

Efficient leaching and separation of iron, aluminum, and calcium from carbon-rich components in coal gasification fine slag using organic acids

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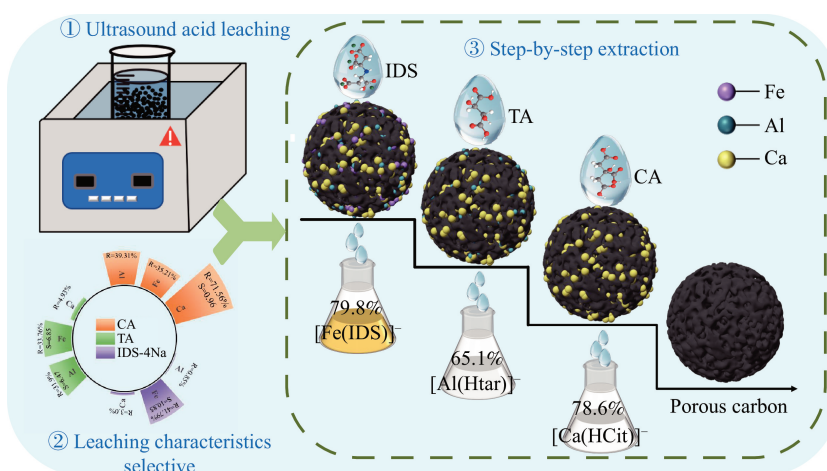
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Abstract: The efficient extraction and separation of valuable metal elements from coal gasification fine slag (CGFS) are crucial for the comprehensive high-value utilization of its constituents. This study focused on the carbon-rich components of CGFS (CGFS-H) and systematically investigates the selective leaching behavior of Fe^{3+} , Al^{3+} and Ca^{2+} using three organic acid extractants, i.e., citric acid, tartaric acid, and tetrasodium

iminodisuccinate. Additionally, the stepwise leaching of iron, aluminum and calcium from CGFS-H is explored. The selective dissolution mechanisms of these metals by different organic acids are elucidated through X-ray diffraction (XRD), X-ray fluorescence (XRF), and scanning electron microscopy (SEM) analyses. The results indicate that tetrasodium iminodisuccinate exhibits the highest leaching selectivity for Fe^{3+} , while tartaric acid demonstrated a comparable affinity for both Fe^{3+} and Al^{3+} . In contrast citric acid shows superior selectivity toward Ca^{2+} . The leaching yield of Fe^{3+} , Al^{3+} and Ca^{2+} after sequential leaching with the three organic acids were 79.8%, 65.08% and 78.6%, respectively. These findings confirm that effective and selective separation of Fe^{3+} , Al^{3+} and Ca^{2+} from CGFS-H can be achieved via optimized organic acid-based leaching strategies. This advancement provides a critical foundation for developing Ca/Fe/Al hydrotalcite materials using CGFS-H as a sustainable feedstock, thereby facilitating the transformation of waste residue into high-value functional materials and promoting resource-efficient utilization of coal gasification fine slag.

Key words: coal gasification fine slag; carbon-rich components; organic acids; leaching; stepwise extraction



Coal gasification technology serves as a crucial method for the clean and efficient utilization of coal resources, significantly contributing to the transformation of China's energy structure and the production of chemical raw materials^[1]. However, the coal gasification process generates substantial amountsof coal gasification fine slag

(CGFS), which consists of residual carbon and inorganic ash^[2]. This byproduct poses challenges to the sustainable development of coal gasification technology. The ash composition of CGFS is primarily characterized by SiO_2 , Al_2O_3 , CaO , Fe_2O_3 and MgO , along with several minor components. Notably the slag contains a considerable

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proportion of residual carbon, typically comprising 20% to 50% of its total mass^[3]. Currently, in response to the technical requirements for the cyclic co-combustion of CGFS and its application in building material production, numerous studies have been conducted by scholars focusing on methods such as the separation of residual carbon from CGFS and the conversion of this carbon into porous materials^[4–5]. Nevertheless, research on the comprehensive valuable utilization of CGFS remains limited, particularly concerning the high-value extraction of valuable metal elements present in significant quantities. Achieving comprehensive high-value utilization of CGFS necessitates advancements in low-carbon, green, and highly efficient separation methods and technologies.

The pre-separation of residual carbon and inorganic ash from CGFS is a crucial prerequisite for achieving resource utilization of CGFS^[6–7]. Currently, research on carbon-ash separation in CGFS is relatively advanced. Li et al.^[8] proposed a separation method based on differences in apparent density, achieving a separation efficiency exceeding 70%. Dong et al.^[9] introduced a cavitation jet technique to enhance flotation efficiency, thereby facilitating the effective separation of carbon and ash from CGFS. Our research group has previously conducted extensive studies on CGFS separation^[10–13]. The findings indicated that the oil agglomeration separation method can effectively extract carbon-rich components (CGFS-H) with a loss on ignition (LOI) greater than 80% and carbon-poor components (CGFS-L) with an LOI less than 10%. Based on the distinct properties of these two product types, we proposed the concept of full-component materialization and high-value utilization, as depicted in Figure 1. CGFS-H can be employed to produce porous carbon materials^[14–15] and carbon/silicon composite materials^[16]. In contrast, CGFS-L is appropriate for the fabrication of cementitious materials or porous ceramics.

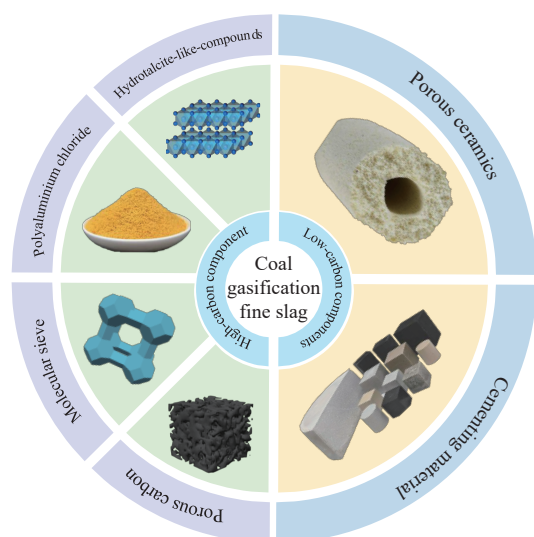


Fig. 1 The utilization diagram of all components of coal gasification fine slag

Additionally, the valuable metallic elements contained in CGFS can be extracted for the production of polyaluminum chloride or layered double hydroxides. Furthermore, silicon can be recovered from the slag for use in the preparation of molecular sieves and other materials. This method ultimately facilitates the comprehensive resource utilization of CGFS.

Layered double hydroxides (LDHs) exhibit significant potential for application in various domains, including CO₂ adsorption and catalysis^[17]. The development of LDHs from solid waste sources aligns with the objectives of the “Dual Carbon” initiative. Currently, Duan et al.^[18] have successfully designed and synthesized LDHs using blast furnace slag as a raw material, thereby providing a novel approach for the utilization of this waste. Additionally, Han et al.^[19] prepared Ca/Fe/Al-LDH adsorbents from polyaluminum chloride waste slag for the purpose of chromium adsorption in water. The chemical composition and structure of CGFS closely resemble those of the aforementioned typical solid wastes. Our research group has previously identified that the metal elements, including Ca, Fe, Al and Mg, present in CGFS-H can serve as essential raw materials for the synthesis of LDHs when preparing porous carbon materials and carbon/silicon composite materials. The extracted calcium, iron, and aluminum can be utilized to produce LDHs, which demonstrate excellent properties for CO₂ adsorption and activation. Nevertheless, the selective extraction of these key metal elements from CGFS-H continues to encounter challenges such as inadequate metal ion selectivity and environmental protection concerns. Thus, investigating the environmentally friendly and efficient method for extracting metal elements such as Ca, Fe, Al and Mg from CGFS-H is of great significance.

Alkali fusion and acid leaching are essential techniques for extracting valuable elements from solid waste at present^[20]. Research indicates that calcination at 875 °C can enhance the acid leaching recovery yield of Al from 8% to 76.72%^[21]. However, these methods are hindered by high energy consumption, substantial additive usage, interference from impurities, and challenges in separation. Inorganic acid systems demonstrate high leaching efficiency for valuable elements. For instance, high-pressure HCl leaching is utilized to effectively extract Al from CGFS for the production of polyaluminum chloride^[22]. Acid leaching with 6 mol/L HCl at 100 °C for 2 h can dissolve over 85% of Fe^[23]. Following the co-roasting of coal gangue and coal gasification coarse slag, the leaching percentages of Fe and Al reached 79.93% and 43.78%, respectively, under H₂SO₄ leaching conditions at 90 °C for 5 h^[24]. However, accompanying elements such as Ca and Mg are also dissolved during this process, which complicates separation and poses challenges for subsequent utilization. Moreover, the leaching process using inorganic acids exhibits low selectivity for metal elements, leading to interference in the utilization of metal elements in the extraction solution.

