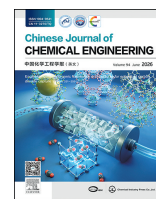




Contents lists available at ScienceDirect

Chinese Journal of Chemical Engineering

journal homepage: www.elsevier.com/locate/CJChE

Full Length Article

Kinetic characteristics and redox performance of iron-based oxygen carriers blending with iron-rich sludge ash

Xiaoying Yuan¹, Xiaoran Wang², Zhihao Zheng^{1,*}, Cuiping Wang^{1,*}¹ Clean Energy Laboratory, Shandong University of Science and Technology, Qingdao 266590, China² Qingdao Yunlu Advanced Material Technology Co. Ltd., Qingdao 266200, China

ARTICLE INFO

Article history:

Received 28 July 2025

Received in revised form

30 December 2025

Accepted 3 January 2026

Available online 6 February 2026

Keywords:

Kinetics

Iron-based oxygen carrier

Iron-rich sludge ash

Reduction

Blend

ABSTRACT

To investigate the redox performance and kinetic characteristics of iron-based oxygen carriers when mixed with iron-rich sludge ash during the sludge chemical looping gasification or combustion, the impregnation method was used to prepare Fe/Al composite oxygen carriers (Fe/Al-OC), and the iron-rich sludge ash (IRSA) was produced by high-moisture sludge burning in Muffle stove. The two types powder were then mixed in a 1:1 mass ratio to obtain another OC of Fe1Ash1. Using a thermogravimetric analyzer, the deep redox processes of the three oxygen carriers were carried out, and their reduction under variable temperature or constant temperature and oxidation processes were analyzed using 13 kinetic models to investigate their kinetic parameters. The results showed that the blending of Fe/Al-OC and IRSA exhibited a synergistic effect, in which the actual oxygen release and oxygen gain amount of Fe1Ash1 both exceed the theoretical values, indicating enhanced oxygen transport capacity. During the reduction process, under non-isothermal conditions, the oxygen release in Fe/Al-OC was controlled by two-dimensional diffusion, while the oxygen release in IRSA and Fe1Ash1 followed a first-order reaction model, with Fe1Ash1 having a slightly lower activation energy ($34.81 \text{ kJ} \cdot \text{mol}^{-1}$) than the individual OCs. During isothermal reduction, the reaction of Fe/Al-OC transitions to contraction model control as temperature increases, IRSA maintains first-order reaction characteristics, while Fe1Ash1 reaction is more compatible with the F3/2 model, with synergistic effects weakening. During the oxidation process, Fe/Al-OC follows a first-order reaction model, while IRSA and Fe1Ash1 both follow two-dimensional diffusion models, but the activation energy of Fe1Ash1 ($34.60 \text{ kJ} \cdot \text{mol}^{-1}$) is significantly lower than that of the other two, resulting in superior oxidation performance. Thus the Fe/Al OC might achieve complementary performance and kinetic characteristics in redox with more sludge ash blending. The highest ash blending proportion that can promote oxygen carrying capacity would be studied in next works.

© 2026 The Chemical Industry and Engineering Society of China, and Chemical Industry Press Co., Ltd. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

1. Introduction

As China advances toward the dual carbon goals, the development of efficient and clean energy conversion technologies has become an urgent priority [1]. Chemical looping combustion (CLC), a novel low-carbon combustion technology, has emerged as a research hotspot since its inception due to its ability to achieve efficient energy conversion while enabling low-cost CO_2 capture

[2]. Unlike traditional combustion methods, CLC achieves indirect contact between fuel and air through the circulation of oxygen carriers (OC), thereby avoiding the mixing of N_2 and CO_2 at the firing process, which significantly reduces the energy consumption of CO_2 capture and effectively suppresses the formation of thermal NO_x [3], making it one of the most promising carbon capture technologies [4].

Oxygen carriers are the key to CLC technology, and their performance directly determines the feasibility of the technology. An ideal oxygen carrier should have high oxygen transfer capacity, high cycle stability, high mechanical strength, low cost, and environmental friendliness [5]. Among numerous candidate OCs, iron-based oxygen carriers are recognized as a distinguished one due to their abundant resource reserves, excellent environmental

This article is part of a special issue entitled: Green Energy and CO_2 Efficient Resource Utilization published in Chinese Journal of Chemical Engineering.

* Corresponding authors.

E-mail addresses: zhengzhihao@sdust.edu.cn (Z. Zheng), wangcuiping21@sdust.edu.cn (C. Wang).

compatibility, moderate redox capacity, and low cost, making them one of the most promising options for industrialization [6]. However, single-iron-based OCs have obvious shortcomings, pure Fe_2O_3 tends to sinter and agglomerate at high temperatures, leading to a significant decline in oxygen transport capacity. Additionally, its reduction reaction kinetics are relatively slow, limiting the operational efficiency of CLC systems. To address this issue, researchers have introduced inert carriers (such as Al_2O_3 [7], SiO_2 [8], ZrO_2 [9], etc.) to construct composite OCs, leveraging the skeletal support function of the carriers to inhibit the agglomeration of active components. For example, Wang *et al.* [10] studied the effects of three inert carriers (ZrO_2 , MgAl_2O_4 , and Al_2O_3) on the performance of iron-based OCs. The three OCs exhibited stable reactivity for ten cycles, and the Fe/Al OCs performed to be the best one. Ma *et al.* [11] also demonstrated that the addition of Al_2O_3 can enhance the redox activity and oxygen-carrying capacity of iron-based OCs. Through studying the initial cycling activation behavior of Fe/Al OCs, they concluded that the activation process is caused by the migration of Fe ions to the surface. Additionally, there is a large amount of industrial waste containing Fe_2O_3 in industry, such as sulfuric acid slag produced during sulfuric acid production, red mud generated by the Bayer process in aluminum production [12], and some iron-rich municipal sludge [13,14]. These can all serve as inexpensive iron-based OCs. Using these industrial wastes as iron-based OCs or modified OCs enables low-cost, large-scale production and achieves the resource utilization of waste [15]. Doping and modifying iron-based OCs to address their existing issues is an important approach to enhancing their reactivity and cycling stability. Feng *et al.* [16] conducted DFT calculations to investigate the effects of 27 dopants on the H_2 reduction process of iron-based OCs, finding that these dopants regulate the formation energy of surface oxygen vacancies by influencing the charge distribution and surface structure of surface oxygen, thereby affecting the performance of OCs. Wang *et al.* [17] investigated the interaction between sludge ash and $\text{CaMn}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ perovskite oxygen carriers, finding that the two exhibit positive synergy. The addition of sludge ash enhances the oxygen-carrying capacity and reactivity of the perovskite oxygen carrier, playing a crucial role in oxygen-carrying performance.

