

Article

Sludge Gasification Using Iron Bearing Metallurgical Slag as Heat Carrier: Characteristics and Kinetics

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Abstract: Waste heat recovery is a key problem to be solved for metallurgical slag. Furthermore, the heat source is a current bottleneck for sewage sludge gasification technology. At present, there is no complete process system for the thermochemical conversion of sludge driven by metallurgical slag waste heat. To recover the waste heat of slag, a granulation and waste heat recovery system using the sewage sludge gasification reaction is proposed in this paper. The sludge gasification kinetics were analyzed using thermogravimetry (TG). The active catalytic components in both Cu and Ni slag were determined using X-ray diffractometry (XRD) and X-ray photoelectron spectroscopy (XPS). The results show that the metallurgical slag could improve the decomposition rate of the sludge gasification reaction. The main catalytic components were Fe₃O₄ and CaO for Cu slag and Ni slag, respectively. The conversion ratio was increased by 7.8% and 11.8%, while the activation energy decreased from 21.09 kJ/mol to 17.36 kJ/mol and 17.30 kJ/mol, respectively, when Cu slag and Ni slag were added. After oxidative modification, the catalytic function was enhanced for Cu slag, whereas it was weakened for Ni slag.

Keywords: sewage sludge; Cu slag; Ni slag; waste heat recovery; gasification



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1. Introduction

Sewage sludge is a semi-solid material derived from urban and industrial sewage treatment. Sludge is a large amount of solid waste with huge output. The first mock exam of sewage sludge treatment was focused on dewatering and landfill [1]; however, through this method, the toxic and harmful substances in sludge caused serious environmental problems. Therefore, recycling treatment methods with reduced environmental impact are needed urgently.

Pyrolysis or gasification technology, as a thermal conversion technology for the energy utilization of solid raw materials, has become an important direction for carbonaceous organic solid disposition [2,3]. Gasification technology is a process of cracking organic units, removing volatile components, and forming solid coke slag under high-temperature reaction conditions with a gasification agent [4]. The gasification process usually coexists with the pyrolysis process [5]. The steam and carbon dioxide produced during the pyrolysis process can be used as gasification agents to participate in the gasification reaction [6]. Pyrolysis gas produced by pyrolysis or gasification is rich in gaseous hydrocarbons, hydrogen, and carbon monoxide [7,8].

Sludge is rich in organic matter and combustible components, which is a sufficient condition for gasification as a raw material [9,10]. Using gasification technology to extract carbon from sludge can convert organic matter into clean and cheap energy while avoiding secondary pollution [11,12]. However, sludge has high ash, high moisture, and low volatile organic compounds. Sludge treatment requires a lot of heat [13]. It requires at least 360 MJ of energy per ton of sludge to be treated with 80% water. It is of great significance to find a stable and economical heat source [14,15].

Furthermore, Cu and Ni slag are typical by-products discharged from the smelting process, whereby about 2.2 tons of slag can be produced for every ton of Cu or Ni [16]. At present, these slags are typically treated by water quenching in smelting enterprises [17]. This treatment method not only fails to recover high-temperature waste heat but also wastes water resources and produces substantial pollution [18]. Slag waste heat recovery and resource utilization are hot issues in the metallurgical industry [6,12,19]. The treatment temperature of slag is about 1300 °C, and the equivalent of about 48 kg of standard coal is needed to provide the heat required for the pyrolysis of one ton of sludge. In addition, Cu slag and Ni slag contain valuable metals such as Fe and Ca; the mass fraction of Fe can reach more than 40%, which can be used as a catalyst and carbon pore structure modifier in the sludge pyrolysis process [20]. Moreover, the gasification reaction can consume oxidation agents (such as CO₂) and produce high value-added gas [21,22]. At present, the catalysts used in sludge gasification or pyrolysis mainly include alkali metal [23], carbon-based catalysts [24], transition metal, and natural ores (such as iron ore [25] and quartz sand [26]). The oxidation agents commonly used for sludge gasification include air, steam, oxygen, CO₂, or a mixture [27].

High-value material cannot be used to process low-value material. Therefore, the key is to treat waste with waste. Moreover, metallurgical slag itself contains alkali metals, representing potential catalytically active components [28,29]. Alkali metal catalysts have a certain ability to decompose tar. However, the composition of metallurgical slag is complex. When it is used as a heat carrier, its catalytic characteristics and active components are difficult to determine. Basic research on the catalysis of blast furnace slag was carried out by Sun [30]; however, the metal content of blast furnace slag is relatively low. In non-ferrous metallurgical industries, the metal content in slag (such as Cu slag or Ni slag) is higher than that in blast furnace slag.

Considering the waste heat recovery demand of non-ferrous metallurgical slag and the treatment demand of sewage sludge, a technical system is proposed as shown in Figure 1. The metallurgical slag granulation and waste heat recovery technology system is shown in Figure 1. It contains a granulator and gasification reactor. Firstly, molten slag is granulated into solid slag particles with a diameter <5 mm at 1100 °C. Then, slag particles enter the gasification reactor. In a gasification reactor, hydrous municipal sludge (the moisture content is about 70%) and CO₂ flow into the reactor. The organic matters (carbon and hydrogen contained in sludge) and fixed carbon react with carbon dioxide. These endothermic gasification reactions take place at this stage. As products, after condensation, a mixture of gas of CO₂, CO, H₂, and H₂O is produced. During this process, slag particles are cooled to 100 °C. The syngas can be used as combustion fuel to provide heat in the smelting process of copper or nickel. With this technology system, slag particles are cooled and can be used as cement additives for resource utilization. Mass and energy analysis of the waste heat cascade recovery of copper slag have been analyzed in the author's previous study [6]. Compared with multi-stage waste heat recovery [6], the device and process of the system in this research are simple. Moreover, the system uses smoke as a gasification agent, which has lower carbon emissions and is a carbon neutralization technology path. By calculation and analysis, 21.0 kg of sludge and 8.48 kg of carbon dioxide are consumed when 1 ton of metallurgical slag is disposed of using the metallurgical slag granulation and waste heat recovery technology system.

