>O<sub>14</sub>) added to the co-combustion of coal and coconut shells. Furthermore, the fixation of HMs is intimately associated with the chemical bonding of the adsorbent and lattice oxygen and oxygen vacancies. On the one hand, a high lattice oxygen concentration can facilitate oxygen activity (LI et al., 2023), which provides a basis for redox reactions that can modify the valence state of HMs to facilitate their fixation. On the other hand, the depletion of lattice oxygen contributes to the formation of oxygen vacancies, and the negative charge generated by the oxygen vacancies also traps positively valenced metal ions, thereby contributing to physisorption (DU et al., 2023). Applying ultrasonic pre-treatment improves sample homogeneity, while glycol pre-treatment promotes elevated oxygen activity (LI et al., 2023). However, there is currently no study on the effect of the two modifications on the fixation of HMs. In this study, we consider the impact of ultrasound modification and pre-treatment with ethylene glycol on the surface active points, which contribute to the adsorption of more metal ions on the surface. Furthermore, the study explores the mechanism of heavy metal fixation during combustion from the oxygen activity point of view.

In this paper, the synthesis, physical modification, and chemical modification of Ca-Al adsorbent ( $Ca_5Al_6O_{14}$ ) are discussed about the fixation of HMs (Cr, Cu, Mn, Ni, Pb, Zn) in the bottom ash. The efficacy of the Ca-Al adsorbent in the fixation of HMs was evaluated by varying the quantity of adsorbent employed and by introducing different adsorbents. Furthermore, simulations were conducted using Factsage software to derive the heavy metal adsorption mechanism model, which provides a starting point for investigating novel heavy metal modification techniques and adsorbents. In parallel, together with environmental risk factors, the three Ca-Al adsorbents' adsorption performance was assessed, resolving the issue of HMs emissions brought on by the co-combustion of coal and biomass.

# 2. Experimental section

#### 2.1. Materials

The coal used as material was obtained from Guangxi Province, China, while coconut shells were collected from the local market in Guangzhou. To ensure the reliability and reproducibility of the experiments, all samples were ground through an 80 mesh sieve and dried at 105 °C for 24 h. The proximate analysis and ultimate analyses of materials from earlier research are displayed in Table S1. Tables S2 and S3 show the compositional characteristics of each material using X-ray fluorescence spectroscopy (XRF). Table S4 displays the heavy metal composition of coconut shells and coal. To balance combustion stability and environmental friendliness, coal and coconut shells (1.25g) were mixed in a ratio of 4:1 (SAIKAEW et al., 2012; ADEWOLE et al.). The thoroughly mixed samples were prepared for thermal adsorption experiments in a tube furnace.

# 2.2. Preparation of Ca-Al adsorbents

 $Ca(NO_3)_2.4H_2O$  and  $Al(NO_3)_3.9H_2O$ , crucial for the experiment, were acquired from the reputable Guangzhou Chemical Reagent Factory. These chemicals, with an analytical purity of  $\geq$  99%, were of the highest quality. The Ca-Al adsorbents were then prepared using the solgel method, with subsequent modification using ultrasound and glycol. The detailed preparation process is as follows:

The corresponding proportions of Ca(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O and Al (NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O were added to an appropriate amount of deionized water to obtain a mixed solution. The citric acid (CA) was then added at a 1:1 M ratio with the metal ions, and the solution was stirred sufficiently at 80 °C until gel formation. The solution was then placed in a drying oven at 120 °C and dried for 12 h. The precursor was removed and placed in a muffle furnace, where it was heated from room temperature to 900 °C at a rate of 2.5 °C/min. It was then calcined under an air atmosphere in the muffle furnace for 5 h. Subsequently, the sample was cooled, crushed, and sieved to obtain particles of 80 mesh or more minor, producing an unmodified Ca-Al adsorbent.

The ultrasound-modified Ca-Al adsorbent was prepared as follows: a mixed solution of Ca(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O and Al(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O and CA was pretreated at 25 kHz for 7 min at room temperature (25 °C). It was then stirred sufficiently at 80 °C until gel formation and dried, calcined, cooled, and milled under the same conditions to obtain the ultrasound-modified Ca-Al adsorbent. Al adsorbent is designated as Ca-Al (UM). For the ethylene glycol modification, the pH was adjusted to 8 ± 0.1 by adding ammonia, and then the same amount of ethylene glycol (EG) as that of CA was added. The mixture was stirred thoroughly at 80 °C until gel formation, and then dried, calcined, cooled, and milled under the same conditions to obtain glycol-modified Ca-Al adsorbent, written as Ca-Al (EG).

# 2.3. Characterization of Ca-Al adsorbents

This study investigated the adsorbent using four characterization methods: XRD, SEM, BET, and XPS. The technical principles of the characterization are presented in the Supplementary Material, and the chosen instruments and the specific setup are shown below.

