

Investigation on the application of by-product steam in iron ore sintering: performance and function mechanism

Yufeng Wu

Central South University

Xiaohui Fan

Central South University

Zhiyun Ji (zhiyunji@sina.com)

Central South University

Min Gan

Central South University

Haoyu Zhou

MCC changtian international engineering co. Ltd

Haorui Li

Central South University

Xuling Chen

Central South University

Yuanjie Zhao

Central South University

Rongchang Zhang

Central South University

Ruisi Lai

Central South University

Research Article

Keywords: iron ore sintering, steam injection, energy saving and emission reduction, mechanism analysis

Posted Date: October 22nd, 2021

DOI: https://doi.org/10.21203/rs.3.rs-935309/v1

License: © 1 This work is licensed under a Creative Commons Attribution 4.0 International License.

Read Full License

Version of Record: A version of this preprint was published at Environmental Science and Pollution Research on April 12th, 2022. See the published version at https://doi.org/10.1007/s11356-022-20059-7.

Investigation on the application of by-product steam in iron ore

2 sintering: performance and function mechanism

- 3 Yufeng Wu^a, Xiaohui Fan^a, Zhiyun Ji^{a*}, Min Gan^a, Haoyu Zhou^{a, b}, Haorui Li^a, Xuling Chen^a, Yuanjie
- 4 Zhao^a, Rongchang Zhang^a, Ruisi Lai^a

- a: School of Resource Processing and Bioengineering, Central South University, 932 Lushan South Road,
- 7 Yuelu District, Changsha City, Hunan Province, China
- 8 b: MCC changtian international engineering co. LTD, No.7 Jieqing Road, Meixi Lake, Yuelu District,
- 9 Changsha, Hunan, P.R. China

Abstract: The combustion-supporting effect of steam to coke breeze in sintering has the potential to improve sinter quality and reduce pollutants emissions. The results show that increasing the by-product steam injection concentration(0.32-0.47vol%) and prolonging the injection time(5min) within a proper range(10-15min) can improve sinter quality. 2.13kgce/t_{-sinter} of the fuel consumption was decreased by reducing coke breeze usage from 5.60% to 5.45% under the recommended parameters, with 15.16% decrease of CO in sintering waste gas. By comparing experimental data with thermodynamic calculations, although the reaction between CO and steam can reduce CO emission and generate H₂, steam tends to react with coke breeze to generate H₂ and CO(react at 674°C), and OH radical produced by H₂ which can reduce the activation energy of CO oxidation reaction is the key to reducing pollutant emissions. The application of steam injection technology, excluding the equipment modification and steam injection cost of \$300,000, can achieve a profit of \$737491.2 per year. Therefore, low-carbon and cleaner iron ore sintering production can be realized through applying by-product steam.

Keywords: iron ore sintering; steam injection; energy saving and emission reduction; mechanism analysis

1 Introduction

Whether in social development or military fields, steel is an indispensable resource for human beings (Denton2014), but the steel industry is the third-largest consumer of fossil fuels, accounting for about 5% of the world's greenhouse gas emissions (Chen et al.2014), and also emits a large number of harmful gases such as NOx and SO₂ (Kristin et al.2015). According to the statistics of the World Bank, the top 10 countries with GDP consumed 80 billion tons of energy in terms of oil equivalent and released 21.82 billion tons of CO₂ (2014), China's steel industry accounted for 15% of China's total energy consumption (Cheng et al.2017). To achieve sustainable development, the United States will reduce CO₂ Emissions from US Steel Consumption by 70% by 2050 (Ryan et al.2020), China has also committed to reducing CO₂ emissions by 60-65% by 2030 in the Paris Agreement (He et al.2018), and most steel mills in India

Email address: zhiyunji@sina.com.

^{*} Corresponding author.

can cut their energy consumption by half (Haider et al.2021). Affected by environmental protection, carbon reduction technologies are also advancing rapidly (Mao et al.2021; Yang et al.2021).

China's iron and steel industry, which uses sinter as the main raw material for making iron, is facing the most stringent environmental requirements. The country has required the steel industry to meet the ultra-low emission standard (PM < 10mg/m^3 , $SO_2 < 35 \text{mg/m}^3$, $NOx < 50 \text{mg/m}^3$) by 2020 (2017), which is a stricter emission standard than the European and American. Sintering is the first high-temperature process in steel production, the dust (Pal2019), SO_2 and NOx emissions account for 35.4%, 67% and 51.1% of the total process emissions (Cai et al.2021). At present, China mainly adopts end-control technology to treat gas pollutants. But it is can not meet the current environmental protection requirements through the above means. In addition, China pays more and more attention to the treatment of COx, the proportion of CO in the sintering flue gas with a mass concentration much higher than NOx and SO_2 is $0.4 \sim 1\%$ (Wang and Zhang.2020).