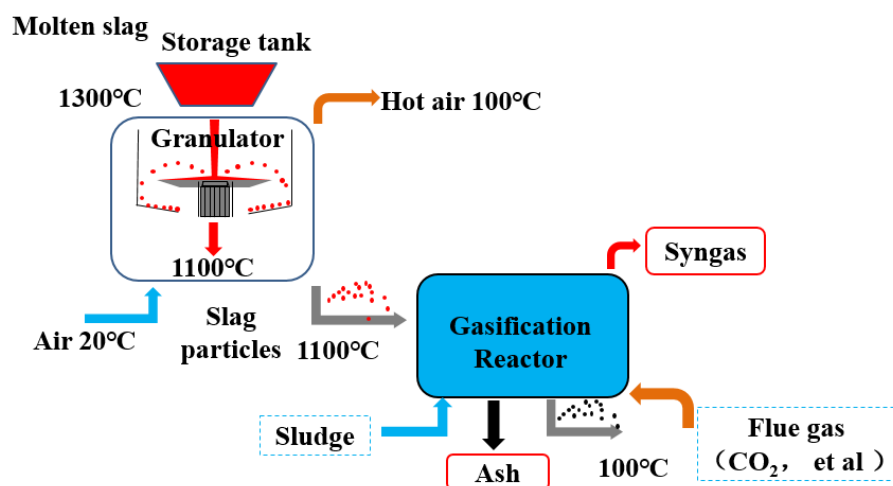


Figure 1. Metallurgical slag granulation and waste heat recovery technology system.

The characteristics of the sludge gasification reaction with CO_2 as an oxidation agent were studied using two kinds of typical raw metallurgical slags as the heat carrier. Mass loss via gasification was analyzed using thermogravimetry (TG). The active components in both Cu slag and Ni slag were determined through phase detection and composition determination using X-ray diffractometry (XRD) and X-ray photoelectron spectroscopy (XPS). Furthermore, the activation energy and kinetic parameters were calculated when the heat carrier was added.

2. Material and Methods

2.1. Material

In this experiment, Cu slag and Ni slag sample were obtained from a flash-smelting metallurgical plant in China. Sludge is collected from a sewage treatment plant in Qingdao, China. The slag and sludge were pulverized (100 mesh) using a mechanical crusher. Then, samples were fully dried in a constant temperature blast drying oven at 105°C for 4 h. The chemical composition of Cu slag and Ni slag are shown in Tables 1 and 2, respectively. As indicated, SiO_2 , FeO , Fe , CaO , and Al_2O_3 were the main components. As there is no dilution treatment for Cu slag, the content of Cu was 0.68%, which meets the standard of copper ore. The composition of Ni slag differed in that CaO , SiO_2 , MgO , FeO , and Fe were the main components. The evaluation was conducted using a proximate analyzer (SDTGA5000). The phases in raw materials were identified by XRD using $\text{Cu-K}\alpha$ radiation operating at 30 kV and 40 mA, and diffraction data were recorded by continuous scanning with a step of $10^\circ \cdot \text{min}^{-1}$. Additionally, the XPS patterns of Cu slag and Ni slag were obtained using an XPS analyzer (spot size $400\ \mu\text{m}$; source gun type, $\text{Al K}\alpha$; energy step size, 1.0 eV for survey results; the number of energy steps, 1361). The XPS test curve was fitted and analyzed using the XPSPEAK41 software, and the spectrum was corrected by setting the C1s binding energy to 284.6 eV.

Table 1. Chemical composition of Cu slag.

FeO	SiO_2	TFe	CaO	Mfe	Al_2O_3	Zn	Na	MgO	Cu
24.63	31.77	27.19	9.58	7.70	6.24	4.85	3.02	2.53	0.68

Table 2. Chemical composition of Ni slag.

CaO	Tfe	SiO_2	MgO	FeO	Mfe	Mn	TiO_2	Cu	Ni
47.28	16.42	13.73	7.15	6.67	6.05	3.45	0.79	0.013	<0.01

Through drying experiments, it was found that the moisture content in municipal sludge was 74.9%. After drying, the industrial analysis results of municipal sludge are shown in Table 3, which highlights the volatile and fixed carbon of municipal sludge at 52.46% and 7.3% as the main gasification reactant, along with low organic content.

Table 3. Proximate analysis of municipal sludge, wt%.

Sample	Moisture	Volatile	Ash	Fixed Carbon
Municipal sludge	0.01	52.46	40.23	7.30

2.2. Methods

A thermodynamic analyzer was employed in this experiment. The slag sample and municipal sludge were first mixed and ground in a crucible. Then they were placed in a high-purity aluminum crucible and mixed sufficiently using an aluminum wire stirrer. The protective gas and reaction gas was N_2 and CO_2 , respectively. The flow rates were both 50 mL/min, as controlled by flow meters. The purity of N_2 used in this study was 99.9%. In each experiment, about 10 mg of the sample was heated from 100 °C to 800 °C~1000 °C at a heating rate of 10~20 °C/min. The mass loss ratio of the sample was detected and recorded. The effects of different heating rates, reaction temperatures, and types of heat carriers on the reaction rate and weight loss rate were investigated. An equal mass of SiO_2 was added as the blank experimental control in the crucible to correct for the baseline of the reaction. The experimental method was the same as described in our previous research work [19].

3. Results and Discussions

3.1. Characteristics of Slag Heat Carrier

As a heat carrier, slag provides energy for the chemical reaction; thus, its phase composition and surface properties were determined by chemical reaction. Figures 2 and 3 present the XRD patterns of the waste slags before the reduction reaction. As shown in Figure 2, fayalite was the main component of the slag. However, the composition of copper slag was complex, and several crystal forms exist. There were many miscellaneous phases in Cu slag, such as magnetite (Fe_3O_4), wüstite (FeO), silicon oxide (SiO_2), and cuprite (Cu_2O). As shown in Figure 3, the main phases detected in the XRD patterns of Ni slag were lamite (Ca_2SiO_4) and calcium silicate (Ca_3SiO_5). Due to the existence of Ca, Mg, and Al, the compound phase of slag was complex, such as $Ca_{54}MgAl_2Si_{16}O_{90}$.