In recent years, organic acids have garnered considerable

attention from researchers due to their high selectivity in metal elements separation. Ali et al.^[25] employed succinic acid to selectively recover lithium from spent lithium-ion batteries. Compared to traditional methods, organic acid leaching combines environmental friendliness with high product purity. Wang et al.^[26] found that approximately 80% of rare earth elements could be extracted from coal gangue in the initial step, while coexisting ions Li and Ga exhibited extraction rates below 7%. Subsequently, the remaining Li and Ga were recovered in a second step. This finding suggests that the stepwise extraction method can effectively facilitate the leaching and separation of metal elements. Building on these advantages, this paper introduces a novel process for organic acid leaching, separation, and regeneration of valuable metal elements in CGFS-H, as illustrated in Figure 2. This process allows for the green and efficient leaching and separation of Fe, Al and Ca in CGFS-H, thereby establishing a robust foundation for the subsequent preparation of LDHs.

This study focused on CGFS-H as the research subject, and investigated the leaching behavior of Fe, Al and Ca elements using three organic leaching agents, i.e., citric acid, tartaric acid, and iminodisuccinic acid tetrasodium (IDS-4Na). The sequential extraction procedure and the underlying mechanisms governing the leaching of Fe^{3+} , Al^{3+} and Ca^{2+} from CGFS-H are discussed. The findings present a novel and environmentally friendly approach for extracting valuable metal ions from CGFS. Moreover, they provide effective support for addressing the technical challenges associated with the preparation of Ca/Fe/Al-LDH using the valuable metal elements from CGFS-H.

1 Experimental

1.1 Raw materials and reagents

In this study, the CGFS sample was from the dry pulverized coal gasification fine slag generated by the Aerospace Furnace at a coal chemical enterprise in Shenmu. The sample was air-dried under natural conditions, thoroughly mixed, and subsequently sealed for storage. The results of the proximate analysis are presented in Table 1. The ash content of CGFS is 51.63%, while the fixed carbon content is 37.64%. The three organic acids utilized in this study were procured from Tianjin Damao Reagent Factory.

1.2 Preparation of carbon-rich components

The carbon-rich components (CGFS-H) was obtained from CGFS through the oil agglomeration method previously developed by our research group^[13]. The proximate analysis results for CGFS-H, both before and after oil removal, along with those for CGFS-L, are presented in Table 1. The ash content of the separated CGFS-H is 17.40%, suggesting a 66.3% reduction compared to CGFS, while CGFS-L exhibits an ash content of 96.25%. This finding indicates that the oil agglomeration method effectively removes ash from CGFS, with the residual carbon components primarily concentrated in CGFS-H. The volatile matter content of CGFS-H is 42.81%, predominantly influenced by the unremoved oil. Following the de-oiling treatment, the volatile matter content decreases to 5.49%.

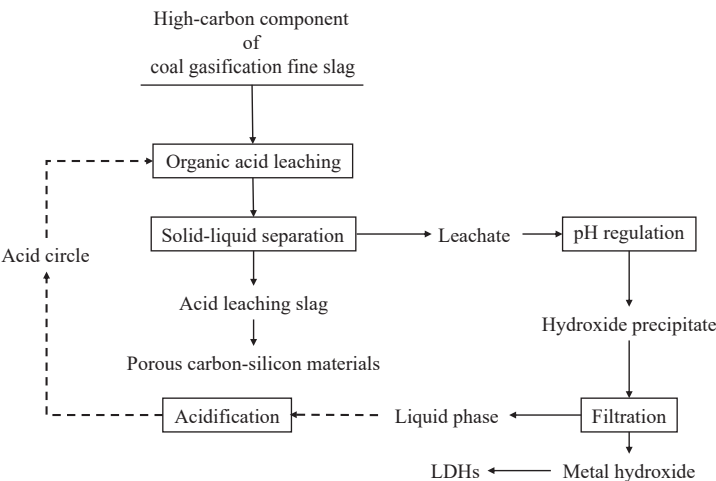


Fig. 2 Process flow chart for recovery of valuable metals from carbon-rich components of coal gasification fine slag

Table 1 Proximate analysis of CGFS

Sample	Proximate analysis $w_{ad}/\%$			
	M	A	V	FC
CGFS	3.70	51.63	7.03	37.64
CGFS-H (before degreasing)	2.25	17.40	42.81	37.54
CGFS-H (after degreasing)	1.86	14.90	5.49	77.75
CGFS-L	0.39	96.25	3.05	0.31

1.3 Leaching experiment

The leaching experiment for valuable metal ions was conducted using oil-untreated CGFS-H as the research sample and citric acid, tartaric acid, and iminodisuccinic acid tetrasodium (IDS-4Na) as leaching agents through the ultrasonic acid leaching method^[17]. The specific experimental procedures were as follows: a 5 g sample of CGFS-H was mixed with varying concentrations of organic acids at a liquid-solid ratio of 10:1 and homogenized *via* agitation. Subsequently, this mixture was subjected to ultrasonic leaching in an ultrasonic instrument, operating at a power of 240 W, a treatment duration of 0.5–24 h, and a frequency of 40 kHz. Following the ultrasonic acid leaching, the mixture was filtered using a 0.45 μm filter membrane. Then, washing and volume fixation were performed to obtain leachate and leached residue samples. The leached residues of CGFS-H, extracted with IDS-4Na, tartaric acid, and citric acid, are designated as CGFS-H-IDS, CGFS-H-TA and CGFS-H-CA, respectively. However, the leached residues, sequentially extracted with IDS-4Na, tartaric acid, and citric acid, are referred to as CGFS-H-IDS, CGFS-H-IDS-TA and CGFS-H-IDS-TA-CA, respectively. Following ultrasonic alkali washing preformed three times to eliminate residual organic acid macromolecules, these residues were utilized to assess their specific surface area and pore characteristics. The concentrations of Fe^{3+} , Al^{3+} and Ca^{2+} in the leachate were quantified. The leaching rate was calculated using equation (1), while the selectivity was calculated using equation (2)^[27].

$$R(\%) = \frac{c \times v}{m \times \alpha} \times 100\% \quad (1)$$

$$S = \frac{R_a}{R_b} \times 100\% \quad (2)$$

In the equation, R denotes the leaching yield of various metals, c represents the concentration of elements in the leaching solution, v indicates the volume of the solution and m signifies the mass of the sample utilized in the leaching experiment. Additionally, S refers to the selectivity of the target element, where a represents the target element ($a = \text{Ca}, \text{Fe}$ or Al), and b encompasses all other elements excluding the target element.

1.4 Characterization and analysis methods

The mineral composition of the carbon-rich components sample was characterized using X-ray diffractometry (XRD). Sample tablets for the X-ray diffractometer, equipped with a Cu target (Bruker D8 Advance, Germany), were prepared using the powder pressing method. XRD patterns were obtained by scanning within the diffraction angle range of $2\theta = 5^\circ$ to 80° at a rate of $0.2(^\circ)/\text{min}$. The structure characteristics of the functional groups for CGFS-H were determined by a Tensor 27 Fourier transform

infrared spectrometer (Bruker, Germany). The test conditions included sample preparation *via* the KBr pellet pressing method, a spectral resolution of 4 cm^{-1} , 32 scans, a measurement range of $4000\text{--}400 \text{ cm}^{-1}$, equipping with a DTGS detector (deuterated triglycine sulfate). The elemental composition and content of the samples were determined through X-ray fluorescence spectroscopy (XRF, Rigaku ZSX Primus III+, Japan). Ash preparation adhered to the national standard GB/T212—2008 Industrial Analysis Method of Coal. The sample was ground to a particle size of less than 0.074 mm , pressed into tablets, and then tested. The X-ray tube target was rhodium (Rh), with an X-ray tube voltage of 60 kV and a tube current of 150 mA. The morphology analysis of the leached residues was conducted using a JSM-6460LV tungsten filament scanning electron microscope (SEM, JEOL, Japan). The analysis was conducted under the following conditions: as follows: an electron beam current of 0.1 nA and an acceleration voltage of 15 kV. The specific surface areas of CGFS and stepwise extraction residues were measured by low-temperature nitrogen adsorption using an ASAP 2020 fully automatic physical adsorption analyzer. The test conditions included adsorption temperature of -195.8°C , a degassing temperature of 200°C , and a degassing duration of 8 h. The determination of iron ions in the leachate was conducted in accordance with the Water Quality-Determination of Fe-1,10-Phenanthroline Spectrophotometric Method (HJ/T 345—2007). The determination of Al^{3+} was performed referring to General Method for Determination of Aluminum in Inorganic Chemical Products-Chrome Azurol S Spectrophotometric Method (GB/T23944—2023). The determination of Ca^{2+} adhered to the Water Quality-Determination of Calcium and Magnesium-EDTA Complexometric Titration Method (GB7477—87).

2 Results and discussion

2.1 Composition and structure of carbon-rich components

The compositional and structural characteristics of CGFS-H are illustrated in Figure 3. Figure 3(a) displays the compositional characteristics of both CGFS and CGFS-H. The XRD pattern of CGFS-H exhibits broad diffraction scattering features^[28], suggesting the presence of residual carbon and amorphous vitreous materials. In contrast, the strong diffraction peaks in the CGFS pattern correspond to minerals including quartz, calcite, hematite, goethite, kyanite, and corundum. Following oil agglomeration separation, the hydrophilic minerals (such as lime, calcite, and diaspor) in CGFS-H are diminished, while the diffraction peaks of hematite, magnetite, kyanite, corundum, and diaspor are weakened, indicating that the contents of these substances are relatively low.