Sintering gas pollutants mainly come from fuel combustion. Scholars have studied and numerically simulated the fuel combustion of iron ore sintering. With thermal power industry or generally fixed bed fuel combustion is different (Hobbs et al.1993; Pugh et al.2017), fuel in sintering material layer is scattered distribution, generally accounts for only 3-5% of total material weight, and most of the solid carbon particles are wrapped by inert ore materials. The combustion regularity of fuel is between monomer char combustion and char layer combustion, which belongs to heterogeneous reactions (Fernandez et al.2017). Fan et al.(2021) studied the relationship between ignition and low-carbon sintering and found that prolongation of ignition time can reduce fuel consumption and pollutant emission. Toda et al. believed that sintering mixture at high temperature would form melt, which would reduce the diffusion efficiency of oxygen in the material layer, affect the fuel combustion rate, and make it easier to generate CO (Hideo and Kimio 1984). Zhu et al. (2006) found that the CO content in flue gas was related to the amount of coke powder. With the increase of the amount of coke powder, there was a reducing atmosphere around the coke powder particles and it was easy to form CO. Li et al. (2020) found in their study that CO would be oxidized to CO2 by NO on the reduced surface of the reduced calcium ferrite. Gan et al.(2016) found that CO and NOx emissions could be reduced by performing fuel pellets during sintering, which was achieved by covering the fuel with quicklime and controlling the fuel surface atmosphere. It can be seen that the emission of CO in the sintering process is related to the combustion rate and the fuel surface atmosphere, but the combustion rate is related to the sintering rate and the high temperature retention time of the fuel layer, which should not be changed. If the fuel combustion efficiency is improved by changing the fuel surface atmosphere in the fuel layer, the emission of CO can not only be reduced, the heat released by the oxidation of CO can also be used to increase the temperature of the feed layer. It is beneficial to improve the quality of sintered minerals.

In the field of coal burning, fuel combustion has been studied deeply. Although it is very different from sintering conditions, some technologies are worth referring to. Buhre et al.(2005) studied the oxygen-coal combustion system. By using pure oxygen and circulating flue gas to control the temperature and heat flow distribution, the fuel combustion efficiency can be improved and NOx emissions can be significantly reduced. An analysis of pressurized coal burners by Hong et al.(2009) showed that high pressure can improve energy efficiency. Oxy-steam combustion is a promising next generation oxy-fuel combustion technology. Wang et al. studied the effect of steam concentration on the combustion process of oxy-steam. At low steam concentration, the decomposition of H₂O molecules is conducive to the formation of C(O) on the particle surface and the conversion to CO and new active sites, which can accelerate the reduction rate of NO at high temperatures (Wang et al.2019). Li et al.(2012)

used PFR model to simulate the reduction path of NO by H_2O and CO, showing that CO is the key to the generation of H free radical and the reduction of NO when the $[H_2O]$ is less than 1%.

It is unreasonable to use pure oxygen or change the pressure in the sintering process of iron ore, the use of pure oxygen will greatly increase the production cost, while the pressure of sintering directly affects the sintering speed and the quality of sintered minerals. There have been many studies on the application of circulating flue gas. Li et al.(2014) showed through experiments that circulating flue gas would concentrate SO₂ in flue gas and achieve higher removal efficiency. Fan et al.(2019) calculated the composition of circulating flue gas and established a fine circulation mode. The emissions of NOx and SO₂ can be reduced by 28.6% and 8.15% without worsening the sintering index. Steam is seldom used in sintering. Pei et al.(2018) analyzed the influence of sintering surface steam spraying technology, and the results showed that steam can reduce CO emissions and increase fuel combustion efficiency, but the specific performance and emission reduction mechanism needs to be further studied.

In this paper, the influence of steam injection on sintering performance was studied, and the appropriate injection system was determined. In addition, HSC software was used to analyze the possible reaction after the addition of steam, the mechanism of CO emission reduction was analyzed. Suggestions were put forward for the practical application of steam spraying sintering technology. The research results will provide effective support for the wide application and improvement of the technology in steel sintering plants.

2 Materials and methods

2.1 Raw material properties

The raw materials used in the test included iron-containing materials, fluxes (dolomite, limestone and quicklime) and coke breeze. Table 1 shows the chemical compositions of raw materials and their proportions. As can be seen from Table 1, the iron contents of mixed iron ores decided the final iron content in the sinter product, while the fluxes were used to adjust the basicity (CaO/SiO₂ mass ratio) and MgO of sinter to 1.80 and 1.80%. Table 2 shows the ultimate and proximate analyses of coke breeze, the fixed carbon and calorific value of which were 82.71% and 28.69MJ·kg⁻¹.