X-ray diffractometer (XRD): The crystalline phase of the Ca-Al adsorbent was determined by Cu-K $\alpha$  radiation ( $\lambda = 1.54056$  Å) using a Rigaku Smartlab X-ray diffractometer. Measurements were performed at a scanning speed of 10°/minute over a scanning range of 5–90°.

Scanning electron microscopy-energy spectrum analysis (SEM-EDS): A scanning electron microscope (FEI QuantaTM 400 FEG) was used to characterize the morphological structure of the Ca-Al adsorbent.

Surface area and porosity analysis: The Ca–Al adsorbent's surface area, average pore size, and total pore volume were measured using nitrogen adsorption/desorption isotherms. These measurements were done on a Micromeritics ASAP 2460 automated surface area and porosity analyzer.

X-ray Photoelectron Spectroscopy (XPS): The Ca-Al adsorbent's elemental composition and valence state were analyzed using an X-ray photoelectron spectrometer (Thermo Scientific K-Alpha). The XPS spectra were calibrated against the C 1s peak (284.8 eV).

#### 2.4. Experimental apparatus and methods

#### 2.4.1. Adsorption experiment

The combustion adsorption test was conducted using a horizontal tube furnace, as illustrated in Fig. 1. Initially, the quartz glass tube ( $\Phi$ 50  $\times$  1100 mm) was heated to 900 °C, with a gas flow rate of 1 L/min of air passed through. The quartz boat containing the mixture was then pushed into the center of the tube and burned fully for 30 min. Subsequently, the sample was cooled, weighed, collected, and labeled. This process was repeated in parallel to ensure the accuracy of the conclusions. In this instance, the mixture comprised 1 g of coal and 0.25 g of coconut shell. The corresponding mass fractions of Ca-Al, Ca-Al (UM), and Ca-Al (EG) adsorbents were then added to the material, which was noted as xCa-Al, xCa-Al (UM), and xCa-Al (EG), respectively (x is 3%, 5%, and 10%).

# 2.4.2. Analysis of experimental results

The ash obtained after co-combustion was carefully transferred to a PTFE beaker and moistened with deionized water.  $HNO_3$ ,  $H_2O_2$ , and HCl were then added for the ablation process. 40 mL of deionized water were added, and the heating was kept up till 10 mL of solution were left. The solution was transferred to a 25 mL volumetric flask through volumizing and filtration. The solution was injected with an ICP-OES (Model 5100, Agilent Technologies, USA).

The experimental data were processed following Equations (1) and (2).

The ash yields A: The ratio of the mass of the sample ash after combustion to the quality of the sample before combustion.  $m_{ash}$  is the quality of ash after the experiment.  $m_{fuel}$  is the mass of the sample preceding the experiment.

$$A = \frac{m_{ash}}{m_{fuel}} \times 100\%$$
 (1)

$$CE = \frac{C_{ash}}{C_{fuel}} \times A \times 100\%$$
<sup>(2)</sup>

Capture efficiency CE: HMs fixation rate is defined as the content of HMs contained in the bottom ash as a percentage of the total content of HMs in the sample. The amount of HMs in the ash following the combustion ( $C_{ash}$ ) and the amount of HMs in the samples before the combustion ( $C_{ash}$ ) are both expressed in mg/kg. A higher fixation rate is indicated by a larger CE.

Factsage 7.3 is a software that simulates and analyzes experimental heavy metal compounds using the Gibbs minimum free energy approach. This technique minimizes the system's Gibbs free energy as an equilibrium criterion at isothermal pressure and temperature. The composition and concentration of the content of the components are



Fig. 1. Schematic diagram of tube furnace thermal adsorption experiment.

then calculated using Lagrange's coefficient determination method.

#### 3. Results and discussion

# 3.1. Characterization of Ca-Al adsorbents

# 3.1.1. Results of XRD

Fig. 2 demonstrates the XRD characterization results of three adsorbents: Ca-Al, Ca-Al (UM), and Ca-Al (EG). The figure shows that the main component of the three calcium-aluminum type adsorbents is Ca<sub>5</sub>Al<sub>6</sub>O<sub>14</sub> (JCPDS-70-0801), which contains a small amount of other calcium-aluminum oxides. The characteristic peaks of Ca<sub>5</sub>Al<sub>6</sub>O<sub>14</sub> are observed at  $2\theta = 24.2^{\circ}$ , 26.6°, 27.1°, 28.6°, 31.0°, 32.6°, 34.8°, 36.2°, 38.4°, 42.2°, 46.2° and 59.1°. Consequently, the crystal structure of the Ca-Al adsorbent was slightly modified following ultrasonication and ethylene glycol modification, yet the characteristic peaks of Ca<sub>5</sub>Al<sub>6</sub>O<sub>14</sub> were generally retained.

# 3.1.2. Results of SEM and BET

This study used SEM and BET characterization to investigate the microscopic morphology and pore characteristics of Ca-Al adsorbent and modified Ca-Al adsorbent. The results are shown in Fig. 3 and Table 1.