During the chemical looping gasification or combustion of iron-rich sludge, the accumulated ash in reactor is growing and mixed with OC particles. Like the effect of biomass ash on OC performance [18], the iron-rich sludge ash also should be focused on the synergistic effects or antagonistic effects of OCs to control the circulation amount of Fe/Al OC. Systematic and in-depth exploration in this area is still lacking. Kinetic analysis is often utilizing data from thermogravimetric analysis (TGA) and model fitting to obtain kinetic parameters. Moed *et al.* [19] determined the kinetic model of the $\text{Fe}_2\text{O}_3\text{-CuO/Al}_2\text{O}_3$ OCs reduction in TGA under H_2/CO conditions, accurately describing the characteristics of the reduction process. The mechanisms for the reduction of prepared OCs by hydrogen and carbon monoxide are proposed based on kinetic analysis. Liang *et al.* [20] employed reaction kinetics methods to analyze the reduction and oxidation processes of perovskite oxygen carriers. The final reaction model accurately predicted the conversion curves for all reaction types.

In previous studies of our research group, the synergistic effects of iron-rich sludge ash and Fe/Al oxygen carriers in terms of oxygen-carrying capacity and cycling stability were demonstrated [21]. To describe the underlying mechanisms, an in-depth analysis was conducted using reaction kinetics, with 13 kinetic models as references. The kinetic mechanisms of Fe/Al oxygen carriers when iron-rich sludge ash blending were systematically investigated for

non-isothermal reduction, isothermal reduction, and oxidation processes, thereby elucidating the synergistic effects and mechanisms of the blended system.

2. Experimental

2.1. Experimental materials

2.1.1. Preparation of Fe/Al OC

The iron-based oxygen carrier was prepared using the impregnation method (as shown in Fig. 1). Al_2O_3 spherical particles with a particle size of 0.5–0.85 mm were used as the inert carrier, and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was the precursor of the active component. First, depending on the ambient temperature, an appropriate amount of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in deionized water (100 ml) and thoroughly stirred in a magnetic stirrer until completely dissolved to form a saturated solution. Then, 80 g of Al_2O_3 spherical particles are immersed in the saturated solution for 6 h, during which vacuum impregnation treatment is performed. The particles are then placed in an isothermal drying oven at 105 °C for complete drying, resulting in spherical particles loaded with the active component precursor. Finally, they are calcined at 850 °C in a muffle furnace for 4 h, yielding the Fe/Al composite oxygen carrier (denoted as Fe/Al-OC). The loading amount of Fe_2O_3 is influenced by ambient temperature and impregnation time, with the Fe_2O_3 content in Fe/Al-OC being approximately 20%.

2.1.2. Preparation of iron-rich sludge ash

The high-moisture sludge used in this paper was obtained from a municipal sewage treatment plant in Qingdao. Industrial analysis was performed in accordance with GB/T 212–2008 Industrial Analysis Methods for Coal, and elemental analysis was conducted using an elemental analyzer. The results are shown in Table 1.

The sludge is mechanically squeezed into strips firstly, and then a disc granulator is used to prepare sludge particles with a diameter of 1–2 mm. These particles are then incinerated in a muffle

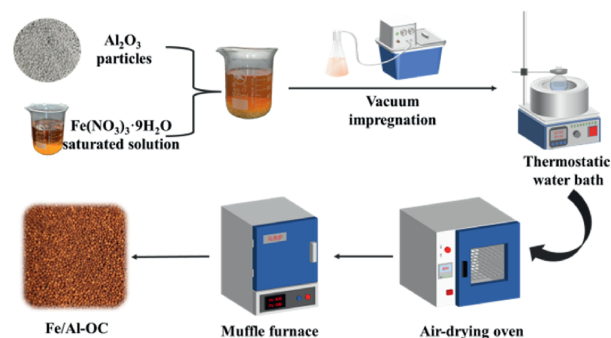


Fig. 1. Preparation process of Fe/Al-OC.

Table 1
Industrial and elemental analysis of sludge.

Industrial analysis/%(mass)(ar)				Elemental analysis/%(mass)(ar)				
M	V	FC	A	C	H	N	S	O [⊙]
79.82	10.03	2.33	8.82	4.61	0.71	0.69	0.46	4.89

Note: M: moisture content; V: Volatile content; FC: fixed carbon content; A: ash content; ar: as-received basis.

[⊙] Calculated by difference.

Table 2
Elemental analysis of IRSA.

Element	Content/ %(mass)	Element	Content/ %(mass)	Element	Content/ %(mass)
SiO ₂	29.516	Fe ₂ O ₃	20.096	P ₂ O ₅	16.726
CaO	12.664	SO ₃	7.246	Al ₂ O ₃	6.379
MgO	4.000	K ₂ O	1.698	TiO ₂	1.001
MnO	0.262	ZnO	0.249	SrO	0.101

furnace at 850 °C to obtain iron-rich sludge ash (IRSA). A laboratory standard sieve is used to select IRSA particles with a diameter of 0.6–0.9 mm. Elemental content was tested using an X-ray fluorescence spectrometer (XRF, Shimadzu EDX-7200, Japan), with results shown in Table 2.

2.2. Experimental methods

2.2.1. Thermogravimetric analysis

To investigate the influence of iron-rich sludge ash on iron-based OCs, IRSA and Fe/Al-OC were mixed in a mass ratio of 1:1 and designated as Fe1Ash1. Performance testing was conducted in the thermogravimetric analyzer shown in Fig. 2 under the same conditions as for IRSA and Fe/Al-OC reacting separately. The experimental data obtained from the individual samples were weighted (averaged) to obtain theoretical weighted values, which were then compared with the data obtained from the mixed samples. If differences were observed, this indicated that an interaction existed between the sludge ash and the oxygen carrier [22].

First, deep oxidation-reduction was employed to determine the total oxygen transferring capacity of the three OCs. During the oxygen release test, OCs were heated from room temperature to 1173 K at a rate of 5 K·min⁻¹ under a 36%(vol) H₂/N₂ atmosphere, and maintained at this temperature for 30 min to ensure OCs fully reduced state. The reduced OCs were then subjected to the same heating program in air environment, maintained for 10 min to ensure complete oxidation. During the cycle process, 50 ml·min⁻¹ of N₂ was introduced as a protective gas, and the additional reduction/oxidation gas flow rate was 100 ml·min⁻¹.

When performing the isothermal kinetic parameters experiments, OCs are placed in a 250 μl Al₂O₃ crucible. To eliminate the influence of layer diffusion, the sample height is kept below two-thirds of the crucible's height. Under these conditions, the temperature is increased at a rate of 20 K·min⁻¹ from room

temperature to 800, 825, 850, 875, and 900 °C. Then OCs are then held at 900 °C with a H₂ flow rate of 100 ml·min⁻¹ for 50 min.