Table 1Chemical compositions and LOI of raw materials

Raw materials	Chemical composition/%						
Kaw materials	TFe	SiO_2	CaO	MgO	Al_2O_3	FeO	LOI/%
Mixed iron	62.42	6.05	0.21	0.32	0.96	9.63	3.82
Dolomite	0.55	1.70	32.10	18.04	0.20	0.14	45.58
Limestone	0.53	3.45	54.58	0.57	0.26	.0.17	40.69
quick lime	0.10	1.02	80.52	3.19	0.18	0.02	8.10
Sinter returns	56.68	5.67	10.58	2.06	1.66	9.41	0.10
Blast furnace returns	57.00	5.17	10.52	2.11	1.59	8.54	0.48
Coke breeze	1.40	6.03	0.80	0.18	3.94	0.05	86.24

LOI: loss on ignition

111 Table 2

112 Industrial analysis of coke and its element content analysis results

	Proximate analysis /%			Calorific		Ultimate analysis /%				
Components	venents V A FC		value / (MJ/kg)	C	Н	О	N	S		
Value	3.44	13.76	82.80	28.69	83.68	2.00	1.02	0.75	0.22	

V: volatile matter, A: ash content, FC: fixed carbon

2.2 Test methods

2.2.1 Sintering test

A laboratory sintering cup with a size of Φ 180×700 mm was used to simulate the practical sintering process, as shown in Fig. 1. Sinter materials are mixed as shown in Table 3. The composition of sinter material is represented by external distribution. Since the return fines need to be constant, sintering returns and blast furnace returns are used as external distribution materials for the convenience of calculation.

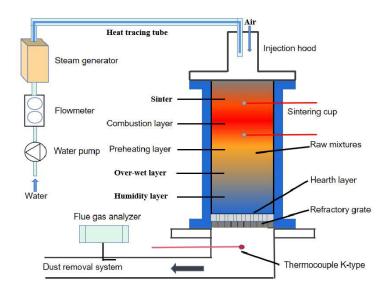


Fig. 1 Schematic diagram of steam injection sintering test research device

Table 3

Composition ratio of sinter material

Components/%	Coke breeze	Mixed iron	Dolomite	Limestone	quick lime	Sinter returns	Blast furnace returns	Σ
Value	5.60	77.17	5.71	7.02	4.50	18.00	12.00	130

After manual blending, the raw materials were granulated using a drum of $\Phi600\times1400$ mm, with a speed of 15 r/min for 4min. Add 80% of the total water during the mixing process, and the rest was added to the granulating process. Add 1kg hearth and then charging the granulated mixture. Igniting at 5kPa for 1 min (ignition temperature is 1050°C) and sintering at 10kPa. The main evaluation indexes of sintering included sintering speed, productivity, yield and tumbler index.

Sintering speed is the ratio of sintering height to sintering time, as shown in formula (1). (ν : Sintering speed, mm/min; H: The height of the sintering layer without the thickness, mm; t: Sintering time, which

means the time interval from ignition to the maximum temperature of the exhaust gas, min.) In this paper, H=680mm.

$$v = \frac{H}{t} \tag{1}$$

- The productivity is the output index of sinter per unit time and per unit area, as shown in formula (2).
- 138 (y: Productivity, $t/(m^2h)$; S_S : Quality of sinter with particle size greater than 5mm, kg; D: Diameter of
- sintering cup, mm.) In this paper, D=180mm.

140
$$\gamma = 7.65 \times 10^4 \frac{s_S}{D^2 t}$$
 (2)

The yield is the proportion of sinter with the size of 5mm or more after screening, as shown in formula (3). (η: Yield, %; S₀: Quality of sinter without hearth, kg.)

143
$$\eta = \frac{s_s}{s_0} \times 100\% \tag{3}$$

And the tumbler index represents the strength of sinter, as specified by ISO3271(2007), as shown in formula (4). (TI: Tumbler index, %; m_1 : The quality of sinter with particle size greater than 6.3mm after drum, kg; m_0 : The quality of sinter added to the drum, kg.) In this paper, m_0 =7.5kg.

$$TI = \frac{m_1}{m_0} \times 100\% \tag{4}$$

Fig. 1 shows that in the sintering process, the flue gas temperature is tested by a thermocouple installed in the flue gas pipeline and the composition of the flue gas was analyzed by a portable infrared flue gas analyzer (Madur Photon) consisting of two units, a Photon II flue gas analyzer and a PGD-100 flue gas preprocessor.

2.2.2 Steam Injection Method

Moving the injection hood above the sintering cup to spray steam on the sintering surface. The steam was generated by the LEP-800 liquid evaporator of Nanjing Boyun-Pass Instrument Technology Co., LTD., and the amount of water is controlled by the attached BT101L flow intelligent peristaltic pump (driver BT101L, pump head YZ15). To prevent condensation of steam before injection, an electric tracing tube is connected between the outlet and the injection hood. The temperature of tracing tube is set at 150 °C. Two thermocouples are set 100mm and 300mm away from the material surface to detect the temperature change of the material layer after spraying steam.