Fig. 3(a) and (b) show the surface structure of Ca-Al, the calciumaluminum adsorbent prepared by the sol-gel method has an interconnected chain-like porous structure. The sol-gel method can promote the homogeneous mixing of the various components in the system at the molecular level, resulting in the realization of the active ingredients' homogenous distribution (LI et al., 2023). In addition, thanks to the spontaneous combustion of the gel during the preparation process (which occurs at temperatures of 200–500 °C) that generates and spills large amounts of CO<sub>2</sub> and N<sub>2</sub> (LI et al., 2023), the Ca-Al adsorbent produces many pores. Fig. 3(c) and (d) illustrate the surface shape characteristics of Ca-Al (UM), which exhibits a flatter and denser inter-stacked chain-like structure after physical modification by ultrasound. This is due to the fact that ultrasonic modification promotes dispersion and homogeneous distribution between particles, making it easier to release gases, thus increasing porosity (WANG et al., 2019), which also facilitates the provision of more reaction sites for the chemisorption of HMs (CHAN et al., 2022). Fig. 3(e) and (f) show the surface structure of Ca-Al (EG), which was chemically modified by adjusting PH and the complexing agent ethylene glycol, which produced complexation that helped to regulate the structure and morphology of the sols and prevented the aggregation and precipitation of the sol particles (LI et al., 2023; KUMAR et al., 2009), resulting in the formation of a large pore structure that was distributed in the center of the plane.



Fig. 2. Xrd of Ca-Al and Ca-Al(UM) and Ca-Al (EG).



Fig. 3. SEM scans of (a), (b) Ca-Al and (c), (d) Ca-Al(UM) and (e), (f) Ca-Al(EG).

Table 1	
Pore characteristics of Ca-Al and Ca-Al(UM) and Ca-Al(UM)	a-Al(EG)

material	Specific Surface Area (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	Mean Pore Size (nm)
Natural limestone	0.6300	0.0002	11.1100
Ca-Al	4.7270	0.0322	27.2603
Ca-Al(UM)	4.4231	0.0284	25.6684
Ca-Al(EG)	4.5405	0.0253	22.3505

The structure of BET is shown in Table 1. It has been demonstrated in a previous study (YANG et al., 2023) that enlarging the specific surface area, pore volume, and pore size creates a larger physical adsorption space inside the material, which facilitates the fixation effect of the adsorbent on HMs. The specific surface area, average pore volume, and pore size of adsorbents modified by sol-gel method, ultrasound, and ethylene glycol pretreatment were significantly increased compared to the conventional calcium-based adsorbent limestone (ZHENG et al., 2018). While comparing Ca-Al adsorbents, it was found that Ca-Al (UM) and Ca-Al (EG) samples showed a slight decrease in specific surface area after ultrasonic and ethylene glycol pretreatment. The combined enhancement of the adsorption performance with subsequent modifications suggests that the modifications may lead to a more homogeneous distribution of active sites, mainly due to the enhanced chemisorption effect of the modifications.

# 3.1.3. Results of XPS

In the fixation of HMs using adsorbents, the chemisorption process mainly depends on the adsorbent's oxygen activity, which is directly related to its lattice oxygen concentration and oxygen vacancy concentration (ZHU et al., 2010). To investigate the surface chemical composition and state as well as the lattice oxygen concentration of the Ca-Al adsorbent and the modified Ca-Al adsorbent, the peak deconvolution of the adsorbent was studied and analyzed by XPS in this paper.

Table 2O1s analysis results of the Ca-Al and Ca-Al(UM)and Ca-Al(EG) from XPS.

Samples	Peak area (%)			OI/(OII + OIII)		
	OI	OII	OIII			
Ca-Al	19.89	53.76	26.34	0.25		
Ca-Al(UM)	23.08	59.17	17.75	0.30		
Ca-Al(EG)	25.13	52.36	22.51	0.34		

Table 2 and Fig. 4 display the results. According to the XPS survey spectra, all fresh samples have elements of Ca, Al, O, and C (Fig. 4a). The element C can be attributed to residual carbon in the precursors and exotic hydrocarbons in the XPS apparatus.