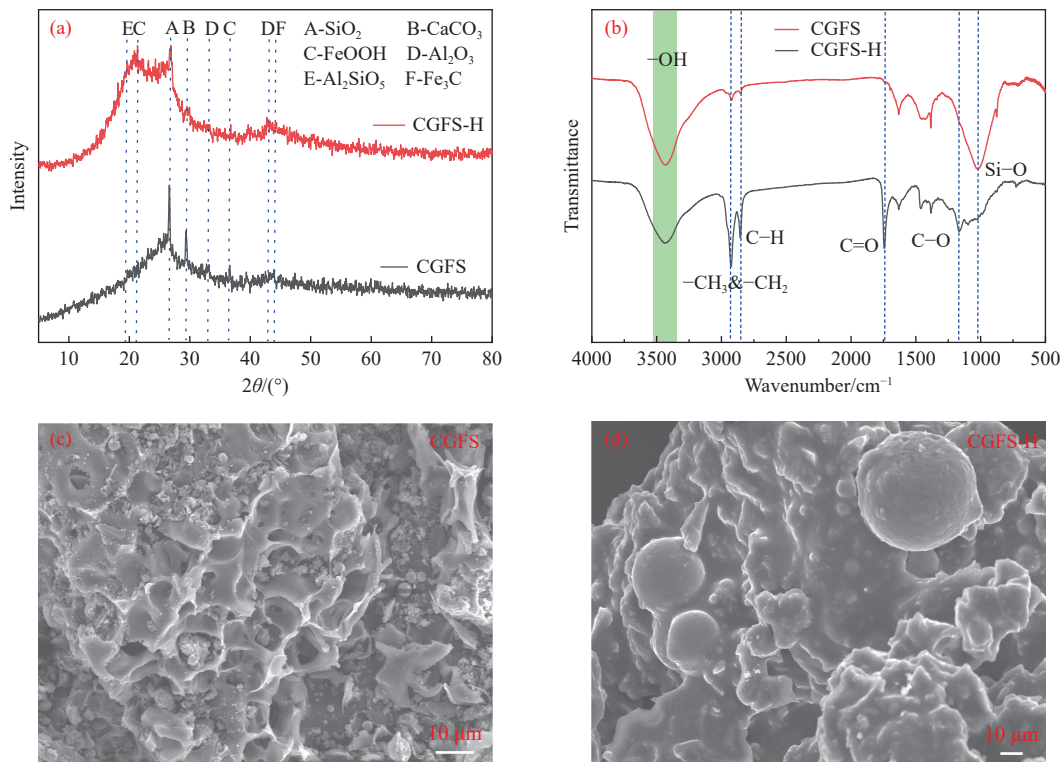
The infrared spectra of CGFS and CGFS-H, as shown in Figure 3(b), reveal a broad absorption band at 3443 cm^{-1} ,

which is attributed to the stretching vibrations of adsorbed water molecules and $-\text{OH}$ groups^[29–30]. The CGFS-H sample exhibits absorption peaks at 2928 and 2855 cm^{-1} , corresponding to the stretching vibrations of $-\text{CH}_2$ and $-\text{CH}_3$ groups, as well as $\text{C}-\text{H}$ bonds, respectively^[13]. Additionally, the peak at 1170 cm^{-1} is assigned to the stretching vibration of $\text{C}-\text{O}$ ^[31], indicating the presence of residual oil in CGFS-H. The peak at 874 cm^{-1} indicates the presence of carbonates, while the peak at 712 cm^{-1} arises from the stretching or bending vibrations of $\text{Si}-\text{O}-\text{Si}$ (Al). In comparison to CGFS, the absorption peak of $\text{Si}-\text{O}$ at 1015 cm^{-1} is absent in CGFS-H, and a new strong peak near 1744 cm^{-1} corresponds to the stretching vibration of $\text{C}=\text{O}$. This observation indicates a reduction of quartz phase and an enrichment of residual carbon components in CGFS-H.

The micromorphology of CGFS is presented in Figure 3(c). CGFS predominantly consists of irregular porous block structures and flocculent particles. The residual carbon displays a highly porous structure. In addition to the ash particles that adhere to the carbon surface, a significant quantity of ash residue is retained

within the carbon pores^[4]. As depicted in Figure 3(d), following oil agglomeration separation, the residual carbon in CGFS-H aggregates, resulting in the formation of large particle structures, with the surface coated by an oil film.

The ash composition of CGFS-H is shown in Table 2. CGFS-H is primarily composed of SiO_2 , Al_2O_3 , Fe_2O_3 and CaO , along with trace amounts of MgO , Na_2O and SO_3 . The element contents of various components, as detailed in Table 2, indicates that mineral components also undergo migration during the enrichment process. This phenomenon is primarily attributed to the diverse forms and varying densities of these components. However, the enrichment of metal elements cannot be accomplished through the oil agglomeration method. Meanwhile, LOI of CGFS-H is 83.80%. Following the oil agglomeration separation of CGFS, the ash content decreases from the initial 51.63% to 17.4%. These findings align with the results of proximate analysis, XRD and FT-IR. Collectively, these results confirm that oil agglomeration separation facilitates an enrichment of residual carbon and ash components.



(a): XRD patterns; (b): FT-IR spectrogram; (c): SEM image of CGFS; (d): SEM image of CGFS-H.

Fig. 3 The compositional and structural characteristics of CGFS and CGFS-H

Table 2 Chemical composition of CGFS and CGFS-H

Sample	Content w/%								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	SO_3	others	LOI
CGFS	36.09	16.14	16.06	22.30	1.29	0.44	3.20	4.48	37.64
CGFS-H	41.96	18.65	12.56	17.55	1.07	0.87	2.92	4.42	83.80
CGFS-L	35.26	16.14	14.65	25.94	1.39	0.47	1.84	4.31	96.64

2.2 Leaching characteristics of iron, aluminum and calcium in CGFS-H by organic acids

2.2.1 Study on citric acid leaching characteristics

To explore the influence of citric acid on the ultrasonic acid leaching of Fe, Al and Ca from CGFS-H under varying conditions, the effects of citric acid concentration, leaching time, temperature, and liquid-solid ratio on the leaching yield of metal elements in CGFS-H were examined at a pH value of 1.0. The results are presented in Figure 4.

Figure 4(a) shows the differences in the leaching ability of three metal ions under different concentrations of citric acid. It is evident that as the concentration of citric acid increases, the leaching yields of Ca^{2+} , Fe^{3+} and Al^{3+} all exhibit an upward trend. However, the increases in the leaching yields of Fe^{3+} and Al^{3+} are more gradual compared to Ca^{2+} . This observation can be attributed to the predominant presence of Al^{3+} in the lattice of aluminosilicates within CGFS. Furthermore, as a recognized nucleation element, aluminum is primarily situated in the core of fine slag particles, which complicates its leaching process^[32]. The stable Si–O–Al bonds can only be disrupted under stronger acidic conditions or in presence of ligands with greater complexation ability, while the efficacy of citric acid within this concentration range

remains limited. As the concentration of citric acid increases, calcite is gradually dissolved, resulting in a greater complexation of Ca^{2+} . To maintain the constant solubility product of calcite, the system's pH also rises^[33], thereby impeding the leaching yield of Ca^{2+} .

With the citric acid concentration maintained at 1 mol/L, Figure 4(b) illustrates the effect of leaching time on the leaching behavior of metal ions at 30 °C and 10 mL/g. The leaching yield of Ca^{2+} increases rapidly during the first hour, with most of the calcium carbonate in CGFS-H dissolving. Reaction equilibrium is achieved at 1.5 h, indicating a rapid leaching process of Ca^{2+} . In contrast, the leaching yields of different metal ions in the citric acid solution exhibit notable variations. The leaching yield of Fe^{3+} increases gradually before stabilizing at approximately 35.4%. A similar trend is observed for Al^{3+} , although its leaching yield exhibits the slowest increase and the least variation over time.

Figure 4(c) illustrates the effect of temperature on the leaching behavior of metal ions under conditions of 1 mol/L citric acid, a leaching duration of 1.5 h, and a liquid-solid ratio of 10 mL/g. It is evident that as the temperature increases from 30 to 70 °C, the leaching yields of the three metal ions gradually rise. This phenomenon can be attributed to the enhancement of the average kinetic energy of molecules with increasing temperature, leading to more frequent and vigorous collisions, thereby accelerating the reaction^[34].