In this paper, different injection schemes were adopted to explore the influence of injection concentration, injection time and injection interval on sintering index and pollutant emission. According to the industrial application, four groups of different steam injection time schemes were studied (the initial injection time was set as 10min, and the injection concentration was set as 0.6%, which means 1 m³ of air contains 0.006 m³ of steam), as shown in Fig. 2.

Although several sintering plants in China have tested steam injection technology in industry, the optimal strategy has not been explored in the technology, and there is still a great possibility of improvement. Bai et al.(2020) studied steam sintering technology at China Anyang Iron and Steel Co., Ltd., and found that compared to early injection, steam injection 7min after ignition had a better sintering index (1min ignition). However, Huang et al.(2019) installed 7 injection pipes (within No. 7-14 bellows) in the industrial test, and the injection time range was 10~20min for sintering, and the sinter yield increased by 2%. As shown in Fig. 2, according to industrial application, 10min after ignition was taken

as the starting time of steam injection, and four different injection schemes were set to explore the optimal strategy.

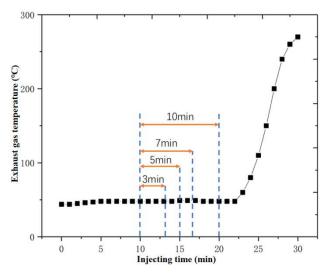


Fig. 2 Steam injecting schemes during sintering process

2.2.3 Calculation Method

In this paper, HSC Chemistry was used to evaluate the possible reactions in the sintering process after the addition of steam, mainly to calculate the Gibbs free energy of each reaction. Based on the sintering time of $10\sim15$ min, the sintering temperature can reach more than $800\,^{\circ}$ C, the steam and free radicals are defined as gaseous states.

3 Results and discussion

3.1 Effect of steam injection on sintering performance

3.1.1 Effect parameters on sintering quality

Fig. 3 gives the influence of steam injection time on sintering index, where the steam injection concentration is 0.6%. When the injection time increased from 0 min to 5min, the productivity, tumbler index and yield all showed an increasing trend, from 1.38t/(m²h), 65.37% and 70.70% to 1.46t/(m²h),65.64% and 71.67%. Prolonging the injection time further, sintering index showed a decrease. Therefore, the recommended injection time is 5min.

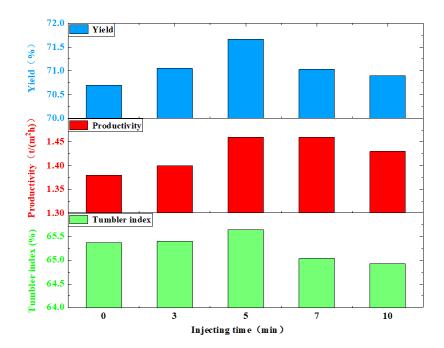


Fig. 3 Influence of injection time on sintering index

Fig. 4 gives the influence of steam injection concentration on sintering index, where the injection time is 5min and the injection interval is 10-15min. When the steam injection concentration increased from 0 to 0.32%, the sintering indexes improved. When increasing the concentration further to 0.47%, sintering indexes were improved slightly, while the tumbler index dropped by 2.17% compared with the base case when increasing the concentration to 0.6%. Therefore, the recommended injection concentration is 0.32~0.47%.

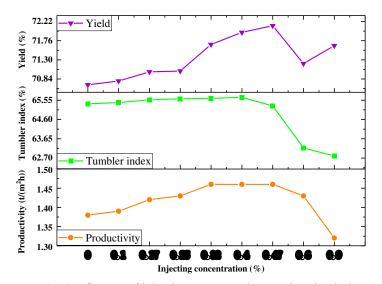


Fig. 4 Influence of injection concentration on sintering index

Fig. 5 gives the influence of steam injection interval on sintering index, where the injection time and concentration were 5min and 0.6%. It can be found that compared with the base case, the optimal injection interval is 10-15min, under which the sintering indexes can be improved to a greater extent. It

should be mentioned that when injecting the steam in the earlier stage, such as 5-10min and 8-13min, the sintering index presented a dropping tendency. Therefore, the appropriate steam injection system is 0.32~0.47% of injection concentration, 5 min of injection time, 10~15min of injection interval.

72.0 – Yeild Yeild (%) 71.4 70.8 70.2 Tumbler index (%) 69.6 Tumbler index 65.6 64.8 64.0 63.2 Productivity (t/m²h) Productivity 1.46 1.44 1.42 1.40 1.38 8-13 10-15 13-18 15-20 no injecting Injecting interval (min)

Fig. 5 Influence of injection interval on sintering index

210211

212

213

214

215

216

217

218

219 220

221222

223

224

209

206

207

208

3.1.2 Effect on coke consumption and CO emission

Productivity (t/(m2h))

The sintering index obtained under the optimal parameters was better than the base level. Under the recommended injecting conditions, the influence of steam injection on proper coke breeze rate was studied, as shown in Fig. 6. It can be obtained that the coke breeze content can be reduced from 5.6% to 5.45%, without affecting the sintering indexes, and the fuel consumption can be reduced by 2.13 kgce/t. sinter.