Fig. 4b shows the detailed spectra of O1s. According to (LIANG et al., 2023b; YAN et al., 2023), O is divided into lattice oxygen OI (~529 eV), chemisorbed oxygen OII (~531 eV), and physisorbed oxygen OIII (~532 eV). The OI image of Ca-Al (EG) is shifted towards the higher energy of Ca-Al, suggesting that the glycol modification induces the loss of electrons from some lattice oxygens, making it easier for lattice oxygens to be released to participate in the reaction (YAN et al., 2022). Table 2 shows the peak area share of the three O's and the OI/(OI + OII + OIII) (LI et al., 2023). The lattice oxygen concentration Ca-Al(EG) >Ca-Al(UM) > Ca-Al suggests that ultrasonic physical modification and ethylene glycol chemical modification improved the oxygen activity in favor of HMs chemisorption. Furthermore, according to the MVK model (DU et al., 2023), the reaction of the reactants with the lattice oxygen leads to the consumption of the lattice oxygen and the formation of oxygen vacancies. The above two points lay the foundation for carrying out redox reactions to change the valence state of HMs to achieve the fixation of HMs and form a negatively charged environment to attract positively charged metal ions for adsorption. In addition, Table 2 shows that the ultrasonically modified Ca-Al(UM) has the highest amount of chemisorbed oxygen OII, which again favors the formation of oxygen vacancies. Fig. 4c shows a detailed spectrum of Al2p, detected to contain Al (~72.7 eV) (TAGO et al., 2017; ROSENBERGER et al., 2008). The figure shows that the peaks of Al2p1/2 and Al2p3/2 are shifted towards the high binding energy shift after ultrasonic modification and ethylene glycol modification. Interestingly, the peaks of Al2p3/2 of Ca-Al (UM) and Ca-Al (EG) increased. In contrast, the peaks of Al2p1/2 decreased, with a significant difference from Ca-Al, which may enhance the activity of Al-related oxides and improve the fixation of HMs. Fig. 4d shows the detailed spectrum of Ca2p, showing the presence of Ca2p1/2 (~350 eV) versus Ca2p3/2 (~346 eV). After modification, the results show that Ca-Al(EG) and Ca-Al(UM) move towards higher energies (WEI et al., 2021).

#### 3.2. Adsorption of HMs by Ca-Al adsorbents

The impact of the Ca-Al adsorbents on the fixation of six heavy metals (HMs) during the co-combustion of coal and coconut shells can be observed in Fig. 5. Higher CE (Capture efficiency) values indicate better fixation. Table S5 shows the gaseous and solid products of HMs in the co-combustion process calculated by Fastage 7.3 software.



Fig. 4. XPS spectra of survey spectrum (a), O1s (b), Al2p (c), and Ca2p (d) for the Ca-Al, Ca-Al(UM), and Ca-Al(EG).



Fig. 5. Fixation rate of HMs by Ca-Al and Ca-Al(UM)and Ca-Al(EG).

Combining the experiments and software calculations, the effect of Ca-Al adsorptions on the fixation of six HMs and its mechanism will be investigated in the following.

#### 3.2.1. Fixation of Cr by Ca-Al adsorbents

For Cr, the fixation effect of Ca-Al adsorbent on Cr decreases with the increase of the addition amount, and the best effect of 75.85% is observed at 3%Ca–Al. A negative effect was observed at 10%Ca–Al. After ultrasonic modification, Ca-Al (UM) showed an overall positive impact on Cr adsorption. Still, the effect was insignificant compared to Ca-Al, which was only slightly higher than that of unmodified Ca-Al with the same addition amount at 5%. The impact of ethylene glycol-modified Ca-Al (EG) showed a considerable increase in the fixation rate of Cr at 5% and 10%, especially at 5%, where more than 90% of the Cr was fixed in the bottom ash. This is in agreement with the XPS characterization results. As Ca-Al(EG) has the highest lattice oxygen concentration, the high lattice oxygen content facilitates the formation of oxygen vacancies. This promotes the redox reaction, converts the 6-valent chromium to 3-valent chromium, and fixes it in the bottom ash. In addition, this process significantly reduces the toxicity of Cr.

The **reactions in 3 and 4** show that after adding Ca-Al adsorbent, Cr remained in the remaining ash, mainly in the form of  $Cr_2O_3$  with AlCr<sub>2</sub>O<sub>4</sub>(1+). Combining the reactions with the experimental results, adding Ca-Al facilitates the fixation of more  $CrO_2(OH)_2$  in  $Cr_2O_3$  and AlCr<sub>2</sub>O<sub>4</sub>(1+). The gaseous heavy metal product is predominantly  $CrO_2(OH)_2$ , which agrees with the results of Chen (CHEN et al., 2019) and Oger (OGER et al., 2022). CrO<sub>2</sub>(OH)<sub>2</sub> is the main species formed in air between 600 and 900 °C (FRYBURG et al., 1977). Increasing Ca-Al may cause  $Cr_2O_3$  to become partially gaseous when converted to AlCr<sub>2</sub>O<sub>4</sub>(1+), reducing the rate of Cr fixation.

$$2Ca_{5}Al_{6}O_{14} + 12CrO_{2}(OH)_{2} = 6Cr_{2}O_{3} + 10Ca(2+) + 9O_{2} + 24OH(-) + 4Al_{3}O_{4}(+)$$
(3)

 $\begin{array}{l} 2Cr_{2}O_{3}+8CrO_{2}(OH)_{2}+Ca_{5}Al_{6}O_{14}=6AlCr_{2}O_{4}(+)+5Ca(2+)+16OH\\ (-)+O_{2} \end{array} \tag{4}$ 

### 3.2.2. Fixation of Cu by Ca-Al adsorbents

As a volatile heavy metal, Cu easily enters the atmosphere through the co-combustion process, causing environmental pollution. As shown in Fig. 5, Cu's fixation rate was low without adding an adsorbent. After the addition of Ca-Al adsorbent, Cu's fixation rate was significantly improved, and the best effect was 10% Ca–Al, with almost 20% improvement. After ultrasonic and ethylene glycol modification, Ca-Al (UM) and Ca-Al (EG) showed a small enhancement of Cu fixation rate compared to unmodified.