To determine the surface atomic type and concentration of Cu slag and Ni slag, XPS analysis was carried out as shown in Figure 3. Based on the results of peak splitting XPS results, the basic information of atoms with different orbitals was obtained as shown in Table 4. We could also determine semi-quantitatively from the peak areas that the Fe, Si, and Cu contents were higher in Cu slag than in Ni slag. Furthermore, the Ca content in Ni slag was much higher than that in Cu slag. This is consistent with the results of elemental analysis. We found that the SiO_2 in Cu slag was mainly present in the form of $2FeO \cdot SiO_2$. The Ca in Ni slag was mainly present in the form of CaO. Both of them are potentially catalytic components.

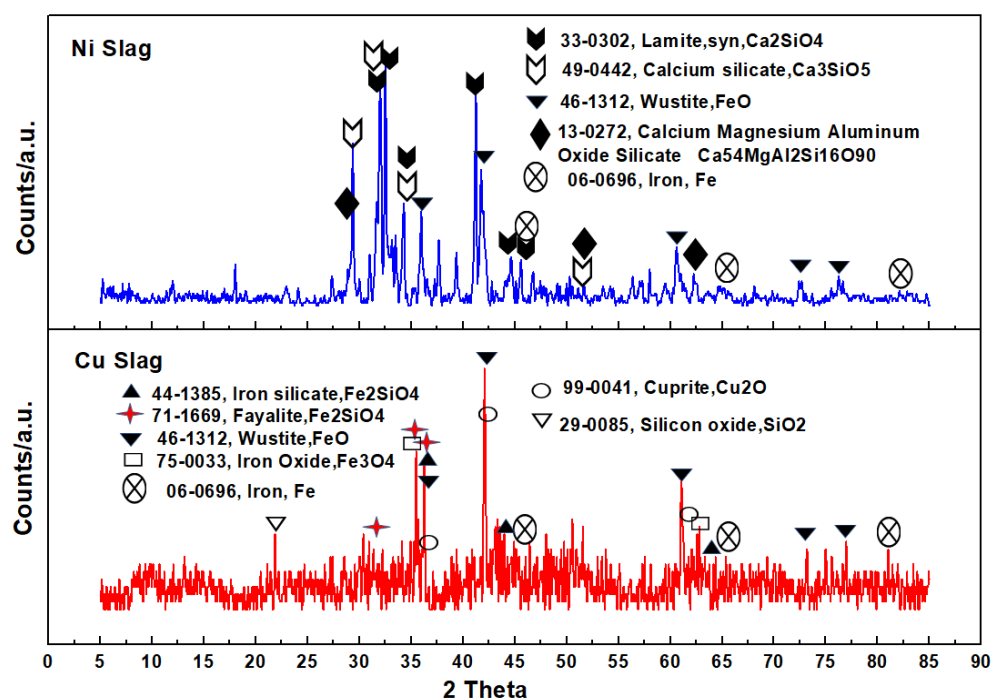


Figure 2. XRD patterns of Cu slag and Ni slag.

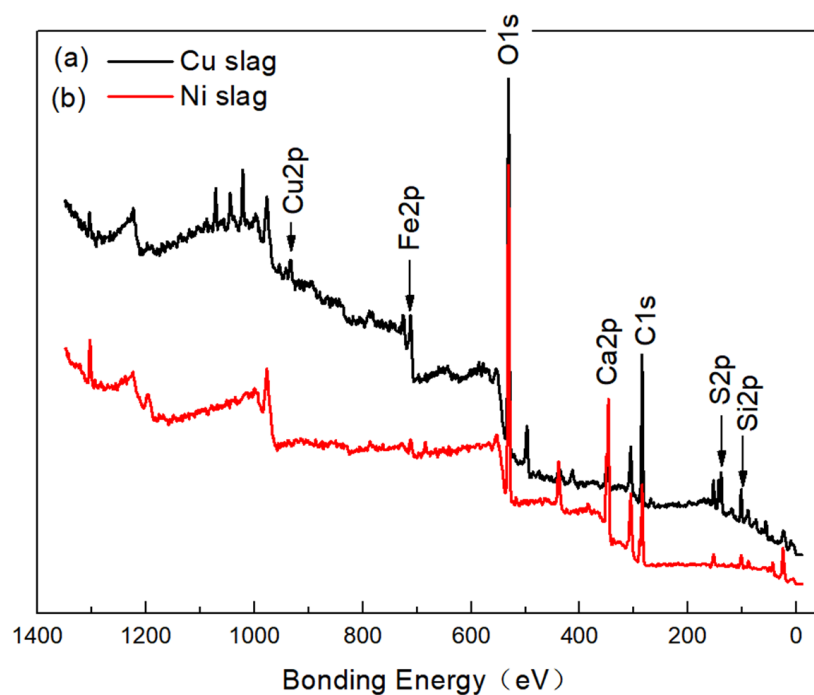


Figure 3. Survey scan XPS spectra of Cu slag and Ni slag.

Table 4. Peak table of Cu slag and Ni slag.