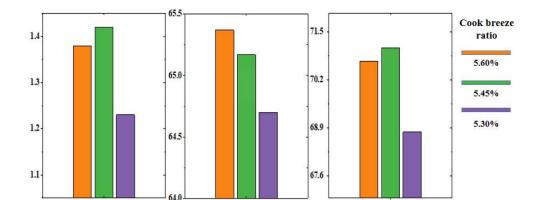


Fig. 6 Influence of steam injection on sintering indexes with different coke breeze contents

Yeild (%)

Under the recommended steam injection time and intervals, the influence of steam injection concentration on CO emission was studied, and the results were shown in Fig. 7. With the increase of steam concentration, CO emission concentration appeared an obvious decrease. Compared with the base

Tumbler index (%)

case, when the injecting concentration was 0.40%, the average CO emission concentration in the interval obviously drops from 11690mg/m³ to 9918mg/m³, with a decrease of 15.16%. With the further increase of 0.90% of steam concentration, the average CO emission concentration in the interval decreases as high as 3435mg/m³, with a decreasing proportion of 29.38%. As can be seen from Fig. 7, when the steam concentration increases, the CO emission reduction rate increases gradually slowly, combined with the research data, the CO emission reduction rate obtained between 0.4 and 0.6% steam concentration is effective.

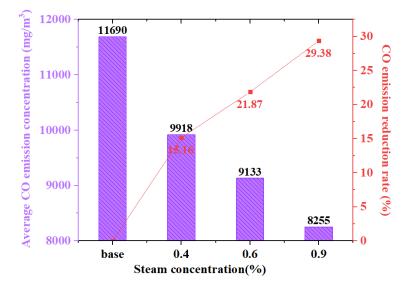


Fig. 7 Effect of injection concentration on CO emission

3.2 Function mechanism of steam injection during sintering process

3.2.1 Influence mechanism on sinter quality

Fig. 3 and Fig. 4 shows with the increase of steam injection concentration and time, the sintering index was improved, the potential reason can be described that the specific heat capacity of steam was larger than the air (Escudero et al.2021), which was conducive to the heat transfer of the sintered layer, the addition of an appropriate amount of steam promoted the combustion of fuel. When the concentration of injection was 0.32~0.47% and the injection time was 5min, the indicators were improved, but when the concentration exceeded 0.6% or the injection time exceeded 5min, it would have adverse effects. Heat transfer occurred when steam passed through the sintered layer and then reached the combustion layer. In addition, the excessive concentration of the injection has a great influence on the combustion temperature of the fuel (Li et al.2020), and the steam also carries a lot of heat when it finally enters the flue gas, increasing the heat loss. Fig. 8 shows the temperature curves of the material layer at 100mm and 300mm after spraying steam (0.40% steam concentration), it shows spraying steam in 5-10 minutes will not only reduce the maximum temperature of the upper sintered bed (58°C reduced) but also shorten the high temperature retention time (more than 800°C), spraying steam in 10-15 minutes can accelerate the temperature rise and increase the maximum temperature of the middle-sintered bed by 15°C.

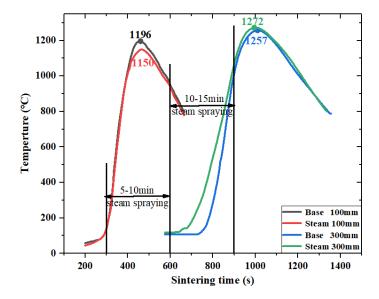


Fig. 8 Influence of spray steam at different time on temperature of sintered bed

Fig. 5 shows during the steam injecting interval of 10-15min, sintering indexes all reached an improvement while injecting steam in the earlier sintering stage worsened the sintering performance. Fig. 9 shows the curve of the flue gas composition (CO, CO₂, O₂, NOx) when steam is injected during the interval of 5-10min. It can be obtained that CO, CO₂ and NOx of the sintering flue gas were all dropped and O₂ content is increased, which indicates that the fuel combustion in the sintered layer deteriorates in 5-10min. At early, the upper layer accumulates less heat, which presented lower highest temperature and duration (Pei et al.2018). Since the temperature of the steam is far lower than the combustion layer, physical heat absorption occurs when steam is close to the combustion layer, and chemical heat absorption occurs after steam reaction (C+H₂O=CO+H₂, heat absorption reaction), which causes adverse effects on the sintering of the upper layer, this agrees with the experimental results (As shown in Fig. 8).