#### 3.2.3. Fixation of Mn by Ca-Al adsorbents

Mn attaches to the fly ash in the co-combustion process and is discharged with the fly ash (JAGODZIŃSKA et al., 2019). As shown in Fig. 5, the fixation rate in the absence of added adsorbent is not high. After adding Ca-Al adsorbent, there is a slight increase at 3% and 5% and a slight decrease at 10%. Following physical or chemical modification, the Ca-Al (UM) fixation rate increases, reaching its highest at 5%Ca-Al (UM). Ca-Al (EG) was similarly improved, with more significant improvements at 5% and 10%, and both modifications provided more lattice oxygen, which was beneficial for the fixation of MnCl<sub>2</sub>. Comparing the two modifications, the effect of ethylene glycol modification on Mn fixation was not as pronounced as that of ultrasonic modification. This may be because ultrasonic modification improves the dispersion uniformity of Ca and Al while providing more pores and reaction sites (SARAVANAN et al., 2023), which provides more favorable conditions for the chemisorption of Mn. The BET results showed that the specific surface area of the two modified adsorbents decreased slightly compared to that before modification. This indicates that the adsorption

of Mn by Ca-Al is mainly due to chemisorption.

When Ca-Al adsorbent is added, the gaseous products are mainly  $MnCl_{2,}$  and the solid products are  $Mn_2O_3$  with  $CaMn_2O_4$ . Possible reactions 5 and 6 are as follows:

$$5O_{2} + 20MnCl_{2} + 6Ca_{5}Al_{6}O_{14} = 10CaMn_{2}O_{4} + 20CaCl_{2} + 18Al_{2}O_{3}(5)$$
$$Ca_{5}Al_{6}O_{14} + 5Mn_{2}O_{3} = 5CaMn_{2}O_{4} + 3Al_{2}O_{3}$$
(6)

#### 3.2.4. Fixation of Ni by Ca-Al adsorbents

As shown in Fig. 5, the combustion of coal and coconut shells results in higher volatilization of the semi-volatile heavy metal Ni into the atmosphere (OBOIRIEN et al., 2016). After adding Ca-Al adsorbent, the fixation was significantly improved, showing a tendency to decrease and then increase with the increase of the amount added, reaching a maximum of 10%. According to Factsage calculations, the gaseous products of Ni after the addition of Ca-Al adsorbent are Ni(OH)<sub>2</sub>, NiCl<sub>2</sub>, and the solid products are AlNi<sub>2</sub>O<sub>4</sub>[1-], NiAl<sub>2</sub>O<sub>4</sub>, FeNi<sub>2</sub>O<sub>4</sub>[1-], FeNi<sub>2</sub>O<sub>4</sub>[2-], Ni<sub>3</sub>O<sub>4</sub>[2-]. Ca-Al adsorbent-related reactions may be in **reactions 7, 8, and 9**.

The Ca-Al adsorbent after ultrasonication and ethylene glycol pretreatment showed a significant increase in the effect of Ni. Among them, Ca-Al (UM) increased significantly with the rise in added amount, and the best effect was found at the high addition rate of 10%. At the same time, the best effect was reached at 3% Ca–Al (EG), while the minimum value was reached at 5%. The comparison of the Ni fixation effects of the two modification methods showed that both the physical and chemical modifications showed positive effects compared to the unmodified Ca-Al adsorbent, which indicates that the modification is beneficial to improve the active sites and promote the fixation of Ni.

$$2H_2O + 3Ni(OH)_2 + Ca_5Al_6O_{14} = 3NiAl_2O_4 + 5Ca(OH)_2$$
(7)

$$3\text{NiCl}_2 + \text{Ca}_5\text{Al}_6\text{O}_{14} = 2\text{CaO} + 3\text{NiAl}_2\text{O}_4 + 3\text{CaCl}_2 \tag{8}$$

 $2Al_2O_3 + 20Ni(OH)_2 + Ca_5Al_6O_{14} = 10AlNi_2O_4(-) + 20H_2O + 5Ca(2+)$  (9)