Sample	Name	Start BE	Peak BE	End BE	Height CPS	FWHM (eV)	Area (P) CPS. eV
Cu slag	Si2p	109.76	102.06	94.86	3261.75	1.75	6695.26
	S2p	174.76	162.82	156.86	387.82	3.04	2406.07
	C1s	297.76	284.8	278.86	16,680.03	1.26	27,618.2
	Ca2p	359.76	347.35	339.86	3143.93	1.62	11,346.11
	O1s	544.76	531.06	524.86	33,295.91	2.32	85,416.3
	Fe2p	739.71	711.09	699.91	4352.76	4.19	40,033.9
	Ni2p	887.71	862.3	843.91	409.43	0.12	7407.4
	Cu2p	966.71	932.34	924.91	3363.35	2.1	22,266.04
Ni slag	Si2p	109.41	102.03	94.51	896.45	2.46	2533.86
	S2p	174.41	169.1	156.51	178.68	0.15	668.68
	C1s	297.41	284.8	278.51	7267.74	1.54	16,835.57
	Ca2p	359.41	347.03	339.51	12177.8	1.84	38,357.95
	O1s	544.41	531.27	524.51	25,476.15	2.35	68,628.93
	Fe2p	739.36	710.81	699.56	1014	4.29	11,257.13
	Ni2p	883.36	863.02	843.56	330.64	0.31	5168.47
	Cu2p	966.36	940.41	924.56	404.94	0.52	5524.79

3.2. Sludge Gasification Characteristics Based Slag as Heat Carrier

Firstly, blank control group experiments were conducted. Figures 4 and 5 show the TG and DTG curves of sludge gasification and pyrolysis reactions. The pyrolysis reaction of sludge occurred in the N₂ atmosphere while the gasification reaction of sludge occurred in the CO₂ atmosphere. According to the decomposition degree of sludge, the gasification reaction was more thorough than the pyrolysis reaction. The main factor involved in the pyrolysis reaction is the precipitation of volatile substances in sludge. In contrast, the gasification reaction also includes the reaction of carbonaceous substances with the gasification agent, i.e., oxygen. For example, carbon substances in sludge can react with CO₂ to produce CO. Following the pyrolysis reaction, the ash and fixed carbon in the sludge were retained, accounting for 72.11% of the sample mass. Following the gasification reaction, they accounted for 58.85% of the sample mass. The quality difference was greater than the content of fixed carbon in the industrial analysis as shown in Table 3. This is because the gasification of CO₂ involves some refractory macromolecular organics that escape from the reactor. Furthermore, through the DTG curve, we can see that the temperature corresponding to the maximum weight loss rate of sludge pyrolysis and gasification was almost the same. Moreover, it can be seen from Figures 4 and 5 that the weight loss range of sludge gasification in carbon dioxide atmosphere is mainly in 200–600 °C, and two peaks of weight loss appear at 200–400 °C and 400–600 °C, respectively. The temperature range of the peak is consistent with the TGA profile obtained by Zhao et al. [31] in air atmosphere. The termination temperatures of pyrolysis and gasification reactions were different; about 800 °C and 700 °C, respectively. Luo et al. [32] found that the gas production of sludge and metallurgical slag continued to increase above 800 °C. The reason for this difference is that the fixed carbon content in the sludge used in this paper is lower than that in the reference, and the gasification agent used is different.

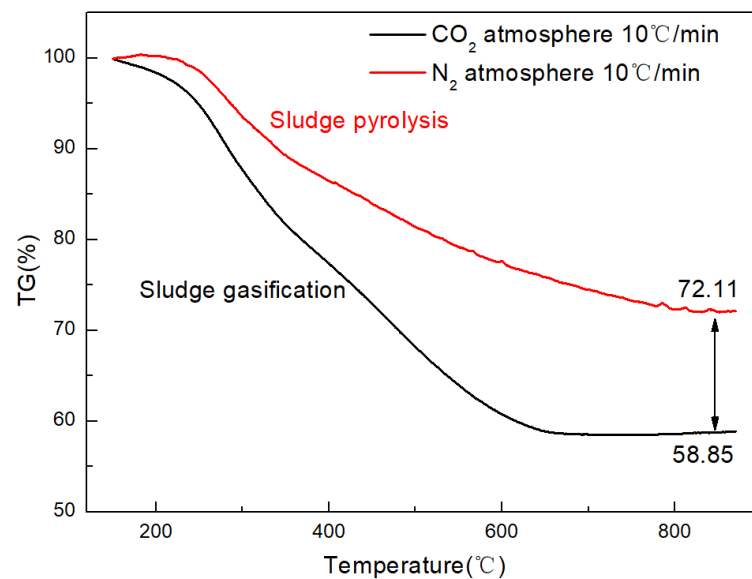


Figure 4. TG curves of sludge gasification and pyrolysis reactions.

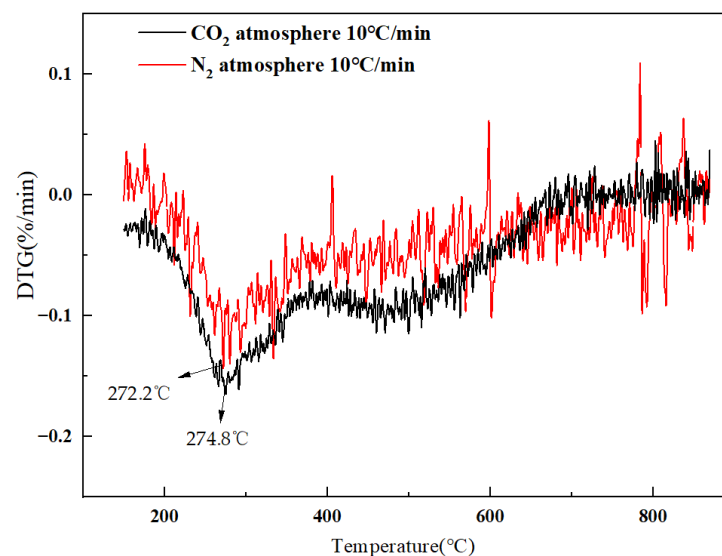


Figure 5. DTG curves of sludge gasification and pyrolysis reactions.

The TG and DTG curves of sludge gasification with different heating rates are shown in Figures 6 and 7. To reflect the real situation of catalysis, we introduced a mixture of equal-quality sludge and silica as a blank control. We can see that the addition of metallurgical slag improved the decomposition rate of the sludge gasification reaction. This confirms the catalytic effect of metallurgical slag on the sludge gasification reaction. Without the slag heat carrier, the terminal mass of the sample is 79.32%. When Cu slag was added at the same heating rate, the terminal mass of the sludge sample decreased to 77.70%. In contrast, when Ni slag was added at the same heating rate, the terminal mass of the sludge sample decreased to 76.88%. The conversion ratio was increased by 7.8% and 11.8% when using Cu slag and Ni slag as the heat carriers, respectively. Through the comparison of different heating rates, it can be found that the conversion ratio at 10 °C/min was higher than that at 20 °C/min, which was mainly because sufficient time was left for the gasification reaction at a lower heating rate. Catalysis caused a change in conversion but the reaction rate changed little, as shown in Figure 7. At 10 °C/min and 700–800 °C, the catalytic action of Cu slag caused a secondary reaction.