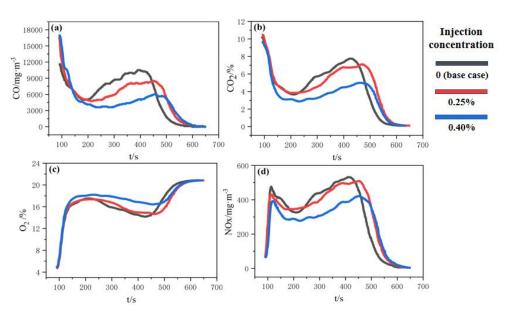


Fig. 9 Emission characteristics curve of sintering flue gas at different injection concentrations

3.2.2 Influence mechanism on CO reduction

269

270

271

272

273

274 275

276

277

278

279

280 281

282 283

284

285

286 287

288

289

290

291

292

293

For the carbon-oxygen reaction system, a new reaction path occurred after injecting steam, which exerted an influence on the flue gas composition, as shown in Fig. 10. Fig. 10(a) and (b) show the reaction path of the carbon-oxygen system without and with steam injection. It can be seen that after injecting steam, the thermodynamics aspect to reduce CO emissions through CO + H₂O □CO₂ + H₂. In the combustion layer, steam reacted with coke breeze to generate hydrogen. In addition, the diffusion coefficient of steam molecule was higher (Wang et al.2013), and the contact area with coke breeze was larger, which promoted the combustion of coke breeze and improved the combustion efficiency of coke breeze through the reaction $C+H_2O \rightarrow CO_2+H_2$.

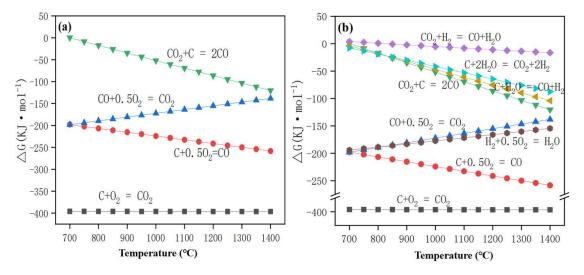


Fig. 10 Changes of reaction pathways after water vapor addition

After injecting steam in the sintering, the combustion reaction formula of coke breeze can be expressed as (Zhang et al.2016):

$$C+(\alpha)O_2+(\beta)H_2O \rightarrow 2(1-\alpha)CO + (2\alpha-1)CO2 + (\beta)H_2O$$

In the formula, the value of α is between 0.5 and 1, and the burning efficiency of coke breeze is expressed by the ratio of CO₂/(CO+CO₂).

Yukihiro (1980) studied CO_X concentration at different positions on the surface of coke breeze particles during combustion, as shown in Fig. 11. It can be seen that at 900 °C, the CO concentration on the surface of coke breeze is about 6%, and the CO₂ concentration is about 17%. At this time, the combustion efficiency of coke breeze is 74%, and α is 0.87. When 1mol C is burned, 0.87mol O₂ is required to participate in the reaction.

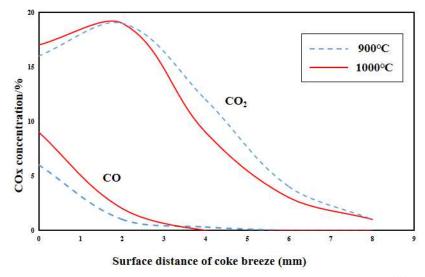


Fig. 11 CO_X concentration at different distances of coke breeze surface^(Yukihiro et al.1980)

The mechanism of the above reaction is an exothermic reaction, so temperature has a great influence on this reaction. Under the conditions of 0.87mol of oxygen (74% combustion efficiency) and 0.50% of steam concentration, the effect of temperature on CO emission reduction was investigated, as shown in Fig. 12. Increase the temperature from 700°C to 1400°C, the CO emission decreased from 2514 mg/m³ to 950 mg/m³. That is not conducive to the forward reaction, the results and analysis are consistent.

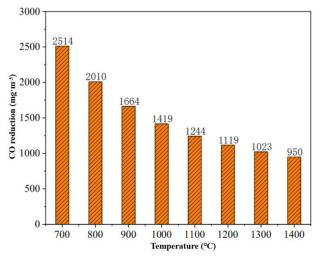


Fig. 12 Effect of temperature on CO emission reduction

However, during sintering process, the temperature is not stable or uniform and can be as high as 1350°C or higher. It can be analyzed that the O₂ content in the sintering flue gas was maintained at 14% and 7% oxygen was consumed in the sintering process, which is only equivalent to the normal concentration of oxygen in 1/3 of the air. Therefore, the maximum CO emission reduction concentration calculated theoretically is 838mg/m³(at 700°C), which is quite different from the CO emission reduction when the steam injection concentration is 0.40% (Fig. 7 shows 1772mg/m³). Therefore, it can be speculated that the presence of steam can reduce CO emissions, but the reaction products produced by steam in sintering are the key factor.