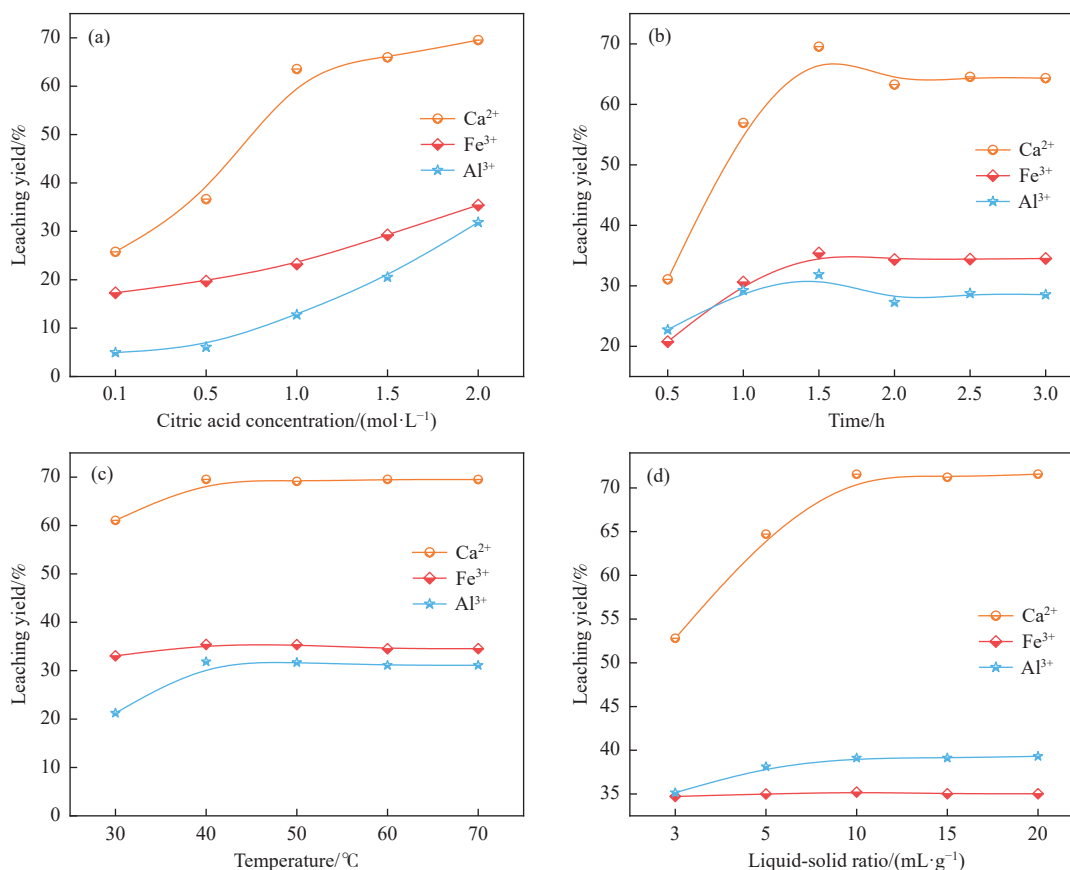


Fig. 4 The leaching yields of Fe^{3+} , Al^{3+} and Ca^{2+} in CGFS-H affected by (a) citric acid concentration, (b) time, (c) temperature, (d) liquid-solid ratio

When the temperature exceeds 40 °C, the leaching yield stabilizes, primarily due to the complexation reaction between citric acid and calcium ions being nearly thermoneutral, with its stability constant showing minimal sensitivity to temperature^[35]. Consequently, the optimal leaching temperature is identified as 40 °C.

The effect of the liquid-solid ratio on the leaching process is shown in Figure 4(d). As the liquid-solid ratio increases from 3 to 10 mL/g, the leaching efficiency of Ca^{2+} increases significantly from 52.8% to 71.6%, stabilizing once the liquid-solid ratio exceeds 10 mL/g. This phenomenon occurs because the initial stage of leaching, governed by mass transfer diffusion, is affected by the liquid-solid ratio. When the ratio reaches 10 mL/g, it signifies that the effective concentration of citric acid has achieved reaction equilibrium. In contrast, the leaching efficiency of Al^{3+} experiences only a modest increase of 5%, as Al^{3+} exists primarily in stable aluminosilicates or vitreous forms. The chemical states of Fe^{3+} and Al^{3+} in CGFS-H exhibit greater stability compared to that of Ca^{2+} ^[36], resulting in low leaching yields for Fe^{3+} and Al^{3+} within the citric acid system.

2.2.2 Study on the leaching characteristics of tartaric acid

Tartaric acid is a dibasic carboxylic acid characterized by

the presence of two hydroxyl groups and two carboxyl groups in its molecular structure, enabling the formation of a five-membered ring chelate^[37]. Its complexation ability is controlled by pH^[38]. The effect of tartaric acid solution on the leaching ability of Ca^{2+} , Fe^{3+} and Al^{3+} under different conditions is shown in Figure 5. The effect of solution pH is shown in Figure 5(a). When the pH value exceeds 2, the leaching yields of the three metal ions are decrease to varying extents. This phenomenon can be attributed to the diminished ionization degree of tartaric acid as the solution pH increases, which results in a reduced effective ligand concentration in the system. At lower pH values, stable complexes readily form between Fe^{3+} and tartaric acid. Nevertheless, as the pH value rises, Fe^{3+} gradually hydrolyzes to form $\text{Fe}(\text{OH})_3$ precipitates. These precipitates adsorb onto carbon, leading to a decrease in the leaching yield^[39]. When the pH value exceeds 5, the leaching yield declines more rapidly due to enhanced hydrolysis of the metal ions. Simultaneously, when the pH exceeds 4, Al^{3+} hydrolyzes to form $\text{Al}(\text{OH})_3$, which weakens the coordination ability of tartaric acid under near-neutral conditions.

Under the condition of maintaining the solution pH value at 1.0, the effect of tartaric acid concentration is shown in Figure 5(b). Increasing the tartaric acid concentration from 0.2 to 1.0 mol/L resulted in significant rise in the leaching yields of Fe^{3+} and Al^{3+} , reaching to 38.0% and 34.2%, respectively.

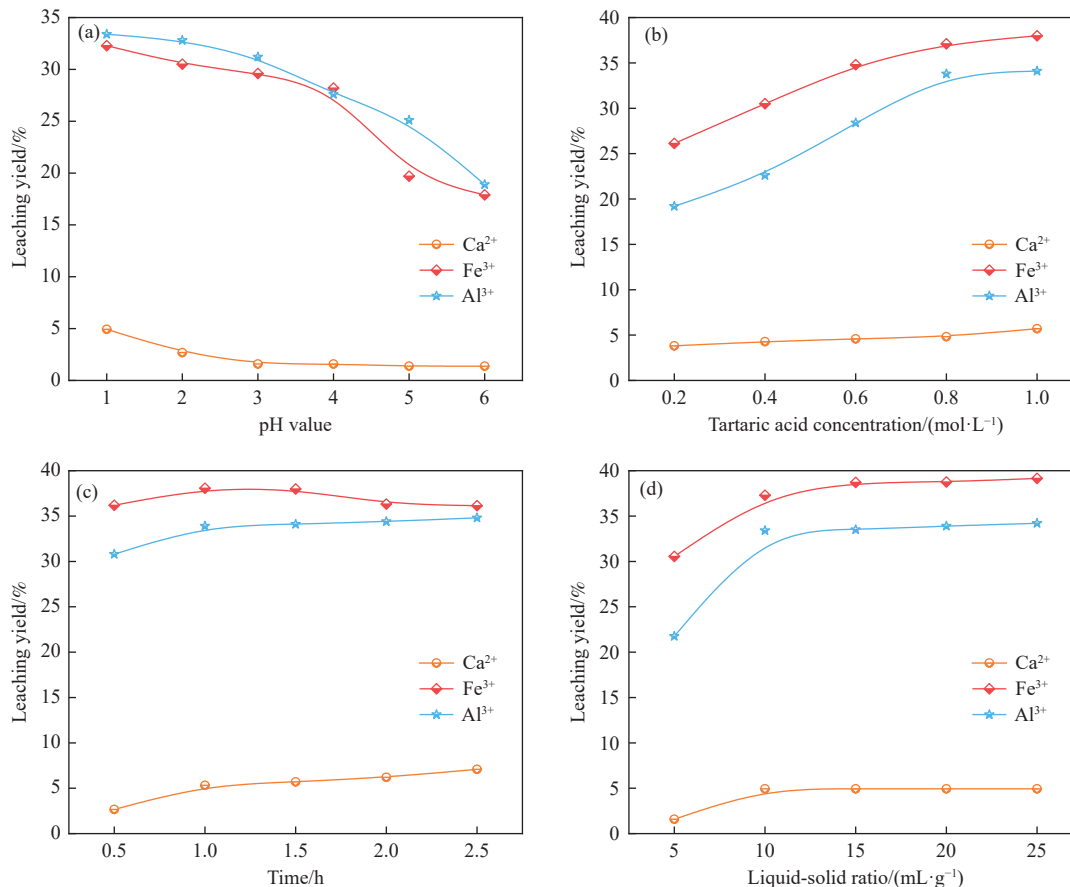


Fig. 5 The leaching yields of Fe^{3+} , Al^{3+} and Ca^{2+} in CGFS-H affected by (a) solution pH value, (b) tartaric acid concentration, (c) time, (d) liquid-solid ratio

It was demonstrated that the dissolution of Al and Fe from CGFS-H was facilitated by tartaric acid. This enhancement is primarily attributed to the increased H^+ concentration, which promotes the protonation of the mineral surface and facilitates the formation of metal-chelate complexes. Concurrently, the release of protons onto the mineral surface further enhances mineral dissolution, thereby increasing the leaching yield. At this concentration, the leaching yield of Ca^{2+} remains relatively low at 5.71%, resulting in a selectivity ratio of Fe^{3+} and Al^{3+} to Ca^{2+} of 12.6. Consequently, the tartaric acid system exhibits a favorable leaching selectivity for Fe^{3+} .