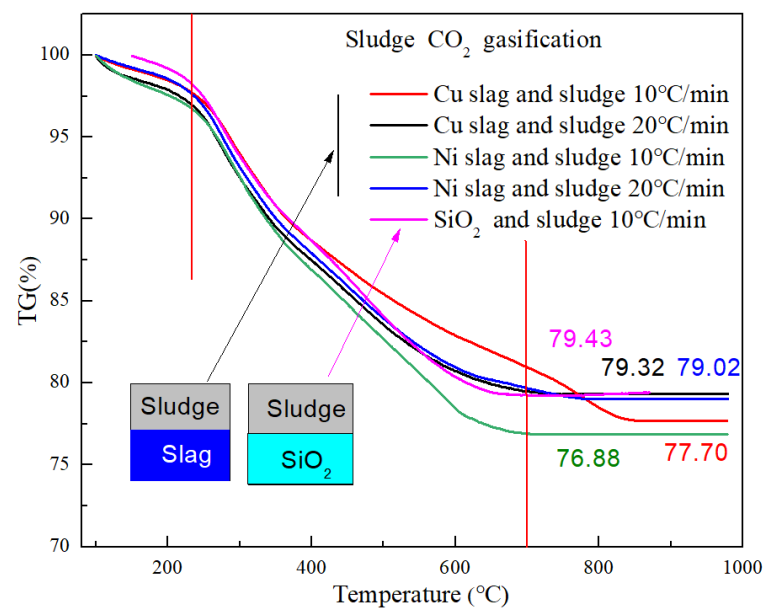


Figure 6. TG curves of sludge gasification with different heating rates.

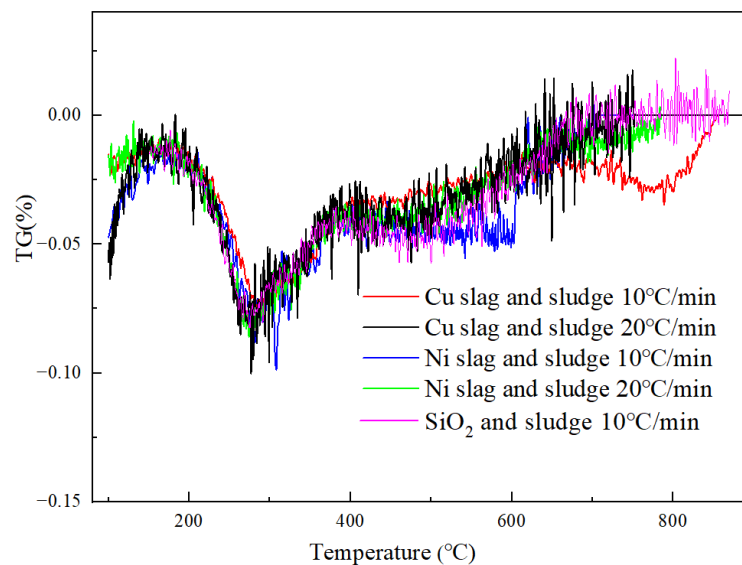


Figure 7. DTG curves of sludge gasification with different heating rates.

Cu slag is rich in metals, such as iron. Thus, modifying the metal in slags via calcination can improve the content of iron oxide and its catalytic performance. From the perspective of engineering application, the effective oxidation of metals can be realized by blowing enough air into the granulator. Cu slag and Ni slag were calcined fully at 1000 °C in a furnace for 1 h and then taken out. The sludge gasification reaction experiment was carried out. TG and DTG curves of sludge gasification with calcined slags are shown in Figures 8 and 9. In the comparison between Figures 6 and 8, it can be seen that the catalytic capacity of oxidized Cu slag is improved. The quality of terminated materials was further reduced from 77.70% to 76.33%. The catalytic effect of copper slag after oxidation is more obvious, which is consistent with the finding of Deng et al. [33]. The conversion ratio was increased by 14.5% and 2.9% when using calcined Cu slag and Ni slag as heat carriers, respectively, compared with sludge gasification using SiO₂ as the heat carrier.

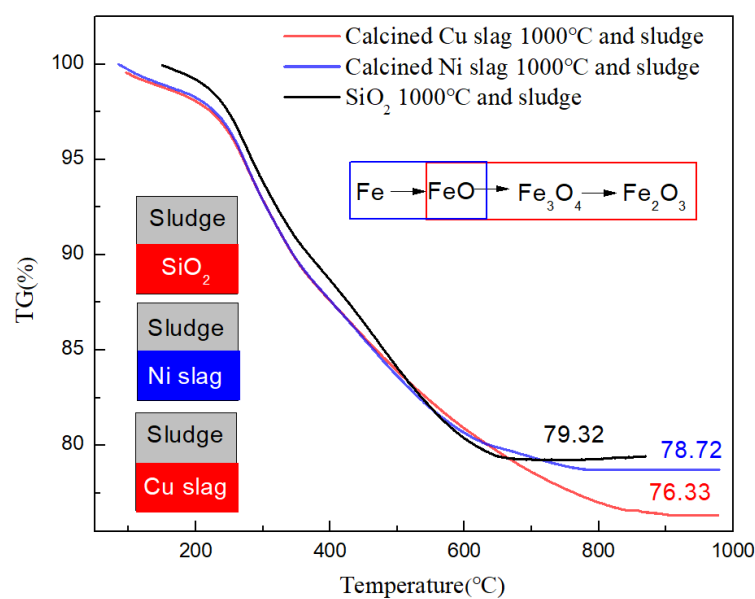


Figure 8. TG curves of sludge gasification with calcined slags.