According to Fig. 13, in the presence of (OH), CO would react with it to generate (H) and CO₂. However, there are many views on the generation pathway of (OH) and (H). Zhang et al.(2010) believed that high concentration of steam would react with volatiles/tar in gas phase to form (H) radicals. Li et al.(2012) suggested that (H) and (OH) were produced by the decomposition of steam. Through thermodynamic analysis, it is very difficult to decompose steam at high temperature, and the concentration of steam sprayed in sintering is very low, so it is difficult to refer to the above viewpoints. As can be seen from Fig. 13, when the temperature is higher than 674°C, H₂ will be continuously generated, which means that (OH) will also be continuously generated. Compared with the decomposition of steam at high temperature, it is a more reasonable speculation to regard H₂ as the source of (OH).

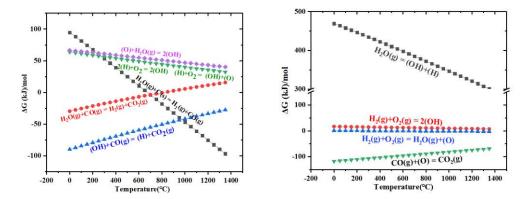


Fig. 13 Thermodynamic analysis of sources of free radicals

In the sintering process, oxygen is sufficient, but due to the limitations of the technological process and the generation of high-temperature melt, oxygen is difficult to reach the surface of coke powder, and there is a local reducing atmosphere around the coke powder. Compared with oxygen, steam diffuses more rapidly in the sinter bed, which can improve the combustion atmosphere of coke powder and at high temperatures, it reacts with C to produce hydrogen, H₂ and O₂ produce not only (OH) but also (O), and both of these free radicals oxidize CO, thereby reducing CO emissions. The reaction formula is as follows:

$$\begin{split} H_2O(g)+C=H_2(g)+CO(g) & \text{ (High temperature spontaneous process)} \\ & H_2(g)+O_2(g)=2(OH) \\ & H_2(g)+O_2(g)=H_2O(g)+(O) \\ & (OH)+CO(g)=(H)+CO_2(g) \\ & (O)+CO(g)=CO_2(g) \end{split}$$

From the above analysis, CO production will be inhibited after steam injecting in the sintering process, and CO emission will be affected by two factors. Fig. 14 is the schematic diagram of the reaction mechanism.

1) At high temperature, CO produced by incomplete combustion of coke breeze will react with steam to produce CO_2 and H_2 ($H_2O(g) + CO(g) = H_2(g) + CO_2(g)$), by calculation, this pathway cannot occur spontaneously at temperatures higher than 800°C, so this is not the main way to reduce CO emission.

2) When the temperature is higher than 674°C, steam reacts with coke breeze to form H_2 , which reacts with O_2 to form (OH) and (O). These two free radicals will rapidly oxidize CO, which is the key to reduce CO emissions.

3) Both reactions can occur between 674°C and 800°C. Considering that the temperature interval is less than 30 seconds during the sintering heating process, it is considered that the reaction tends to proceed in 2) as the temperature increases.



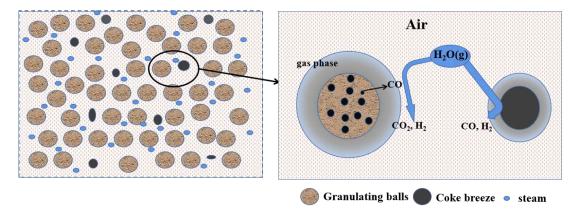


Fig. 14 Mechanism diagram of CO emission reduction by steam

3.3 Further Discussion and Recommendations on Industrialization

During the sintering process, the CO emitted from incomplete combustion of coke breeze can be reduced through steam injection. However, the high temperature region is constantly changing from top to bottom, only by injecting steam in a suitable area can desirable emission reduction effect be achieved.

In industrial production, steam can be preheated by the hot sinter, according to the temperature curve of the sintered layer (Fig. 8), it can be seen that the highest temperature and high temperature retention time of the upper sintered layer are worse than those of the middle and lower layers, so it is not suitable for low-temperature steam injection. It is better to inject steam when the combustion layer reaches the middle of the sintering layer, where the hot sinter layer has the ability to heat the steam to a higher temperature. After steam reaches the high temperature area, it can react with C to generate H₂, and it's going to form (OH) and (O), which releases heat of reaction. Due to the addition of extra heat, the sintering energy consumption and pollutant emissions can be reduced through reduce the ratio of coke breeze.

In industrial application, the influence of steam temperature, the height of the injecting device from the sinter surface and the pressure of injecting should be considered comprehensively. However, this study provided effective production and operation parameter guidance for steam injecting in iron and steel sintering plants.