Figure 5(c) depicts the influence of reaction time on the leaching rates of Ca^{2+} , Fe^{3+} and Al^{3+} under the conditions of pH value=1 and 1 mol/L tartaric acid. Evidently, the leaching yields of Ca^{2+} , Fe^{3+} and Al^{3+} increase gradually with extended reaction time, ultimately reaching a stable state. This phenomenon can be attributed to the initial stage of the reaction, during which tartaric acid fully interacts with the mineral surface, enabling a rapid reaction. As the reaction time increases, the number of active sites on the mineral surface diminishes. The leaching yields of Ca^{2+} , Fe^{3+} and Al^{3+} tend to stabilize due to the influence of solid product coatings, mineral structure densification, and diffusion limitations. In heterogeneous reactions, the reaction rate is affected by factors such as surface contact

area, viscosity, and surface tension, with the liquid-solid ratio serving as a crucial parameter affecting these variables^[40]. When the liquid-solid ratio is low, the CGFS-H sample does not achieve complete contact with tartaric acid. This limitation hinders the rapid and homogeneous mixing of the solution. As a result, the effective contact area of the solution is reduced, leading to a deceleration of the reaction process. Notably, the leaching yield of Ca^{2+} in the tartaric acid system is less than 7%. This is primarily attributable to the weaker complexation ability of tartaric acid with Ca^{2+} compared to citric acid. Due to its low charge density and absence of empty d -orbitals, Ca^{2+} struggles to form stable chelates.

2.2.3 Leaching characteristics of IDS-4Na

As a novel type of amino-carboxylic acid chelating agent, IDS-4Na exhibits strong chelating performance, high water solubility, and environmental friendliness. Recent studies have revealed its extensive applications^[41–42]. This study investigated the effects of several factors, including solution pH value, IDS-4Na concentration, reaction temperature, and leaching time, on the complexation and leaching performance of valuable metal elements in CGFS-H. The results are presented in Figure 6.

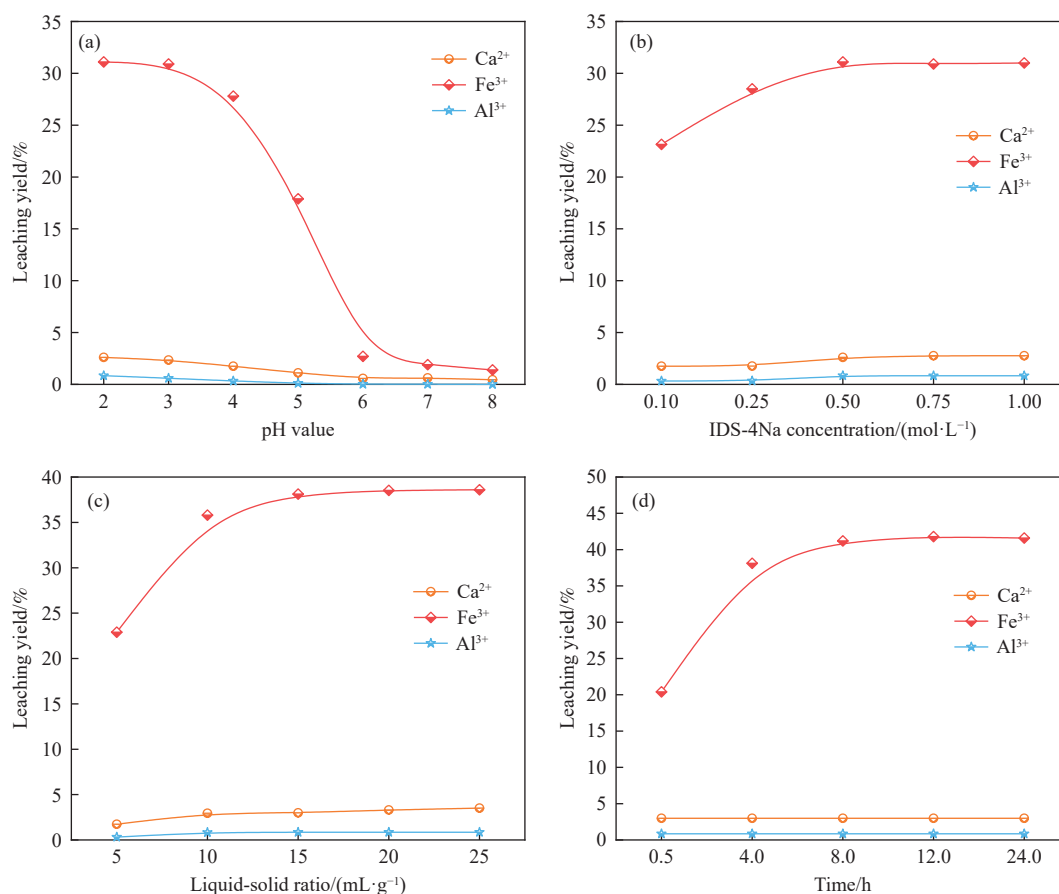


Fig. 6 The leaching yields of Fe^{3+} , Al^{3+} and Ca^{2+} in CGFS-H affected by (a) solution pH value, (b) IDS-4Na concentration, (c) liquid-solid ratio, (d) time

The influence of solution pH value is depicted in Figure 6 (a). Under pH value ranging from 2 to 4, IDS-4Na demonstrates the strongest complexation ability toward Fe^{3+} . In contrast, its complexation capacity for Ca^{2+} and Al^{3+} is relatively feeble, highlighting a pronounced selectivity for Fe^{3+} . At pH value = 2, the selectivity ratios for Ca^{2+} and Al^{3+} are 11.96 and 37.11, respectively. This phenomenon can be attributed to the increased protonation of functional groups in IDS-4Na, such as carboxyl ($-\text{COOH}$) and amino ($-\text{NH}_2$), in an acidic environment, which enhances its complexation ability with Fe^{3+} . When the pH value exceeds 5, Fe^{3+} begins to hydrolyze, forming $\text{Fe}(\text{OH})_3$ precipitates. This results significantly reduces the concentration of free Fe^{3+} in the solution, subsequently decreasing the leaching rate. At this juncture, even though the complexation ability of IDS-4Na may be enhanced due to the complete dissociation of carboxylic acid groups, it still fails to compete effectively with the precipitation reaction.

Figure 6(b) depicts the impact of varying concentrations of IDS-4Na on the leaching efficiency of three metal ions. The leaching yield of Fe^{3+} increases from 23.1% to 31.1%. Meanwhile, the leaching yields of Ca^{2+} and Al^{3+} rise from 1.8% and 0.3% to 2.6% and 0.8%, respectively. Notably, the leaching agent exhibits a selectivity of 9.15 toward Fe^{3+} . This phenomenon can be attributed to the fact that IDS-4Na, as a polydentate ligand, has significantly higher complexation stability constants with Fe^{3+} than with Ca^{2+} and Al^{3+} [43–44]. At elevated concentrations, IDS-4Na preferentially forms stable octahedral complexes with Fe^{3+} as the ligand concentration increases. When the concentration reaches 0.50 mol/L, the leaching yield approaches a stable state, indicating that a dynamic equilibrium between dissolution and complexation is established within the system.

The influence of the liquid-solid ratio on the leaching yield of Fe^{3+} , Al^{3+} and Ca^{2+} is depicted in Figure 6(c). As the liquid-solid ratio increases, the leaching yield of Fe^{3+} rises gradually and stabilizes upon reaching 15 mL/g. In contrast, the leaching yields of Ca^{2+} and Al^{3+} increase slightly, remaining below 3%. This phenomenon can be attributed to the limited the contact area per unit volume of the reaction system at low liquid-solid ratios, resulting in a substantial mass transfer resistance at the reaction interface. With the

liquid-solid ratio increases, the concentration of the leaching agent becomes sufficient to react effectively with the solid particles[45].

To enhance the understanding of the complexation leaching process of IDS-4Na for three metal ions, an investigation was carried out on the leaching efficiency of these ions at various time intervals. Figure 6(d) illustrates the temporal variation trends in the extraction efficiencies of the three metal ions. The extraction of metal ions by IDS-4Na exhibits a distinctive characteristic. Specifically, the leaching rate of Fe^{3+} stabilizes after 8 h. This phenomenon can be attributed to the large volume of IDS-4Na as a complexing ligand, which introduces significant steric hindrance and results in a relatively low diffusion rate across the mineral layer/liquid interface[37]. Owing to its relatively weak complexation ability with Ca^{2+} and Al^{3+} , the leaching yields of Ca^{2+} and Al^{3+} only reach 3.0% and 0.9%, respectively, during the 24 h extended leaching process. This finding offers a novel approach for the selective complexation and leaching of Fe^{3+} from the carbon-rich components of coal gasification fine slag.

2.2.4 Leaching characteristics of carbon-rich components after oil removal

Studies have shown that the leaching rates of Ca^{2+} , Fe^{3+} and Al^{3+} in the aforementioned three organic acid systems require enhancement. Based on this foundation, an in-depth investigation was conducted to examine the leaching characteristics of the de-oiled carbon-rich components under the optimal leaching conditions of the three organic acids. The detailed findings are presented in Figure 7.