#### 3.2.5. Fixation of Pb by Ca-Al adsorbents

Pb is a very toxic and volatile heavy metal (CHENG et al., 2020). It can be read from Fig. 5 that the low fixation rate of Pb when no adsorbent is added means that a larger proportion of Pb will drift into the atmosphere with the co-combustion process, which may cause serious harm to human beings. Therefore, adding adsorbents is necessary to control Pb in the bottom ash during co-combustion. The fixation rate of Pb increased with the addition of Ca-Al adsorbent, with the best results at 5% Ca-Al. Among the relevant gaseous products of Pb are PbO, PbCl<sub>2</sub>, and solid products are Pb<sub>2</sub>FeAl<sub>2</sub>O<sub>7</sub>[1-], Pb<sub>2</sub>AlSi<sub>2</sub>O<sub>7</sub>[1+], Pb<sub>2</sub>Al<sub>3</sub>O<sub>7</sub>[1-], Pb<sub>2</sub>AlFe<sub>2</sub>O<sub>7</sub>[1-]. Reactions 10, 11, 12, and 13 show the relevant reaction equations. The addition of Ca-Al adsorbent can chemisorb with the gaseous heavy metal products PbO and PbCl<sub>2</sub> and fix them in the remaining ash in the form of silicate and oxide to improve the fixation rate of Pb, which is consistent with the experimental results. The fixation rate of Ca-Al with Ca-Al(EG) decreased at 10% addition instead, in combination with reaction 13, which may be due to the increase of CaCl<sub>2</sub> by reaction 10, resulting in the conversion of some Pb back to the gaseous product PbCl<sub>2</sub>.

The effect of the ultrasonically modified Ca-Al(UM) adsorbent decreased at low additions (3%, 5%) compared to the unmodified one, probably due to the decrease of the specific surface area, which reduced the physical adsorption, whereas when the additions reached 10%, the chemical adsorption dominated. The fixation rate of Pb by Ca-Al(UM) was improved. The fixation rate of Pb by ethylene glycol-modified Ca-Al(EG) was significantly improved, and the Ca-Al adsorbent prepared by

adjusting the pH and adding complexing agents improved the chelation process of metal ions, the homogeneity of the gel and the purity of the oxide phase, which were all conducive to the physical and chemical adsorption of Pb.

$$Ca_{5}Al_{6}O_{14} + 4PbCl_{2} = 2Pb_{2}Al_{3}O_{7}(-) + 5Ca(2+) + 8Cl(-)$$
(10)

$$12Al_2O_3 + 20PbO + Ca_5Al_6O_{14} = 10Pb_2Al_3O_7(-) + 5Ca(2+)$$
(11)

 $\label{eq:2.1} \begin{array}{l} 3Ca_{5}Al_{6}O_{14}+20PbCl_{2}+20SiO_{2}=10Pb_{2}AlSi_{2}O_{7}(+)+40Cl(-)+15\ Ca \\ (2+)+4Al_{2}O_{3} \end{array} \tag{12}$ 

 $PbSO_4 + CaCl_2 = PbCl_2 + CaSO_4$ (13)

#### 3.2.6. Fixation of Zn by Ca-Al adsorbents

As a highly volatile heavy metal, most of the Zn volatilizes to a gaseous state at high temperatures (JAGODZIŃSKA et al., 2019). Fig. 5 also shows that the total fixation rate of Zn is lower than that of other HMs, with less than 20% in the case of no adsorbent addition. With the addition of Ca-Al adsorbent, the fixation rate of Zn increased, reaching a maximum value at 5% addition and starting to decrease with a negative effect at 10% addition. The gaseous products associated with Zn are ZnCl<sub>2</sub> and the solid products are ZnAl<sub>2</sub>O<sub>4</sub>, Ca<sub>2</sub>ZnSi<sub>2</sub>O<sub>7</sub>, Ca<sub>2</sub>ZnAl<sub>2</sub>O<sub>7</sub>[2-], Ca<sub>2</sub>FeAl<sub>2</sub>O<sub>7</sub>[1-]. Relevant reactions are shown in **reactions 14 and 15**.

The effect of the ultrasonically modified Ca-Al (UM) adsorbent decreased at low additions (3%, 5%) compared to the unmodified one, similar to the Pb fixation results, which may be related to the reduction of physical adsorption. When the addition reached 10%, the fixation rate of Zn by Ca-Al (UM) was slightly increased compared to Ca-Al, and overall, Ca-Al (UM) had a positive effect at all three addition levels. The fixation rate of Zn by ethylene glycol-modified Ca-Al(EG) was much higher than that of Ca-Al and Ca-Al(UM), especially at 10%, which was more than twice the fixation rate of Zn without adsorbent addition. The modification of ethylene glycol is advantageous in providing more active sites.