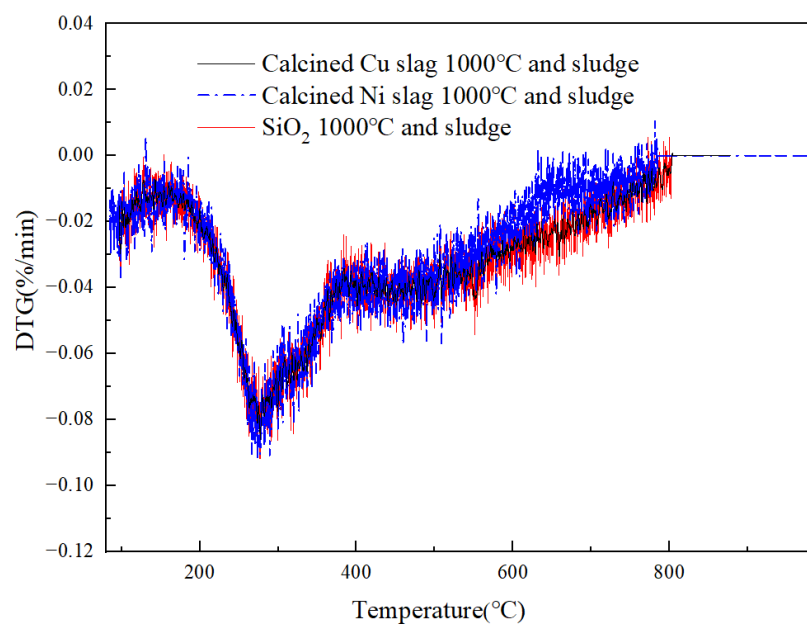


Figure 9. DTG curves of sludge gasification with calcined slags.

The comparison results of the catalytic function of different heat carriers are shown in Figure 10. XRD patterns of calcined Cu slag and Ni slag are shown in Figure 11. According to the change in metal valence on the surface of the heat carrier, its catalytic effect on sludge differed.

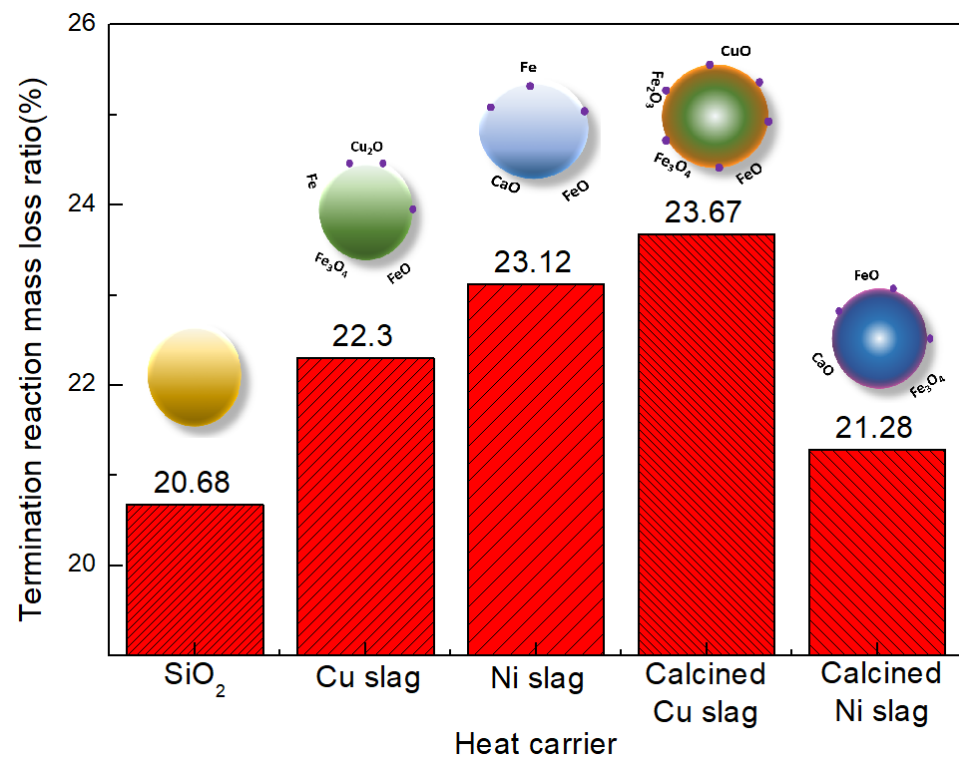


Figure 10. Termination reaction mass loss ratio with different heat carriers.

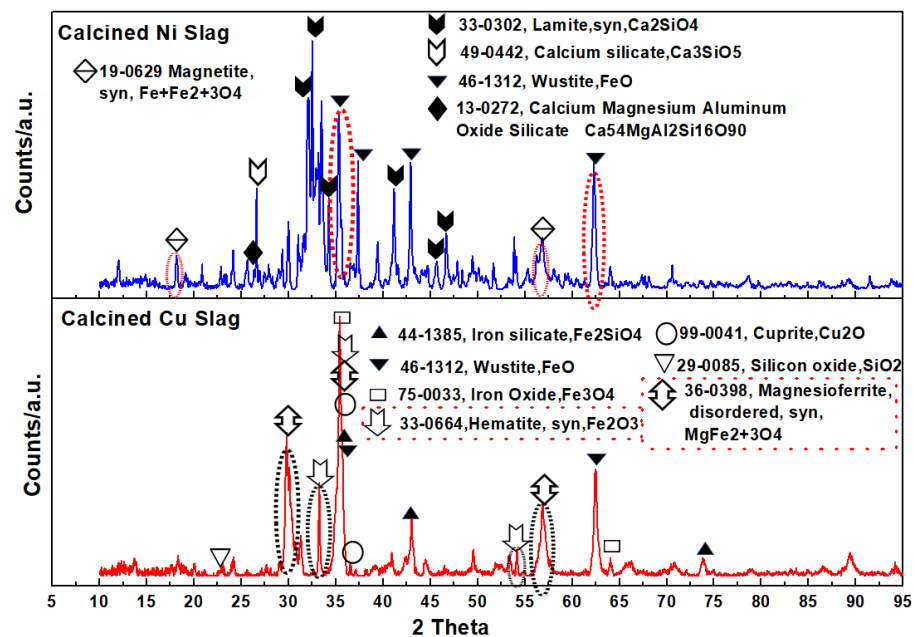
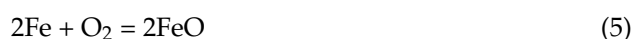


Figure 11. XRD patterns of calcined Cu slag and Ni slag.