As shown in Figure 7, the leaching yields of Ca^{2+} , Fe^{3+} and Al^{3+} are significantly enhanced by the three organic acids when compared to the carbon-rich components without de-oiling. This enhancement is primarily attributed to the presence of an oil film on the surfaces of agglomerated particles, which serves as a hydrophobic barrier. This barrier impedes effective contact between the organic acids and the internal metal oxides, thus reducing the effective reaction area. Once the surface oil film is removed, the effective reaction interface is restored.

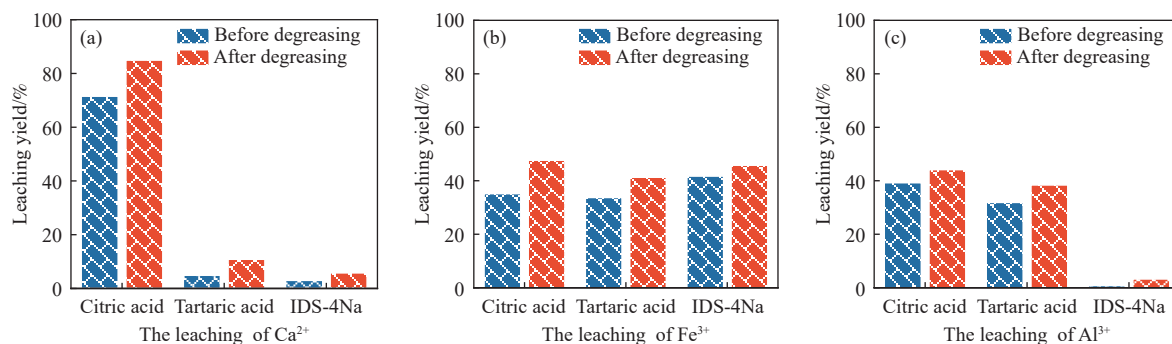


Fig. 7 Comparison of leaching properties of (a) Ca^{2+} , (b) Fe^{3+} , (c) Al^{3+} in CGFS-H before and after degreasing by citric acid, tartaric acid and IDS-4Na

Consequently, organic acids can penetrate more effectively and establish better contact with metals, resulting in an increased dissolution rate of metal ions. Nevertheless, the selectivity of organic acids toward different metal ions remains unchanged.

Furthermore, when other organic solvents, such as acetone, are used for oil removal, it is accompanied by toxicity and pollution issues. This situation not only raises environmental concerns but also increases treatment costs. During the activation process in the subsequent utilization phase, the oil film is converted into a functionalized carbon layer. This transformation eliminates the need for additional pore-forming agents and reduces alkali consumption. Moreover, during the direct combustion utilization process, the ignition point may be lowered due to the high volatile matter content with residual carbon exceeding 40%. The calorific value of the residual carbon can be increased by the presence of an oil film, thereby improving combustion performance. The overall cost of the non-deoiling approach is relatively low, with its primary advantage being the transformation of the oil film from a “polluting liability” into an “energy/material asset”. Under conditions of minimal variance in metal ion leaching yield, waste oil recyclability, and resource utilization of leaching residues, this study adopts a non-deoiling strategy.

2.3 The stepwise extraction process of Fe^{3+} , Al^{3+} and Ca^{2+} in carbon-rich components

Based on the aforementioned research, a stepwise extraction process involving IDS-4Na leaching, followed by tartaric acid leaching and citric acid leaching, is proposed. This process aims to achieve the stepwise enrichment of

Fe^{3+} , Al^{3+} and Ca^{2+} in carbon-rich components. Eventually, Si is enriched in the residue, thereby realizing the comprehensive utilization of multiple resources, as depicted in Figure 8.

2.3.1 Selective extraction of Fe^{3+}

Under the aforementioned optimal process conditions, IDS-4Na demonstrates a high selectivity for Fe^{3+} . To identify the optimal parameters for the selective extraction of Fe^{3+} from CGFS-H, the influence of extraction time was explored, and the results are presented in Figure 9. During the three extraction procedures, the extraction efficiencies of Ca^{2+} and Al^{3+} by IDS-4Na remained below 3%. As the number of extractions increased, the content of Fe^{3+} in CGFS-H gradually decreased, leading to a corresponding decline in the extraction efficiency of Fe^{3+} during the second and third extractions. After three extractions, the cumulative extraction efficiency of Fe^{3+} in CGFS-H reached 79.8%, while the co-extraction efficiencies of Ca^{2+} and Al^{3+} were each less than 8%. These findings confirm the efficacy of IDS-4Na in the targeted separation of Fe^{3+} and provide a sustainable approach for recovering iron resources from CGFS-H.

2.3.2 Selective extraction of Al^{3+}

In the aforementioned tartaric acid leaching system, tartaric acid exhibited selectivity for Fe^{3+} and Al^{3+} . Consequently, leaching experiments utilizing tartaric acid were conducted on the residue CGFS-H-IDS following the extraction of Fe^{3+} by IDS-4Na, with the results presented in Figure 10.

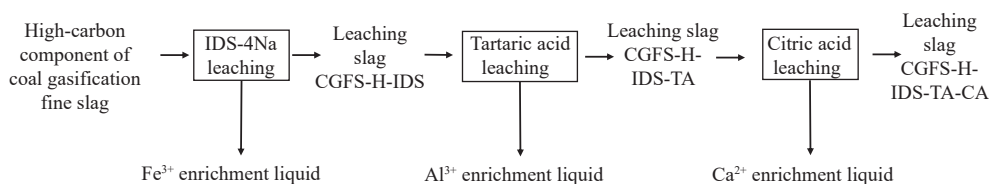


Fig. 8 The stepwise extraction process of Fe^{3+} , Al^{3+} and Ca^{2+} in the CGFS-H

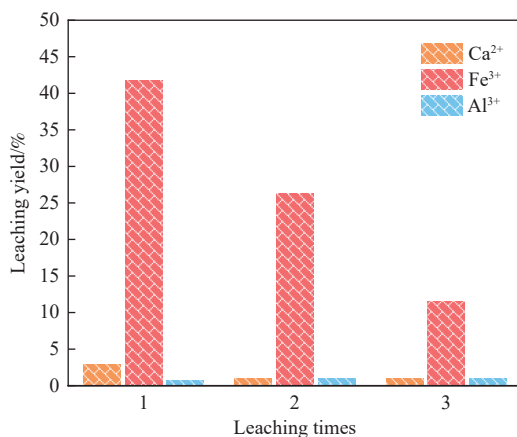


Fig. 9 Three extractions effect of IDS-4Na

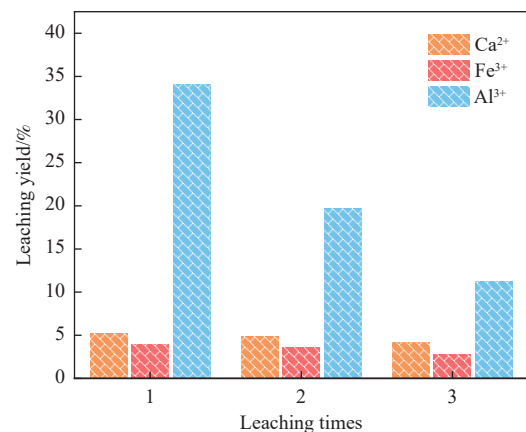


Fig. 10 Three extractions effect of tartaric acid

During the three extraction procedures, the extraction rate of Al^{3+} demonstrated a consistently decreasing trend. This indicates that during these processes, readily soluble components such as amorphous $\text{Al}(\text{OH})_3$ preferentially formed complexes with tartaric acid, indicating that the complexation reaction between tartaric acid and Al^{3+} is relatively complete. Moreover, a cumulative recovery of 65.08% of Al^{3+} was achieved after three extractions, while the loss rates of Ca^{2+} and Fe^{3+} were approximately 10%.

2.3.3 Selective extraction of Ca^{2+}

Following three extractions with tartaric acid as previously described, the residue CGFS-H-IDS-TA was mixed with a citric acid solution. The extraction efficiencies of Ca^{2+} , Fe^{3+} and Al^{3+} are presented in Figure 11. After the three extraction processes, the cumulative extraction efficiency of Ca^{2+} in CGFS-H-IDS-TA reached 78.6%. In contrast, the cumulative extraction efficiencies for Fe^{3+} and Al^{3+} were both below 7.5%. These findings suggest that Fe^{3+} and Al^{3+} were preferentially removed from CGFS-H after extraction with IDS-4Na and subsequent treatment with tartaric acid. Moreover, Ca^{2+} shown a greater tendency for extraction from CGFS-H, facilitating the stepwise selective separation of Fe^{3+} , Al^{3+} and Ca^{2+} from CGFS-H.