2.2.2. Method for calculating dynamic parameters

To determine the kinetic mechanism functions of different OCs in redox processes, 13 common kinetic mechanism functions were selected as candidate models to fit the conversion rates of OCs. Based on the degree of fit with different mechanism functions, the optimal mechanism function was selected, and finally, the activation energy and pre-exponential factor were calculated. The selection of these 13 kinetic models is based on their representation of the main solid-state reaction mechanism categories (reaction order, nucleation-growth, geometrical contraction, and diffusion-controlled models) commonly applied in thermogravimetric analysis. The optimal kinetic model for each redox process was determined by comparing the linear regression goodness-of-fit (R^2) between experimental conversion data and theoretical model fits, and selecting the model with the highest R^2 value.

Define the conversion rate of oxygen carriers as:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \quad (1)$$

where m_0 is the initial mass of the oxygen carrier before the reaction; m_t is the instantaneous mass of the oxygen carrier at time t ; m_∞ is the final mass of the oxygen carrier after complete oxidation/reduction.

The general form of the kinetic equation is:

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \quad (2)$$

k is the rate constant of a chemical reaction that follows the Arrhenius equation, as shown in Eq. (3):

$$k = A \cdot e^{-\frac{E_a}{RT}} \quad (3)$$

$$\frac{d\alpha}{dt} = A \cdot e^{-\frac{E_a}{RT}} \cdot f(\alpha) \quad (4)$$

where E_a is the activation energy, kJ·mol⁻¹; A is the pre-exponential factor, s⁻¹; R is the ideal gas constant, 0.00831 kJ·mol⁻¹·K⁻¹; T is the absolute temperature, K. Using the Coats-Redfern integration rule, this can be converted to:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A \cdot e^{-\frac{E_a}{RT}} \cdot t = k \cdot t \quad (5)$$

Taking the logarithm of both sides of Eqs. (4) and (5), the activation energy E_a and the pre-exponential factor A can be obtained from the slope and intercept of the straight-line relationship $\ln k - (1/T)$.

$$\ln \frac{d\alpha}{dt} = \ln A - \frac{E_a}{RT} + \ln(f(\alpha)) \quad (6)$$

$$\ln k = \ln \left(A \cdot e^{-\frac{E_a}{RT}} \right) = \ln A - \frac{E_a}{RT} \quad (7)$$

3. Results and Discussion

Different kinetic models represent distinct physical reaction pathways: reaction order describing intrinsic chemical rate control,

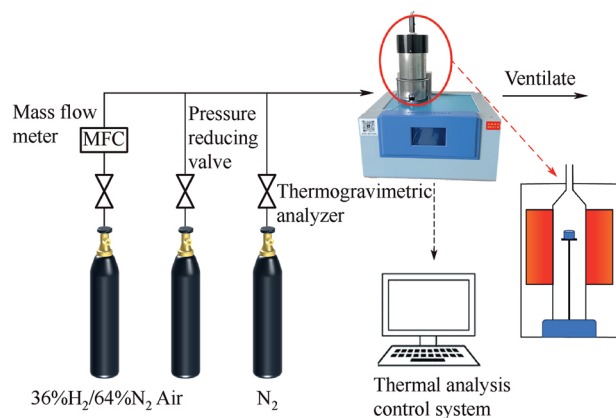


Fig. 2. Schematic diagram of thermal gravimetric analysis system.

nucleation-growth reflecting site formation and expansion, geometrical contraction capturing interface advancement limitations, and diffusion-controlled models indicating mass transport limitation through product layers. Based on the material microstructure differences between Fe/Al-OC and IRSA, and under different experimental temperature conditions, the dominant rate-controlling mechanism may shift, which is reflected in the model selection.

3.1. In-depth oxidation-reduction analysis

The TG results for the deep oxidation-reduction of the three OCs are shown in Fig. 3. Fe/Al-OC begins to lose mass from the start, primarily due to the desorption of surface and internal adsorbed water (mainly occurring between 50 °C and 200 °C) and the decomposition of undecomposed nitrate $\text{Fe}(\text{NO}_3)_3$. Subsequently, it can be clearly observed that around 380 °C, Fe/Al-OC begins to lose mass due to reduction, with a noticeable increase in reaction rate. The reduction process of Fe/Al-OC exhibits two distinct reduction peaks, located in the temperature ranges of 380–450 °C and 520–600 °C, respectively. The low-temperature reduction peak corresponds to the conversion of Fe_2O_3 to Fe_3O_4 , while the high-temperature reduction peak is attributed to the further reduction of Fe_3O_4 to FeO . The overall reduction process is relatively slow compared to IRSA, with a lower oxygen release of approximately 6.5%. In contrast, IRSA exhibits a higher oxygen

release capacity of approximately 14.3%, with oxygen release beginning around 400 °C. Combined with its phase analysis [21], the high oxygen release capacity of IRSA stems from the synergistic effects of multiple components. The reduction of Fe_2O_3 contributes the majority of the oxygen release, while the active components in IRSA, such as CaO , MgO , and sulfides, also undergo reduction reactions. The onset temperature for oxygen release in IRSA is delayed by approximately 20 °C compared to Fe/Al-OC, which may be attributed to the rigid framework formed by SiO_2 potentially restricting the migration of some Fe. The theoretical oxygen release value of Fe1Ash1 was calculated based on the blending ratio, denoted as Fe1Ash1(Th), for comparison with the actual oxygen release value. Fe1Ash1 exhibits a peak similar to Fe/Al-OC at 380–450 °C, with an overall curve resembling that of IRSA, yet showing a higher oxygen release of approximately 10.5%. The actual oxygen release is slightly higher than the theoretical value. This indicates that the mixed Fe/Al-OC and IRSA exhibit a synergistic effect. The alkaline components in IRSA may promote the reduction of Fe ions in Fe/Al-OC, while the stable structure of Fe/Al-OC significantly slows down the agglomeration of species in IRSA, allowing more active oxygen to participate in the reduction reaction.