After calcination and oxidation, the oxidation reaction of iron and copper occurred and the phase peaks of Fe₂O₃ and MgFe₂₊₃O₄ appeared in Cu slag. The catalytic effect on sludge gasification was enhanced by Fe₂O₃ and MgFe₂₊₃O₄. It should be noted that MgFe₂₊₃O₄ is a transition state of Fe₃O₄ and Fe₂O₃ forming a complex with MgO, as shown in Equation (1). Its essence is the transformation from FeO to Fe₃O₄, as shown in Equation (2). Thus, the termination reaction mass loss ratio was further improved from 22.3% to 23.67%. The phase conversion can be proved by the XRD patterns in Figures 2 and 11. The oxidation reaction in Cu slag is shown in Equations (1)–(4). Compared with FeO in the initial Cu slag, the structures of Fe₃O₄ and Fe₂O₃ in the calcined Cu slag are unstable, with

high catalytic activity. The variation of Fe element in copper slag after oxidation calcination obtained from the above XRD patterns is consistent with the discovery of Zhao et al. [34].

After the calcination of Ni slag, oxidation of iron occurred, as shown in Equation (5). The phase peaks of FeO in Ni slag become stronger, as shown in Figure 10. Furthermore, another form of $\text{MgFe}_{2+3}\text{O}_4$ appeared, albeit with low content. FeO can be easy to combine with SiO_2 to form olivine, an extremely stable structure. As an alkaline metal oxide, CaO has good catalytic activity in its original state. However, after calcination and oxidation, the coating of FeO decreased the catalytic activity of CaO. The termination reaction mass loss ratio decreased from 23.12% to 21.28%. In other words, calcination oxidation was beneficial to Cu slag but unfavorable to Ni slag.



3.3. Sludge Gasification Kinetics Using Slag as Heat Carrier

In this research, the Coats–Redfern method is selected to analyze the above dynamic parameters. According to the law of mass conservation, the mass loss rate in the process of sludge gasification reaction can be expressed as:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (6)$$

where n is the reaction order, α is sludge gasification conversion rate (%), and k is Arrhenius constant. The expressions of α and k are as follows:

$$\alpha = \frac{m_0 - m}{m_0 - m_e} \quad (7)$$

$$k = A e^{\frac{-E}{RT}} \quad (8)$$

where m_0 is the initial mass of the material (g), m is the mass of the material at a certain moment in the reaction process (g), m_e is the mass of the material when the reaction is terminated (g), A is pre-exponential factor, E is the activation energy (kJ/mol), R is the molar constant of gas (8.314 J/(mol·K)), and T is the thermodynamic temperature (K).

The heating rate is defined as follows:

$$\beta = \frac{dT}{dt} \quad (9)$$

Combined with the above formula, we can obtain:

$$\frac{d\alpha}{dt} = \frac{A}{\beta} e^{\frac{-E}{RT}} (1 - \alpha)^n \quad (10)$$

Both sides can be obtained by integrating and shifting terms.

$$\int_0^\alpha \frac{d\alpha}{(1 - \alpha)^n} = \frac{A}{\beta} \int_{T_0}^T e^{\frac{-E}{RT}} dT \quad (11)$$

The logarithms on both sides of Equation (11) can be taken. When $n = 1$, the equation can be transformed as follows:

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{E\beta}\left(1 - 2\frac{RT}{E}\right)\right] - \frac{E}{RT}. \quad (12)$$

When $n \neq 1$:

$$\ln\left[\frac{1 - \ln(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\left[\frac{AR}{E\beta}\left(1 - 2\frac{RT}{E}\right)\right] - \frac{E}{RT}. \quad (13)$$

$\frac{E}{RT} \gg 1$, thus, $a = -E/R$, $X = 1/T$, and b is as follows:

$$b = \ln\left[\frac{AR}{E\beta}\left(1 - 2\frac{RT}{E}\right)\right] \approx \ln\left(\frac{AR}{E\beta}\right). \quad (14)$$

When $n = 1$, Y is as follows:

$$Y = \ln\left[-\frac{\ln(1-\alpha)}{T^2}\right]. \quad (15)$$

When $n \neq 1$, Y is as follows:

$$Y = \ln\left[\frac{1 - \ln(1-\alpha)^{1-n}}{T^2(1-n)}\right] \quad (16)$$

Thus, the function ' $Y = aX + b$ ' can be obtained. Through the thermogravimetric curve obtained from the sludge gasification experiment, combined with the fitting Equations (15) and (16), the relationship between the activation energy E and the pre-exponential factor a could be obtained. During the fitting calculation, the reaction orders were calculated, respectively, when the reaction orders were 0.5, 1, 1.5, and 2 so as to compare and determine the actual reaction orders. Lastly, the kinetic fitting curves of the sludge gasification reaction under different experimental conditions were drawn. The appropriate reaction order was selected according to the correlation coefficient R^2 of the curve.