2.4 Complexation leaching mechanism of different leaching agents

2.4.1 Structural properties of different leaching slag

To delve into the compositional and structural changes of

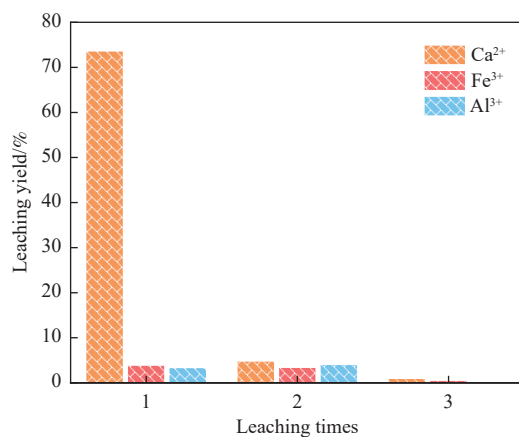


Fig. 11 Three extractions effect of citric acid

leaching residues during the organic acid leaching process, XRD was used for the mineralogical analysis of CGFS-H-IDS, CGFS-H-IDS-TA and CGFS-H-IDS-TA-CA. The findings are presented in Figure 12. It can be clearly discerned that following organic acid leaching, the principal mineral phases, including kyanite, corundum, and diaspore in CGFS-H, were diminished or entirely absent, while amorphous glassy phases persisted along with crystalline phases such as quartz and mullite. This observation suggests that treatment with organic carboxylic acid can effectively dissolve relatively unstable aluminate and aluminosilicate minerals, while exerting minimal impact on stable silicate minerals.

To further understand the content changes of Fe^{3+} , Al^{3+} and Ca^{2+} during the stepwise extraction process using organic acids, we conducted ash composition analysis of the leaching residues *via* X-ray fluorescence spectroscopy (XRF). The results are shown in Table 3. After three extractions with IDS-4Na, the Fe_2O_3 content in CGFS-H-IDS significantly decreased, while the remaining components were mainly SiO_2 , Al_2O_3 and CaO . Subsequent extraction with tartaric acid, led to a notable reduction of Al_2O_3 content in CGFS-H-IDS-TA, with CaO remaining the main component. After citric acid extraction, the CaO content in CGFS-H-IDS-TA-CA was reduced to less than 5%, while SiO_2 became sufficiently enriched, exceeding 79%. The effectiveness of the selective separation of target elements in each acid leaching system can be demonstrated through a combination of XRD and XRF analyses. Additionally, the main residues in the final leaching residue consist of silicate materials, providing a foundation for preparing subsequent carbon/silicon composite materials.

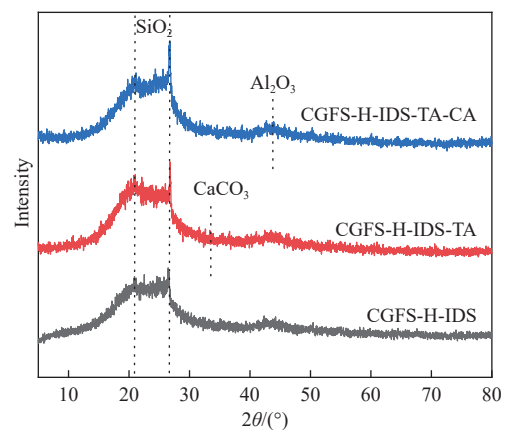


Fig. 12 XRD patterns of the residue after stepwise extraction

Table 3 Chemical composition of CGFS-H from different acid leaching slag

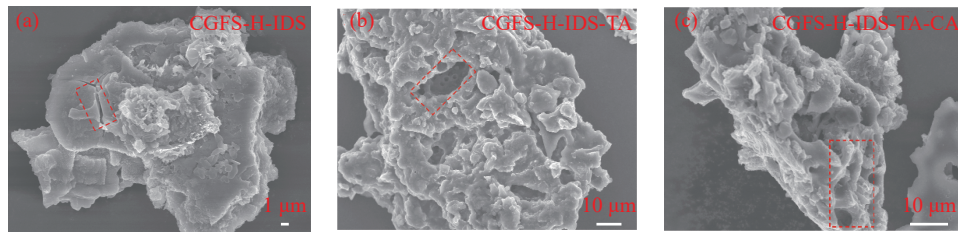
Sample	Content w/%							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	TiO_2	K_2O	SO_3	others
CGFS-H-IDS	47.82	17.13	3.50	23.96	1.24	1.09	2.73	2.52
CGFS-H-IDS-TA	56.64	6.94	3.83	26.01	1.11	0.93	2.00	2.54
CGFS-H-IDS-TA-CA	79.58	7.08	3.82	4.99	0.86	0.84	0.79	2.04

The morphological characteristics of the residues obtained from the stepwise extraction are presented in Figure 13. In comparison to CGFS-H, the acid leaching process effectively removed the oil film from the surface of the residual carbon, thereby exposing its porous structure. As the number of leaching cycles increased, the pore structure gradually expanded. This phenomenon is primarily attributed to the substantial dissolution of Fe^{3+} , Al^{3+} and Ca^{2+} [46]. Moreover, partial cracks formed on the surface of the carbon particles (Figure 13(a)), resulting from the effects of ultrasonic cavitation and shock^[13].

To delve the impact of the stepwise extraction process on pore structure, N_2 adsorption-desorption tests were conducted on CGFS, CGFS-H, and the residues from the stepwise extraction. The findings are presented in Figure 14 and Table 4. As depicted in Figure 14, the adsorption isotherms of CGFS, CGFS-H, and the stepwise extraction residues exhibit an “S”-shaped distribution, with H3-type hysteresis loops emerging at a p/p_0 range of 0.4–1.0. It is indicated that the materials remain classified as the mesoporous adsorption materials, confirming that the type of pore structure is not changed by the acid leaching

process. During the stepwise extraction process, the pore structure gradually expands. Concurrently, the quantities of micropores and mesopores increase, while the distribution characteristics of micropores and mesopores remain unchanged. The pore size of CGFS-H is predominantly concentrated within the range of 10 to 20 nm, which can be attributed to its pore structure arising from the packing voids among aggregates rather than from the pores within the particles themselves.

As presented in Table 4, the specific surface area of CGFS-H is notably lower than that of CGFS. This difference primarily results from the encapsulation of the material by agglomerated oil and the filling of its pores. Regarding the stepwise extraction residues, exhibit a gradual increase in both the specific surface area and pore volume. This trend indicates that the inorganic components are effectively removed by acid leaching treatment, thereby exposing the carbon matrix. Nevertheless, the specific surface area of the residues remains lower than that of CGFS, primarily due to the residual and obstructive effects of organic acid macromolecules on the pores.



(a): CGFS-H-IDS; (b): CGFS-H-IDS-TA; (c): CGFS-H-IDS-TA-CA.

Fig. 13 SEM images of the residues after stepwise extraction

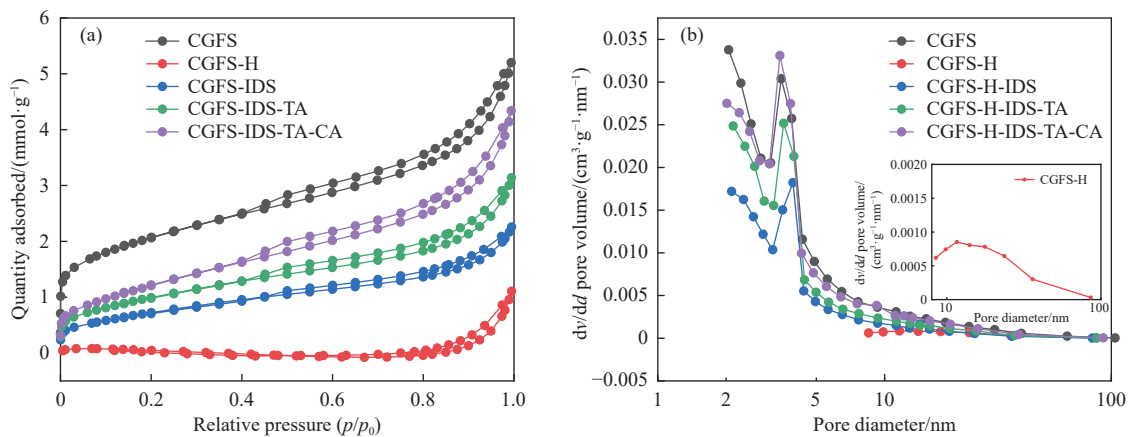


Fig. 14 (a) N_2 adsorption-desorption curves and (b) pore size distributions of CGFS, CGFS-H and stepwise extraction residues

Table 4 Pore structure parameters of CGFS, CGFS-H and stepwise extraction residues

Sample	BET surface area $A/(\text{m}^2 \cdot \text{g}^{-1})$	Pore volume $v/(\text{cm}^3 \cdot \text{g}^{-1})$	Average pore size d/nm
CGFS	158.23	0.18	4.59
CGFS-H	1.69	0.038	90.78
CGFS-H-IDS	60.59	0.078	5.17
CGFS-H-IDS-TA	81.74	0.11	5.32
CGFS-H-IDS-TA-CA	101.94	0.15	5.91

During the leaching process, organic acids not only react with metal ions but may also be retained in the pores of the residual carbon *via* physical adsorption or capillary action. Even after ultrasonic alkali washing, a small quantity of organic acid molecules may persist forming crystals or films that block the pore channels, resulting in a reduction of the specific surface area. Clearly, the hierarchical pore structure of the residual carbon is retained in the stepwise leaching residue, making it a viable precursor for producing porous carbon as a high-value material.