The results of deep oxidation are shown in Fig. 3(b). All three OCs can be regenerated by oxidation at relatively low temperatures. Fe/Al-OC exhibits an oxygen release of approximately 4.6%, demonstrating excellent oxidation-regeneration capability. The

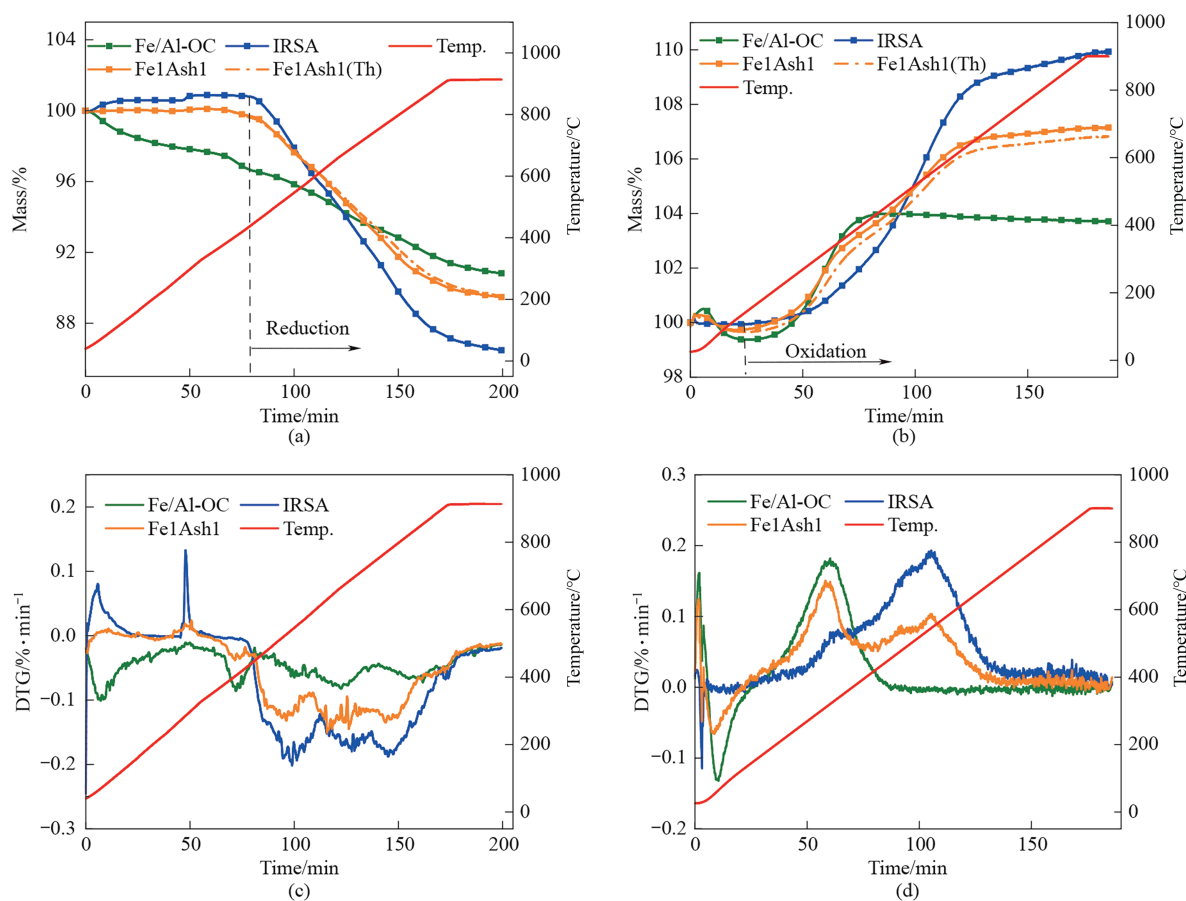


Fig. 3. Mass changes and DTG of three different OCs undergoing deep oxidation-reduction (a) deep reduction with oxygen release, (b) deep oxidation with oxygen gain, (c) DTG of deep reduction, (d) DTG of deep oxidation.

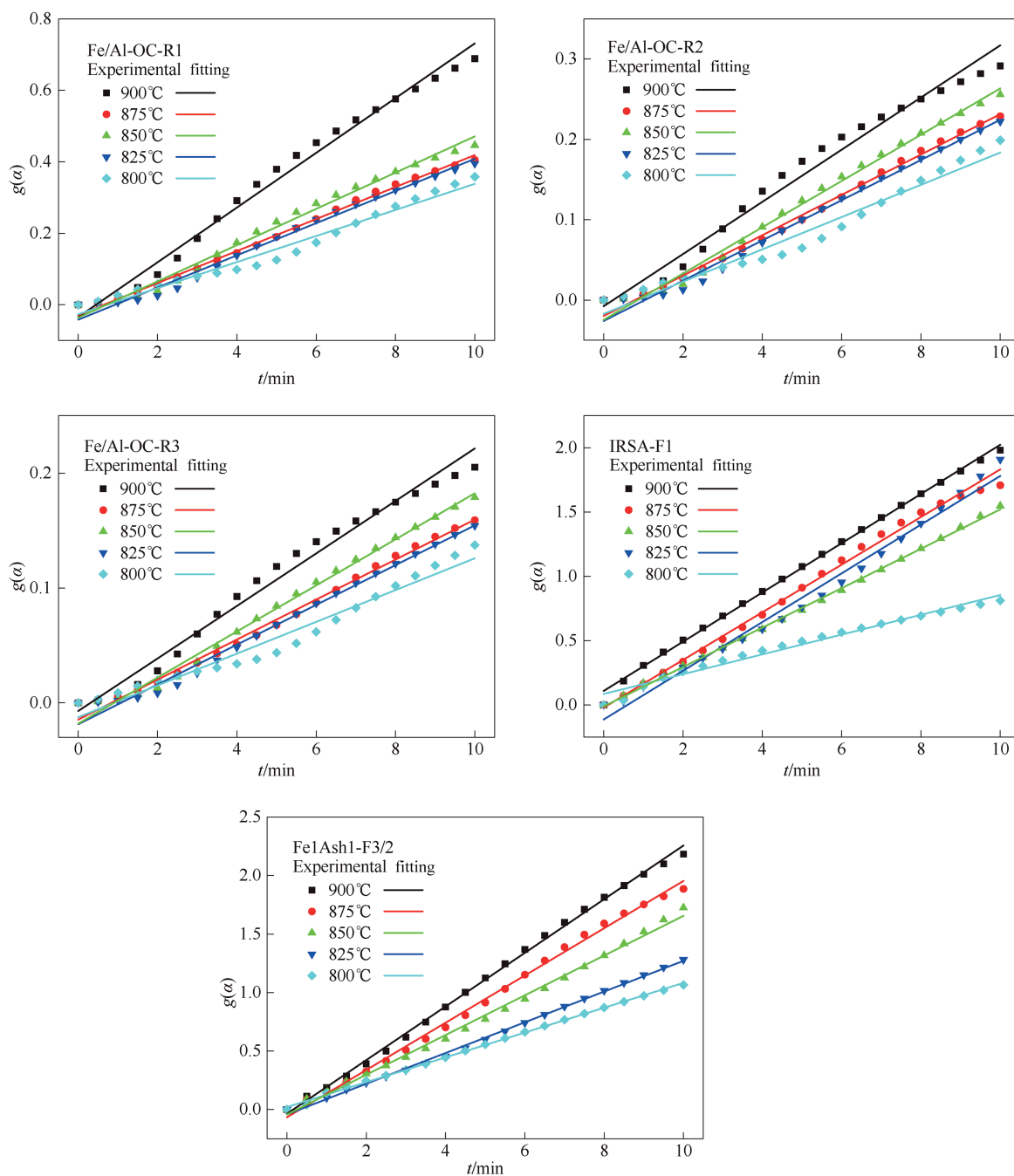


Fig. 4. Fitting curves of $g(\alpha)$ - t for three OCs at different temperatures.