 $Ca_{5}Al_{6}O_{14} + 3ZnCl_{2} = 3ZnAl_{2}O_{4} + 3CaCl_{2} + 2CaO$  (14)

 $7\text{CaO} + \text{Ca}_5\text{Al}_6\text{O}_{14} + 3\text{ZnCl}_2 = 3\text{Ca}_2\text{ZnAl}_2\text{O}_7(2\text{-}) + 6\text{Ca}(2\text{+}) + 6\text{Cl}(-) \eqref{eq:CaO} \$ 

In summary, the three Ca-Al type adsorbents showed different fixation effects on different heavy metals. Specifically, adding Ca-Al adsorbent significantly improved the fixation rate of six heavy metals compared to the condition without added adsorbent, proving that  $Ca_5Al_6O_{14}$  is feasible as a heavy metal adsorbent. Ultrasound and glycol modification improved the oxygen activity of the Ca-Al adsorbent and helped to promote the chemisorption process. Ca-Al(UM) showed the most apparent enhancement for Cn and Ni. Ca-Al(EG) showed the most obvious enhancement for Cr and Ni; the fixation rate of 3% Ca-Al(EG) for Cr was more than 90%.

# 3.3. Ecological risk of HMs

Environmental risk factors are commonly used to visualize and assess the hazards of heavy metals entering the atmosphere (HU et al., 2021). Therefore, in this study, environmental risk factors and risk indices are used to compare the combined heavy metal fixation capacity of Ca-Al, Ca-Al (UM), and Ca-Al (EG).

$$E_r = T_r \frac{C_i}{C_r}$$
(16)

$$R_i = \sum E_r \tag{17}$$

calculation (16) represents the potential ecological risk factor for

gaseous HMs ( $E_r$ );  $T_r$  stands for HMs toxicity response factor;  $C_i$  ( $\mu g/m^3$ ) is the content of HMs emitted to the atmosphere; and  $C_r$  ( $\mu g/m^3$ ) is the content of HMs in the environment (CHEN et al., 2019).  $R_i$  represents the total of the corresponding HMs ecological risk factors in **Calculation** (17). For this experiment, the gas volume was 0.03 m<sup>3</sup>.

Table S6 displays the air concentrations of heavy metals (HMs) and the HMs toxicity response factors, where the atmospheric concentrations of HMs were selected to represent southern China (CHEN et al., 2019).

The calculated results are shown in Table 3. Combined with  $E_r$  and  $R_i$  values, it was found that the more toxic HMs are Cu, Ni, and Pb (CHEN et al., 2019; CHEN et al., 2020; HUANG et al., 2020). The total  $E_r$  and  $R_i$  decreased after the addition of Ca-Al, which demonstrated that the adsorbent significantly reduced the environmental risk of HMs associated with the co-combustion process. This proved the effectiveness of Ca-Al as a mineral adsorbent.

Fig. 6 clearly shows the variation patterns of Ca-Al, Ca-Al (UM), and Ca-Al (EG) adsorbents at different additions concerning the Er values. For Cr, which is a heavy metal with high potential ecological risk and low atmospheric concentration, the addition of Ca-Al adsorbent reduces the ecological risk at low additions (3%, 5%). However, at 10%, the risk is higher than that of the pure sample. Similarly, Ca-Al(UM) showed a similar pattern. On the other hand, Ca-Al(EG) significantly improved in reducing the risk of Cr under all conditions, especially at 5%, with a reduction of 86.01%. For Cu, all three adsorbents showed a reduction in Er values at different additions, indicating that the adsorbents are very effective, with Ca-Al(EG) showing a better-combined reduction. For Mn, the Er value is small and the addition of Ca-Al has no significant effect on the Er value. Still, after ultrasonic modification, Ca-Al(UM) can significantly reduce the  $E_r$  of Mn at 3% and 5% additions by 38.08% and 46.13%, respectively. Ca-Al(EG) has a better effect at 10%. Ni is also a very hazardous heavy metal, and the addition of Ca-Al successfully reduces the Er value of Ni. Ca-Al(UM) and Ca-Al(EG) are more effective in reducing the E<sub>r</sub> value of Ni after physical or chemical modification. 10% Ca-Al(UM) reduces it by 50.43% and 3% Ca-Al(EG) reduces it by 49.02%. For Pb, Ca-Al and Ca-Al(UM) have less effect, but Ca-Al(EG) can reduce it significantly. Zn is not very toxic, 10% Ca-Al(EG) addition showed excellent performance, reducing it by 23.35%.

Since adsorbents have different fixation effects on different HMs, a comprehensive evaluation index is then required to compare the performance of adsorbents. The  $R_i$  of Ca-Al increases and then decreases with the increase of mixing ratio, and the minimum value is 10%, which is about 28.90% lower than that of the case of no adsorbent added. The  $R_i$  of Ca-Al(UM) showed a negative correlation with the addition amount, reaching a minimum  $R_i$  at 10% Ca-Al(UM), about 41.24% lower than that of the case of no adsorbent added. The  $R_i$  of Ca-Al (EG) increases with the increase of the added amount, and the best result is obtained at 3%, which is about 41.24% lower than that of the case of no adsorbent added. The Rai of Ca-Al (EG) increased with the increase in the addition, and the best result was obtained at 3%, which is about 43.2% lower than that of the case without the addition of adsorbent.