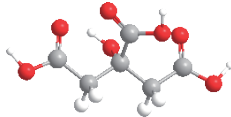
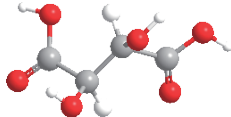
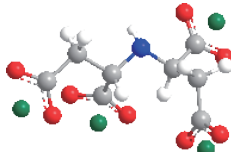
2.4.2 Mechanism of stepwise leaching

The structures of various organic acid leaching agents are presented in Table 5. Based on the above experimental results and considering the structural characteristics of organic acids and complexation equilibrium constants, the stepwise extraction mechanism of metal elements in CGFS-H, as shown in Figure 15, is proposed. The molecular structure of IDS-4Na contains multiple potential coordination groups, including carboxyl, imino and secondary amine groups. Under acidic conditions,

specifically around pH value 2, most carboxyl groups become protonated, resulting in the loss of their coordination ability. In contrast, secondary amines remain in a free state as electron donors and preferentially form coordination bonds with Fe^{3+} ions, which possess a high charge density.

Based on the hard-soft acid-base theory, Fe^{3+} is classified as a hard acid, favoring interactions with hard bases, such as the lone electron pairs on N and O atoms. Conversely, competitive ions such as Ca^{2+} and Al^{3+} have lower charge densities and exhibit relatively weaker affinities for nitrogen. Consequently, Fe^{3+} demonstrates a stronger propensity to form stable complexes with IDS-4Na^[47]. Meanwhile, a stable octahedral FeN_2O_4 chelate can be formed by the α -iminodicarboxylic acid structure of IDS-4Na in conjunction with Fe^{3+} . The chelating ring strain is optimized to accommodate Fe^{3+} . In contrast, the ionic radius of Ca^{2+} is too large to fit within this structure. Thus, in this system, the selective leaching of Fe^{3+} is enabled by IDS-4Na through covalent bonding, primarily contributed by secondary amino groups and the spatial adaptation mechanism.

Table 5 The chemical structure of the selected organic acids

Organic acid	Structure	Complexation constant/logK			Ref.
		Ca	Fe	Al	
Citric acid ($\text{C}_6\text{H}_8\text{O}_7$)		3.5	11.8	7.1	[48–49]
DL-tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$)		2.0	7.5	7.0	[49–50]
Tetrasodium iminodisuccinate ($\text{C}_8\text{H}_7\text{NNa}_4\text{O}_8$)		6.7	16.1	7.1	[51–52]

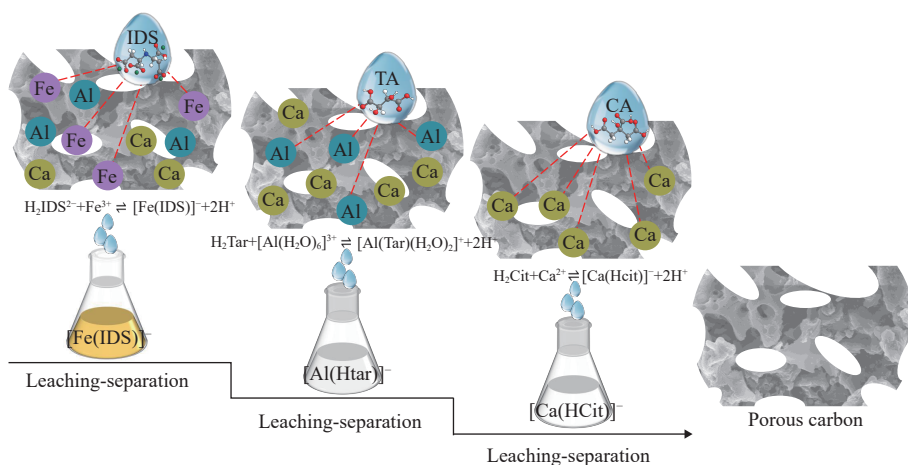


Fig. 15 The stepwise extraction mechanism of Fe^{3+} , Al^{3+} and Ca^{2+} in CGFS-H

The complexation leaching of metal ions from the carbon-rich components in coal gasification fine slag by citric acid and tartaric acid is fundamentally influenced by the interplay of complexation selectivity and mineralogical constraints^[53]. Organic acids facilitate the leaching of metal elements by providing protons and forming chelates, as depicted in Equations (3)–(6)^[54–55]. Notably, metal ions with higher valence exhibit a stronger capacity for complexation with tartaric acid. The distinctive α -hydroxy carboxylic acid structure of tartaric acid aligns well with the high coordination number and charge density of Fe^{3+} and Al^{3+} . Simultaneously, tartaric acid can differentiate between Fe^{3+} and Al^{3+} via steric hindrance, forming stable complexes with Al^{3+} , thereby enabling selective leaching. Structurally, citric acid serves as an asymmetric ligand with seven potential O-donors. Geometrically, the radius of Ca^{2+} is compatible with the carboxyl oxygen atoms of citric acid. During the chelation process, metal ions are coordinated by oxygen atoms in various configurations^[56], resulting in the formation of distinct types of metal complexes.

3 Conclusion

This study investigates the selective leaching characteristics of Ca^{2+} , Fe^{3+} and Al^{3+} from the carbon-rich components (CGFS-H) of coal gasification fine slag using various organic acids. Employing a stepwise extraction method with IDS-4Na, tartaric acid, and citric acid facilitates the efficient leaching, separation, and enrichment of Fe^{3+} , Al^{3+} and Ca^{2+} . The primary conclusions are as follows.

(1) Organic acids with varying structures exhibit distinct complexation leaching selectivities for Fe^{3+} , Al^{3+} and Ca^{2+} in CGFS-H. An investigation into factors such as organic acid concentration, temperature, and leaching duration reveals that IDS-4Na exhibits the highest leaching yield and selectivity for Fe^{3+} . The single leaching yield for Fe^{3+} attains 41.2%, while simultaneously inhibiting the leaching of Ca^{2+} and Al^{3+} to less than 4%. The selectivity ratio of Fe^{3+} to Al^{3+} and Ca^{2+} is 10.73. Tartaric acid effectively leaches both Fe^{3+} and Al^{3+} , achieving single leaching yield of 38.7% and 33.5%, respectively, while the leaching yield for Ca^{2+} remains below 5%. The selectivity of Fe^{3+} and Al^{3+} relative to Ca^{2+} is 14.73. In contrast, citric acid preferentially leaches Ca^{2+} , with a single leaching yield of 71.5%. However, the single leaching yield for Fe^{3+} and Al^{3+} also reach 35.2% and 39.1%, respectively. The selectivity ratio of Ca^{2+} to Fe^{3+} and Al^{3+} is merely 0.96.

(2) A green stepwise separation method has been developed to efficiently leach and separate Fe^{3+} , Al^{3+} and Ca^{2+} from CGFS-H using IDS-4Na, tartaric acid, and citric acid in a sequential manner based on the selective affinities of organic acids for these metal ions. Under optimal conditions, the cumulative leaching yield achieved for Fe^{3+} , Al^{3+} and Ca^{2+} are 79.8%, 65.08% and 78.6%, respectively.

(3) The efficient stepwise leaching and separation of iron,

aluminum, and calcium from CGFS-H using IDS-4Na, tartaric acid, and citric acid occurs through a complexation mechanism. The effect of organic acids on this process primarily results from the synergistic effect of selective coordination complexation between the structurally diverse organic acids and metal ions. Additionally, the stepwise separation facilitates the elimination of competitive complexation among metal ions.

Declaration of Competing Interest

The authors declare no conflict of interest.

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煤气化细渣高炭组分中铁铝钙元素有机酸高效浸出与分离研究

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摘 要: 煤气化细渣 (CGFS) 中有价金属元素的高效提取与分离是实现其全组分高值化利用的关键。本工作以煤气化细渣高炭组分 (CGFS-H) 为研究对象, 重点探究了不同有机酸 (柠檬酸、酒石酸、亚氨基二琥珀酸四钠) 浸出剂对 CGFS-H 中铁、铝、钙元素的选择性浸出特性, 并进一步对 CGFS-H 中铁、铝、钙元素的逐级浸出进行了探究, 结合 XRD、XRF、SEM 等分析, 明晰了不同有机酸对铁、铝、钙元素的逐级浸出机理。结果表明, 亚氨基二琥珀酸四钠对 CGFS-H 中 Fe^{3+} 的浸出选择性最高, 酒石酸则对 Fe^{3+} 、 Al^{3+} 有相近的浸出选择性, 而柠檬酸对 Ca^{2+} 的浸出选择性较高。采用亚氨基二琥珀酸四钠、酒石酸、柠檬酸依次逐级浸出 Fe^{3+} 、 Al^{3+} 、 Ca^{2+} , 其浸出率分别达到了 79.8%、65.08%、78.6%。这表明, 采用不同有机酸逐级浸出方法, 可实现 CGFS-H 中 Fe^{3+} 、 Al^{3+} 和 Ca^{2+} 的高效浸出及逐级分离。研究结果对于突破以 CGFS-H 为原料的 Ca/Fe/Al 类水滑石制备技术, 实现煤气化细渣材料化高值利用具有重要意义。

关键词: 煤气化细渣; 高炭组分; 有机酸; 浸出; 逐级提取

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