rate of change during the oxidation process is significantly steeper than that during the reduction process, indicating that the activation energy required for the oxidation reaction is lower than that for the reduction reaction. In contrast, the oxidation process of IRSA is relatively gentle, especially after 650 °C. This may be due to the complex composition of IRSA, which forms various low-valent species during reduction, which are gradually oxidized during oxidation, and there are differences in the oxidation rates of different species. The oxidation process of Fe1Ash1 is clearly divided into three stages: the first stage, from the onset of oxidation to 350 °C, is dominated by Fe/Al-OC; the second stage, the main oxidation phase, occurs between 350 °C and 650 °C and is dominated by IRSA; the third stage, after 650 °C, is essentially

complete oxidation. Furthermore, the actual oxygen yield of Fe1Ash1 is significantly higher than the theoretical value, approximately 7.2%. This further demonstrates the synergistic effect of their blending, indicating superior oxygen transport performance and cycle stability in redox cycles. This synergistic effect may be the key to enhancing the oxygen transport capability of Fe1Ash1, providing favorable conditions for its application in chemical looping reactions.

3.2. Kinetic analysis of OCs reduction process

The OCs cycle can be divided into initial and subsequent cycles. Generally, the reduction stage in the initial cycle is equivalent to a

non-isothermal reduction process, while the subsequent cycles are conducted at an isothermal process, and temperature fluctuations are not significant. The reduction process of OCs at different temperatures present varies effects [23], and the blending of IRSA and Fe/Al-OC may also have another impacts. Therefore, the kinetic analysis of the reduction process is studied from two aspects: non-isothermal reduction and isothermal reduction at high temperatures.

3.2.1. Non-isothermal reduction

To ensure that all three different OCs are in the reduction phase, kinetic parameters for the reduction process within the temperature range of 450–900 °C were calculated using the 13 kinetic models [24] revealed in Table 3, and the R^2 values for the three OCs during the non-isothermal reduction process were calculated. The results indicate that the non-isothermal reduction process of Fe/Al-OC is controlled by two-dimensional diffusion (D2), meaning that the reaction rate depends on the migration rate of oxygen ions from the Fe_2O_3 crystal lattice to the particle surface, rather than surface chemical reactions with H_2 . In previous studies [21], SEM analysis revealed that the Fe/Al-OC structure is compact, with uniform distribution of Al and Fe elements and continuous composition. Fe_2O_3 , as the active component, is highly dispersed in the inert carrier Al_2O_3 , thereby shortening the diffusion path of lattice oxygen. The activation energy E_a was calculated using Eq. (6) to be $49.36 \text{ kJ}\cdot\text{mol}^{-1}$, slightly lower than the reduction activation energy of pure Fe_2O_3 . This result is attributed to the mesoporous structure of Al_2O_3 , forming diffusion channels, shortening the diffusion path, and reducing the energy barrier for oxygen migration. As the reduction depth increases, the reaction rate gradually decreases, and the product layer formed by Fe_2O_3 gradually thickens, thereby blocking diffusion within the gas phase.

The non-isothermal reduction processes of both IRSA and Fe1Ash1 OCs conform to a first-order reaction model (F1) controlled by interfacial chemical reactions, indicating that the non-isothermal reduction process is dominated by surface chemical reactions rather than diffusion-controlled lattice oxygen. The non-isothermal reduction processes of IRSA and Fe/Al-OC mixed reduction are more similar to those of IRSA, consistent with the results in Fig. 3, indicating that the non-isothermal reduction process of the two mixed OCs is primarily dominated by IRSA. The

Table 4

Parameters and results of kinetic fitting equations for the non-isothermal reduction processes of three OCs.

Parameters	Model	Fitting equations	$E_a/\text{kJ}\cdot\text{mol}^{-1}$	A/s^{-1}
OCs				
Fe/Al-OC	D2	$y = -5939.54x + 0.018$	49.36	0.049
IRSA	F1	$y = -4204.73x + 0.013$	34.94	0.0371
Fe1Ash1	F1	$y = -4188.87x + 0.013$	34.81	0.0367

Note: x is $1/T$ in Eq. (6); y is $\ln k$ in Eq. (6).

activation energies (Table 4) of IRSA and Fe1Ash1 are lower than those of Fe/Al-OC, suggesting that the reduction in the reaction energy barrier is attributed to the enhancement of surface-active sites.

In addition to Fe, IRSA contains various impurity elements, such as approximately 19% Ca and 8% P, among others. These impurities in IRSA play a catalytic role in its reduction process. At higher temperatures, P_2O_5 readily forms amorphous FePO_4 , which undergoes a reduction reaction at 650 °C with an activation energy of approximately $35 \text{ kJ}\cdot\text{mol}^{-1}$. Research has shown that the doping of Ca ions can induce the formation of oxygen vacancies, thereby accelerating the progress of surface redox reactions [25]. The kinetic behavior of Fe1Ash1 is consistent with that of IRSA, which is attributed to the fact that during the reaction, partially fragmented IRSA deposits on the surface of Fe/Al-OC, and the impurity phases of IRSA cover the surface, shielding part of the mesoporous structure of the Al_2O_3 carrier and eliminating diffusion restrictions.

3.2.2. Isothermal reduction

The isothermal reduction process was also fitted to 13 different reaction models. First, the K values and R^2 were calculated at different temperatures using Eq. (5). The models with the best fit at five temperatures were selected, and then the pre-exponential factor A of the activation energy E_a was calculated according to Eq. (7). The results indicate that Fe/Al-OC exhibits good fitting performance for the contraction models, seen in Fig. 4, with an average fitting degree above 0.98. Among these, model $R2 > R3 > R1$. IRSA shows the highest fitting performance for the F1 model, with an average fitting degree above 0.99 at all five temperatures. Fe1Ash1 exhibits the highest fitting performance for the F3/2 model, with an average value above 0.99.

Table 3

R^2 values for three different OCs during non-isothermal reduction at 450 °C–900 °C fitted to different reaction models.