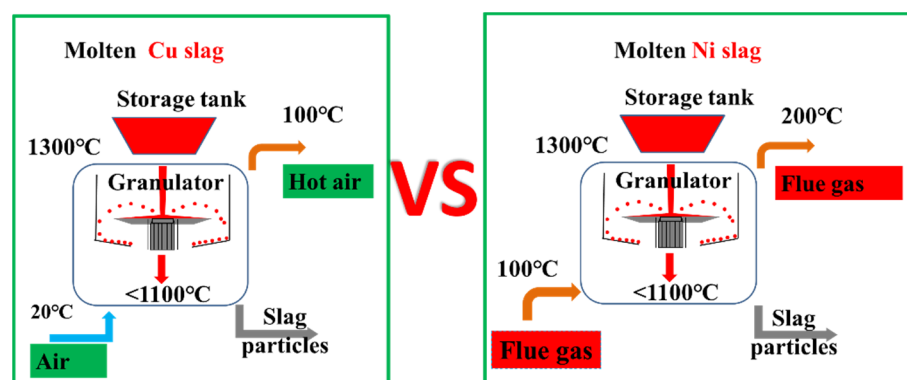
The kinetic parameter values of the sludge gasification reaction under experimental conditions can be derived from the data in Table 5. Heat carrier SiO_2 had little effect on the reaction. This is mainly due to the stable nature of silica. In the actual system process, the existence of a heat carrier may improve the heat and mass transfer rate, but this is not reflected by the dynamics. When the heating rate was $10^\circ\text{C}/\text{min}$, with Cu and Ni slag as the heat carriers, the activation energy decreased from 21.09 kJ/mol to 17.36 kJ/mol and 17.30 kJ/mol, respectively. According to the calculation results of activation energy, we can see that both Cu slag and Ni slag could reduce the activation energy of the gasification reaction, while the catalytic potential of alkali metals in the nickel slag was stronger. Therefore, the activation energy of the gasification reaction catalyzed by the Cu slag heat carrier was lower than that catalyzed by the Ni slag heat carrier. The results also show that the catalytic effect of CaO in Ni slag was stronger than iron oxides in Cu slag.

Table 5. Kinetic parameters of municipal sludge gasification in experiment conditions.

No	Heat Carrier	Heating Rate (°C/min)	Atmosphere	Temperature Region of Maximum Mass loss (°C)		R ²	Activation Energy (kJ/mol)	Reaction Coefficient
1	-	10	N ₂	247	352	0.998	21.18	2
2	-	10	CO ₂	237	347	0.998	21.93	2
3	SiO ₂	10	CO ₂	227	302	0.995	21.09	0.5
4	Cu slag	20	CO ₂	237	352	0.984	17.93	1
5	Cu slag	10	CO ₂	262	367	0.993	17.36	2
6	Ni slag	20	CO ₂	247	347	0.995	18.10	1.5
7	Ni slag	10	CO ₂	252	352	0.996	17.30	2
8	Calcined-Cu slag	10	CO ₂	247	372	0.998	14.53	2
9	Calcined-Ni slag	10	CO ₂	262	372	0.993	17.86	2

Furthermore, after oxidation, a reversal of the activation energy of Ni slag and Cu slag occurred. The activation energy of Cu slag decreased to 14.53 kJ/mol, indicating that the catalytic activity of copper slag is strengthened after oxidation. In contrast, the activation energy of Ni slag increased from 17.30 to 17.86 kJ/mol. This further proves that the catalytic effect of oxidation treatment on Cu slag was strengthened, while that on Ni slag was inhibited, as shown in Figure 11. This was mainly due to the change in catalytic active components.

From the perspective of the catalytically enhanced gasification reaction in the technical system, the treatment methods of Ni slag and Cu slag were different. As shown in Figure 12, Cu slag is metallurgical slag rich in divalent iron with a phase of 2FeO·SiO₂. This kind of slag should be oxidized in the granulation process to transform the internal iron-containing components into magnetite and hematite minerals. Air can be selected as the coolant in the granulation process. Ni slag is a metallurgical slag with low iron content, which exists in the form of metal. This kind of slag should not be oxidized in the granulation process. Flue gas can be selected as the coolant in the granulation process.

**Figure 12.** Comparison of treatment technology Cu slag and Ni slag.

4. Conclusions

A metallurgical slag granulation and waste heat recovery technology system for iron-bearing metallurgical slag was proposed in this research. The system uses smoke as a gasification agent, which provides a path to carbon neutralization technology. The kinetics of the sludge gasification reaction with CO₂ were studied, using two kinds of typical raw metallurgical slags as the heat carriers and catalysts.

- (1) There were many miscellaneous phases in Cu slag, such as magnetite (Fe₃O₄), wüstite (FeO), silicon oxide (SiO₂), and cuprite (Cu₂O). The main phases of Ni slag were lamite (Ca₂SiO₄) and calcium silicate (Ca₃SiO₅). The Fe, Si, and Cu content in Cu

- slag was higher compared to Ni slag. The Ca content in Ni slag was much higher compared to Cu slag.
- (2) Metallurgical slag could improve the decomposition rate of the sludge gasification reaction. The conversion ratio was increased by 7.8% and 11.8% when using Cu slag and Ni slag as the heat carriers, respectively. The main catalytic component were Fe_3O_4 and CaO . The catalytic function of alkali metals in Ni slag was stronger than that of Fe_3O_4 in Cu slag. Correspondingly, the activation energy of the gasification reaction catalyzed by Cu slag was lower than that catalyzed by Ni slag. Using Cu and Ni slag, activation energy decreased from 21.09 kJ/mol to 17.36 kJ/mol and 17.30 kJ/mol, respectively.
 - (3) After modification, the active components changed. Fe_2O_3 and $\text{MgFe}_{2+3}\text{O}_4$ were the active components in the modified Cu slag and the catalytic function was enhanced. After modification, CaO remained the active component in Ni slag, but it was weakened by the generation of FeO . In Ni slag, FeO was combined with SiO_2 to form olivine, which is an extremely stable structure. The conversion ratio increased by 14.5% and 2.9% when using calcined Cu slag and Ni slag, respectively, compared with sludge gasification using SiO_2 .
 - (4) Oxidation modification is beneficial to the catalytic function of Cu slag but unfavorable to that of Ni slag. Thus, different treatment methods should be applied to Cu slag and Ni slag. Cu slag should be oxidized in the granulation process to transform the internal iron-containing components into magnetite and hematite minerals. On the other hand, Ni slag should not be oxidized in the granulation process.

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