# 4. Conclusions

In this study, a new metal ore adsorbent Ca-Al ( $Ca_5Al_6O_{14}$ ) was prepared and modified by ultrasonic pretreatment and ethylene glycol pretreatment to prepare Ca-Al (UM) and Ca-Al (EG). The three adsorbents were used to fix HMs (Cr, Cu, Mn, Ni, Pb, and Zn) from the cocombustion process of coal and coconut shells. The ability of the adsorbents to fix heavy metals was verified experimentally and the combined effect of the three Ca-Al adsorbents was assessed using ecological risk. In addition, the mechanism of Ca-Al and modified Ca-Al adsorbents was investigated in this study by combining Factsage simulation with characterization such as XPS. The main conclusions are as follows.

(1) XRD, XPS, and BET characterization found that the modification significantly changed the morphological characteristics and

# Table 3

Potential ecological risk factors and risk indices for individuals before and after the addition of Ca-Al and Ca-Al(UM) and Ca-Al(EG).

Experimental parameters		E <sub>r</sub>					R <sub>i</sub>	
Adsorbent	mixing ratio	Cr	Cu	Mn	Ni	Pb	Zn	
None	_	1.68E+04	2.00E+04	2.11E+04	3.81E+05	1.14E+04	3.03E+03	4.53E+05
Ca-Al	3%	8.13E+03	1.62E + 04	2.09E+04	3.33E+05	1.10E + 04	2.88E+03	3.92E+05
	5%	1.56E + 04	1.24E + 04	1.92E + 04	3.48E+05	9.32E+03	2.30E + 03	4.07E+05
	10%	1.76E+04	1.51E+04	2.17E+04	2.54E+05	1.09E+04	3.06E+03	3.22E + 05
Ca-Al(UM)	3%	1.53E+04	1.70E+04	1.31E + 04	2.92E + 05	1.15E+04	2.99E+03	3.52E + 05
	5%	1.34E+04	1.39E+04	1.14E + 04	2.62E + 05	1.06E + 04	2.77E+03	3.14E + 05
	10%	2.58E+04	1.95E + 04	1.93E + 04	1.89E + 05	9.94E+03	3.00E+03	2.66E+05
Ca-Al(EG)	3%	1.43E+04	1.70E + 04	2.06E + 04	1.94E + 05	8.62E+03	2.80E + 03	2.57E+05
	5%	2.35E+03	1.39E+04	1.46E+04	2.68E+05	8.03E+03	2.92E+03	3.10E + 05
	10%	1.31E + 04	1.40E+04	1.43E+04	2.24E + 05	8.64E+03	2.32E+03	2.77E + 05



Fig. 6. Er of Ca-Al and Ca-Al(UM)and Ca-Al(EG).

oxygen activity of Ca-Al adsorbents. Among them, the ultrasonic modification helped improve the samples' homogeneity, and Ca-Al(UM) formed a flatter and denser pore distribution with the highest chemisorbed oxygen content under the influence of physical modification. The Ca-Al(EG) modified by the complexing agent ethylene glycol also formed many large pores in the center of the plane and had the highest lattice oxygen content under the influence of chemical modification, which was conducive to promoting the chemisorption process in the fixation of heavy metals and improving the adsorption effect. In particular, improving the fixation effect was particularly significant for Cr and Mn.

(2) Ca-Al, Ca-Al(UM), and Ca-Al(EG) adsorbents showed the effect of adsorption on different HMs at 900 °C and showed different patterns on the fixation rate of HMs with the change of added amount. Considering the ecological risk of HMs comprehensively, the ecological risk of HMs can be significantly reduced after the addition of adsorbents, so it is considered that three kinds of adsorbents are effective. Comparison at the same addition level. It was found that the  $R_i$  values of both modified Ca-Al adsorbents were lower than unmodified ones, which indicates that the two modification methods can significantly reduce the ecological risk and are very effective in fixing HMs. Among them, Ca-Al (EG) at 3% had the best effect on  $R_i$ . 3% Ca–Al (EG) reduced the  $E_r$  value of Ni by 49.02%. 5% Ca–Al (EG) reduced the  $E_r$  value of Cr by 86.01%. 5% Ca–Al (UM) had the best effect on Mn, with a reduction of 46.13%. Adding 10% Ca–Al (UM) reduced  $E_r$  of Ni by 50.43%. Considering the practical application in coal-fired power plants, Ca-Al(EG), which exhibits a higher fixation rate at small additions, is more suitable.

# CRediT authorship contribution statement

Zi You: Writing – original draft, Methodology, Investigation. Zhaosheng Yu: Writing – review & editing, Funding acquisition, Conceptualization. Yijian Hu: Writing – review & editing, Methodology, Investigation. Jinxi Dong: Writing – review & editing, Investigation. Wenchang Yue: Writing – review & editing, Methodology. JingJing Li: Writing – review & editing. Xiaoqian Ma: Supervision, Resources.

# 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.

# Data availability

Data will be made available on request.

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# Appendix A. Supplementary data

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