Reaction mechanism	Model	$f(\alpha)$	$g(\alpha)$	Fe/Al-OC	IRSA	Fe1Ash1
Nucleation model	A3/2	$\left(\frac{3}{2}\right)(1-\alpha)[- \ln(1-\alpha)]^{1/3}$	$[- \ln(1-\alpha)]^{2/3}$	0.80	0.57	0.73
	A2	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$[- \ln(1-\alpha)]^{1/2}$	0.64	0.03	0.29
	A3	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$[- \ln(1-\alpha)]^{1/3}$	0.27	0.30	0.11
Diffusion model	D1	$\frac{1}{2\alpha}$	α^2	0.89	0.73	0.73
	D2	$\frac{1}{[- \ln(1-\alpha)]}$	$(1-\alpha)\ln(1-\alpha) + \alpha$	0.96	0.87	0.90
	D3	$\left(\frac{3}{2}\right)(1-\alpha)^{2/3}[1 - (1-\alpha)^{1/3}]$	$[1 - (1-\alpha)^{1/3}]^2$	0.88	0.87	0.87
Dynamic model	F1	$1-\alpha$	$-\ln(1-\alpha)$	0.92	0.92	0.93
	F3/2	$(1-\alpha)^{3/2}$	$2\left[(1-\alpha)^{-1/2} - 1\right]$		0.90	0.92
	F2	$(1-\alpha)^2$	$(1-\alpha)^{-1} - 1$	0.92	0.89	0.91
Shrink model	F3	$(1-\alpha)^3$	$\frac{1}{2}\left[(1-\alpha)^{-2} - 1\right]$	0.90	0.87	0.89
	R1	1	α	0.23	0.04	0.06
	R2	$2(1-\alpha)^{1/2}$	$[1 - (1-\alpha)^{1/2}]$	0.83	0.77	0.74
	R3	$3(1-\alpha)^{2/3}$	$[1 - (1-\alpha)^{1/3}]$	0.88	0.87	0.87

Table 5

Reaction rates and activation energies of the isothermal reduction process of three OCs at 800–900 °C.

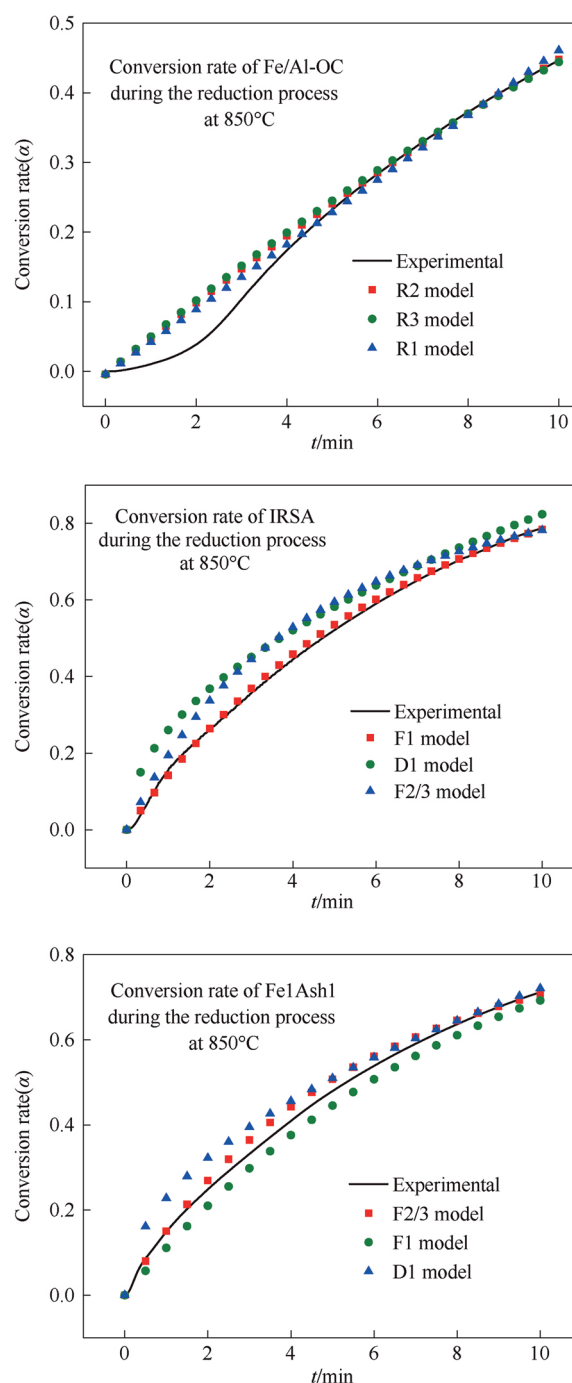
OCs		Fe/Al-OC			IRSA	Fe1Ash1
		R2	R3	R1	F1	F3/2
k/s^{-1}	900 °C	2.0329	1.4290	3.5078	73.5219	13.7532
	875 °C	1.8234	1.2754	3.1858	71.4263	12.1152
	850 °C	1.6275	1.1325	2.8811	69.3011	10.1868
	825 °C	1.4452	1.0002	2.5936	67.1468	7.8756
	800 °C	1.2762	0.8783	2.3234	64.9637	6.3648
R^2		0.9297	0.9363	0.9043	0.9612	0.9900
$E_a/kJ \cdot mol^{-1}$		48.71	50.93	43.10	12.95	82.71

The activation energy for the above models is shown in Table 5. The results indicate that the isothermal reduction process of Fe/Al-OC at 800–900 °C conforms to the contraction reaction model, which is synergistically controlled by interfacial reactions and product layer diffusion. This differs from the diffusion-controlled behavior observed in the non-isothermal reduction process. The reason lies in the accelerated reduction rate of Fe_2O_3 at higher temperatures, which leads to thickening of the product layer and increased gas diffusion resistance, shifting the reaction from bulk diffusion to interface-dominated reactions. Additionally, at high temperatures, the mesoporous structure of Fe/Al-OC undergoes sintering, reducing diffusion pathways and increasing mass transfer resistance in the product layer. Fe/Al-OC exhibits high fitting accuracy for all three contraction models, and the activation energies are similar, ranging from 43 to 50 $kJ \cdot mol^{-1}$. To determine the reaction order, model validation was performed using the three models and experimental data at 850 °C, as shown in Fig. 5. Although the agreement between the three models and experimental data is similar, the contraction model with a reaction order of 1 (R1) is more suitable.

The oxygen release of IRSA also conforms to the first-order reaction model (F1) controlled by interfacial chemical reactions during the isothermal reduction process at 800–900 °C, but the activation energy is reduced, indicating that the catalytic effect on the IRSA surface is enhanced under higher temperatures, and the active impurities in IRSA have a catalytic effect on it. However, the model for Fe1Ash1 changes at high temperatures, shifting to the higher-order F3/2 model (F3/2). This model maintains a goodness-of-fit above 0.99 at all temperatures, with an increase in activation energy. In deep reduction experiments, higher temperatures result in the theoretical and actual values of Fe1Ash1 being closer, with a weakened promotional effect and a slower reaction rate compared to previous conditions. The high degree of agreement further confirms the reliability of this transformation. At higher temperatures, more IRSA components may migrate deeply to the surface of Fe/Al-OC. On one hand, this blocks part of the mesoporous diffusion channels of the Al_2O_3 carrier; on the other hand, it competes with the active sites of Fe/Al-OC for adsorption, reducing the effective pathways for reactive oxygen species to participate in the reaction. Ultimately, this narrows the deviation between the theoretical oxygen release and the actual value, weakening the synergistic promotion effect.

3.3. Kinetic analysis of OCs oxidation process

Using the data from the deep oxidation process in Fig. 3(b), kinetic parameters were calculated, with the results shown in Fig. 6 and Table 6. The results indicate that the oxidation process of Fe/Al-OC is controlled by surface chemical reactions. The lower activation energy compared to the reduction reaction suggests that the oxidation reaction is easier to occur than the reduction

**Fig. 5.** Validation of the best-fit models for the three OCs.

reaction. The lower activation energy is consistent with the steep trend of the oxidation curve. This is attributed to the fact that the oxidation reaction is an exothermic process, with a lower O_2 adsorption energy barrier, the Al_2O_3 pore structure facilitating gas penetration, and the stable structure reducing the agglomeration of active components, thereby ensuring a high oxidation rate.

The oxygen gain of IRSA follows the two-dimensional diffusion model (D2), with an activation energy of 59.17 $kJ \cdot mol^{-1}$. The high activation energy and slow reaction rate are attributed to the stepwise oxidation of its complex components and the restriction of oxygen diffusion by the SiO_2 framework structure. Fe1Ash1 also

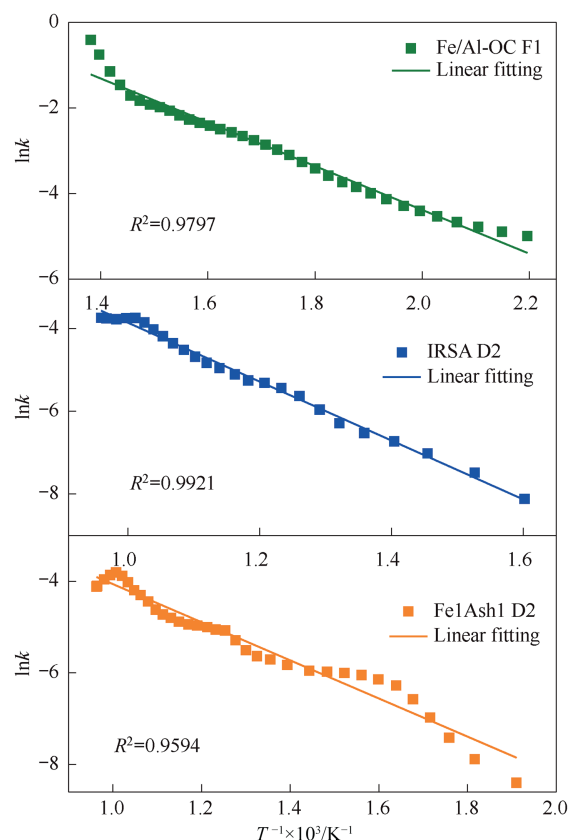


Fig. 6. Fitting curves of the best-fit models for the three OCs.

Table 6

Parameters and results of kinetic fitting equations for the oxidation processes of three OCs.

Parameters	Model	Fitting equations	$E_a/\text{kJ}\cdot\text{mol}^{-1}$	A/s^{-1}
OCs				
Fe/Al-OC	F1	$y = -5123.49x + 0.098$	42.58	5.862
IRSA	D2	$y = -7119.94x + 0.054$	59.17	0.4349
Fe1Ash1	D2	$y = -4163.26x + 0.002$	34.60	0.01845

Note: x is $1/T$ in Eq. (7); y is $\ln k$ in Eq. (7).

fits the D2 model, but with a significantly reduced activation energy. Fe1Ash1 exhibits a more pronounced synergistic advantage during the oxidation stage, retaining the rapid oxidation characteristics of Fe/Al-OC while improving diffusion performance by inhibiting the agglomeration of IRSA. This results in overall oxidation performance superior to that of either single OC, providing theoretical support for its long-term operation in chemical looping systems.

4. Conclusions

This paper prepared Fe/Al OC particles and produced iron-rich sludge ash from high-moisture sludge. Through thermogravimetric analysis combined with kinetic analysis, the redox performance and interaction mechanisms of Fe/Al-OC, IRSA, and their 1:1 mixed system Fe1Ash1 were investigated. The main conclusions are as follows:

- (1) When Fe/Al-OC and IRSA were blended at a mass ratio of 1:1, their actual amount of oxygen release and oxygen gain were both higher than the theoretical mass change values, confirming the existence of a synergistic effect between them. The active components in IRSA promoted the reduction of Fe ions in Fe/Al-OC, while the stable structure of Fe/Al-OC inhibited the agglomeration of IRSA's active components, jointly enhancing oxygen transport capacity.
- (2) The kinetic mechanism of the OCs reduction process varies with reaction conditions. During non-isothermal reduction, the oxygen release in Fe/Al-OC is governed by two-dimensional diffusion, while the oxygen release in IRSA and Fe1Ash1 follow a first-order reaction model. The activation energy of Fe1Ash1 is slightly lower than that of the single OC, indicating that the reaction energy barrier is further reduced after mixing; During high-temperature isothermal reduction, the oxygen release in Fe/Al-OC transitions to contraction model control, reaction in IRSA maintains first-order reaction characteristics, while Fe1Ash1 better aligns with the F3/2 model, with synergistic promotion effects weakening at high temperatures.
- (3) The advantages of the mixture of Fe1Ash1 are prominent during the oxidation process. All three OCs can be oxidized and regenerated at relatively low temperatures. Fe/Al-OC follows a first-order reaction model with an activation energy E_a of $42.58 \text{ kJ}\cdot\text{mol}^{-1}$, and the oxidation rate is faster than the reduction process. IRSA and Fe1Ash1 both follow a two-dimensional diffusion model, but the activation energy of Fe1Ash1 is significantly lower than that of IRSA, indicating that the mixed OC improves diffusion limitations during the oxidation process through structural optimization.

The mixed OC of Fe/Al-OC and IRSA achieve complementary advantages in redox performance and kinetic characteristics, providing a theoretical basis and experimental support for its application in chemical looping systems.

CRediT Authorship Contribution Statement

Xiaoying Yuan: Writing – original draft. Xiaoran Wang: Formal analysis. Zhihao Zheng: Conceptualization. Cuiping Wang: Writing – review & editing.

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.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (52476120) and the Key international Cooperation of Qingdao City (24-1-6-ghgg-9-hz). The author is very grateful for the support of these projects.

Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2026.01.003>.

References

- [1] Q. Zhu, Y. Liang, Q. Zhang, Z. Zhang, C. Wang, S. Zhai, Y. Li, H. Sun, Biochar derived from hydrolysis of sewage sludge influences soil properties and heavy metals distributed in the soil, *J. Hazard Mater.* 442 (2023) 130053.
- [2] A. Zylka, J. Krzywanski, T. Czakiert, K. Idziak, M. Sosnowski, M.L. de Souza-Santos, K. Sztukler, W. Nowak, Modeling of the chemical looping combustion of hard coal and biomass using ilmenite as the oxygen carrier, *Energies* 13 (2020) 5394.
- [3] S. Daneshmand-Jahromi, M.H. Sedghkarder, N. Mahinpey, A review of chemical looping combustion technology: fundamentals, and development of natural, industrial waste, and synthetic oxygen carriers, *Fuel* 341 (2023) 127626.
- [4] J. Adanez, A. Abad, F. Garcia-Labiano, P. Gayan, L.F. de Diego, Progress in chemical-looping combustion and reforming technologies, *Prog. Energy Combust. Sci.* 38 (2012) 215–282.
- [5] M. Tang, L. Xu, M. Fan, Progress in oxygen carrier development of methane-based chemical-looping reforming: a review, *Appl. Energy* 151 (2015) 143–156.
- [6] L. Zeng, Z. Cheng, J.A. Fan, L.-S. Fan, J. Gong, Metal oxide redox chemistry for chemical looping processes, *Nat. Rev. Chem* 2 (2018) 349–364.
- [7] Y. Li, J. Liu, F. Liu, Y. Yang, Influence of doping Al on the reactivity performance of Cu–Fe spinel-type oxygen carrier during chemical-looping combustion, *J. Energy Inst.* 105 (2022) 25–32.
- [8] Z. Wang, W. Liang, M. Li, X. Yang, Z. Sun, B. Yang, B. Sun, Z. Wu, Performance evaluation on chemical looping oxidative dehydrogenation of ethane via $\text{Fe}_2\text{O}_3/\text{SiO}_2$ oxygen carriers, *Fuel* 400 (2025) 135758.
- [9] J. Zhang, Z. Cai, B. Shi, L. Ding, Y. Wang, Mg–Al spinel supported Fe–Zr oxygen carriers for chemical looping hydrogen generation at low temperatures, *Int. J. Hydrogen Energy* 158 (2025) 150419.
- [10] J. Wang, M. Zheng, H. Wang, L. Peng, H. Zheng, M. Liang, Inert supports enhanced sulphur-resistant of iron-based oxygen carriers in chemical looping combustion of element sulphur, *Chem. Eng. Process. Process Intensif.* 196 (2024) 109672.
- [11] Z. Ma, S. Zhang, Y. Lu, Activation mechanism of $\text{Fe}_2\text{O}_3\text{--Al}_2\text{O}_3$ oxygen carrier in chemical looping combustion, *Energy Fuel* 34 (2020) 16350–16355.
- [12] K. Wang, J. Li, S. Yao, L. Chen, Y. Jin, C. Wang, Performance evaluation of red mud-based oxygen carriers in the chemical looping gasification of wet sludge rich in iron, *Fuel* 372 (2024) 132229.
- [13] K. Wang, X. Yuan, W. Liang, S. Yao, J. Li, C. Wang, G. Yue, Red mud-based perovskite oxygen carrier preparation for chemical looping gasification of municipal sludge, *Waste Manag.* 177 (2024) 169–176.
- [14] Z. An, Q. Yuan, H. Liang, K. Wang, X. Yuan, C. Wang, Q. Guo, Investigation and optimization of syngas generation during chemical looping gasification of municipal sludge using Fe/Al oxygen carrier, *J. Energy Inst.* 117 (2024) 101844.
- [15] Y. Niu, Z. Chi, M. Li, Advancements in biomass gasification research utilizing iron-based oxygen carriers in chemical looping: a review, materials reports, *Energy* 4 (2024) 100282.
- [16] Y. Feng, N. Wang, X. Guo, S. Zhang, Characteristics of dopant distribution and surface oxygen vacancy formation for modified Fe_2O_3 in chemical looping combustion, *Fuel* 276 (2020) 117942.
- [17] K. Wang, Y. Jin, L. Zhang, Study on the oxygen release kinetics of iron-rich sludge ash synergistic perovskite oxygen carrier, *Clean Coal Technol.* (2025), <https://doi.org/10.13226/j.issn.1006-6772.FF24121601>. (in Chinese)
- [18] L. Yang, W. Chen, C. Song, C. Li, J. Chen, X. Zhang, F. Liu, Improving attrition resistance of oxygen carriers by biomass ash in chemical looping process, *Fuel* 346 (2023) 128352.
- [19] N.M. Moed, M.-H. Chiang, Y. Ku, Y.-H. Tseng, Kinetics for chemical looping process with fabricated $\text{Fe}_2\text{O}_3\text{--CuO/Al}_2\text{O}_3$ oxygen carriers, *Chem. Eng. Sci.* 258 (2022) 117730.
- [20] W. Liang, F. Wang, C. Wang, H. Yang, W. Cui, G. Yue, Investigation on the oxygen-carrying performance and reaction kinetics of $\text{CaMn}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ perovskites prepared from red mud, *Fuel* 331 (2023) 125929.
- [21] X. Yuan, J. Song, W. Hu, S. Yao, K. Wang, C. Wang, Characteristics of iron phase migration and redox performance of Fe/Al particles blending with iron-rich sludge ash, *Chem. Eng. Sci.* (2025) 121501.
- [22] L. Mu, J. Chen, P. Yao, D. Zhou, L. Zhao, H. Yin, Evaluation of co-pyrolysis petrochemical wastewater sludge with lignite in a thermogravimetric analyzer and a packed-bed reactor: pyrolysis characteristics, kinetics, and products analysis, *Bioresour. Technol.* 221 (2016) 147–156.
- [23] T.A. Jawdekar, I.K. Kndva, S. Gun, S.G. Shinde, A.A. Sunny, Z. Cheng, L.S. Fan, Metal ferrite derivative chemical looping systems: a review towards a multiscale approach for technology readiness enabling clean energy conversion and carbon neutrality, *Chem. Sci.* 16 (2025) 4971–4991.
- [24] X. Hua, W. Wang, F. Wang, Performance and kinetics of iron-based oxygen carriers reduced by carbon monoxide for chemical looping combustion, *Front. Environ. Sci. Eng.* 9 (2015) 1130–1138.
- [25] P. Wang, C. Zheng, Y. Li, Z. Xu, H. Zhao, Exploring the regulation mechanism of Ca/Fe-based oxygen carrier in biomass chemical looping gasification, *Chem. Eng. J.* 498 (2024) 155488.