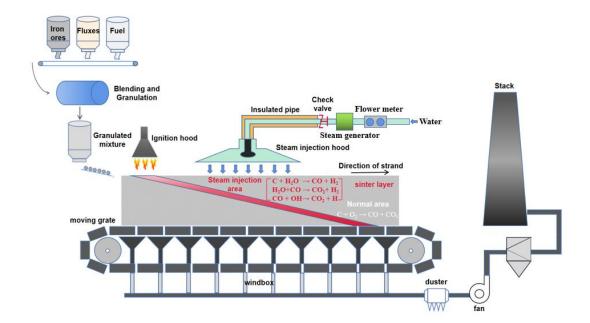


Fig. 15 Schematic diagram of practical application of steam injection in iron and steel sintering plant

Fig. 15 is a schematic diagram of the actual application of steam injection in iron and steel sintering plants. Steam injection device should be installed in the middle of sintering machine, the flowmeter control injection concentration, steam is produced by the industrial recovery wastewater after heating and atomization, water can be heated to 150°C by a heating device or preheating device, the injection device is highly controllable and covers the sintering surface. Industrial reclaimed wastewater mainly includes rolling, steelmaking and coking wastewater, etc.

At present, most iron and steel enterprises have established water circulation systems to treat and recycle the iron and steel industrial wastewater. In addition, the injection device can also be used for gas injection after modification, and better sintering effect can be achieved by exploring an appropriate coupling injection system.

On this basis, the energy consumption of sintering can be reduced by 2.13kgce/t_{-sinter}, in the sintering plant in China, the annual production of a 360m² sintering machine is approximately 3.2 million tons, and the coal price is \$108.2 / ton, the annual economic benefit is estimated at \$737491.2, excluding the cost of equipment modification and steam injection of approximately \$300,000, the profit increased by \$437491.2 in the first year. In short, the method is simple and easy to implement, the steam injection device not only has low cost and low risk but also can bring a profit of \$737491.2 per year. It is a technology worth popularizing and applying.

4 Conclusion

- (1) The influence of steam injection on sintering indexes is found: during sintering process, increasing the steam injection concentration and prolonging the time will improve the sintering indexes, the recommended value is $0.32 \sim 0.47\%$ of injection concentration, 5 min of injection time, $10 \sim 15$ min of injection interval.
- (2) The application of steam injection technology reduces the content of coke breeze and fuel consumption. The ratio of coke breeze can be reduced from 5.60% to 5.45%, the average emission concentration of CO was reduced by 1772 mg/m^3 , with a decrease of 15.16%, the emission of CO_2 , NO_x can be reduced when all the indexes of sinter are guaranteed.

104	(3) When T<800°C, steam will react with CO to generate H ₂ and CO ₂ , when T>674°C, steam tends to react with coke to generate H ₂ , and then generate (OH) and (O) radicals, which can rapidly oxidize
104	CO at high temperature.
105	(4) With the application of steam injection technology, excluding the equipment modification and
106	steam injection cost of \$300,000, the profit can be increased in the first year by reducing solid fuel
107	consumption by 2.13kgce/t-sinter, and the annual profit is \$737491.2.
108	Ethics approval and consent to participate: Not applicable
109	Consent for publication: Not applicable
110	Availability of data and materials
111 112	The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.
113	Competing interest
114 115	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.
116	Authors' contributions
117	Chen Xuling is in charge of project management. Fan Xiaohui proposed conceptualization. Gan
118	Min and Zhou Haoyu are in charge of project supervision. Ji zhiyun mainly provides methodology,
119	funding acquisition, writing review and editing.Li Haorui and Lai Ruisi investigated samples from the
120	project Wu Yufeng is mainly responsible for verification, formal analysis and writing-preliminary
121	draft preparation. Zhao Yuanjie is responsible for data management. Zhang Rongchang controls
122	resources. All authors read and approved the final manuscript.
123	Acknowledgement
124	This work was financially supported by the National Natural Science Foundation of China (Grant
125	No.51804347 and No.51974371), and the Foundation supported by Central South University
126	(No.2021zzts0903). These funds provide money for the purchase of experimental materials and
	equipment, and testing of experimental materials.
127	
127 128	References:
	References: Bai Xiaojun, Guo Junwei, Liu Yuejian (2020) Test and effect analysis of steam jet on sintered material
128	
128 129	Bai Xiaojun, Guo Junwei, Liu Yuejian (2020) Test and effect analysis of steam jet on sintered material
128 129 130	Bai Xiaojun, Guo Junwei, Liu Yuejian (2020) Test and effect analysis of steam jet on sintered material surface. Henan Metallurgy 28(03):4-7 (in chinese)
128 129 130 131 132	Bai Xiaojun, Guo Junwei, Liu Yuejian (2020) Test and effect analysis of steam jet on sintered material surface. Henan Metallurgy 28(03):4-7 (in chinese) Buhre BJP, Elliott LK, Sheng CD, Gupta RP, Wall TF (2005) Oxy-fuel combustion technology for coal-fired power generation. Progress in Energy and Combustion Science 31:283-307 http://doi.org/10.1016/j.pecs.2005.07.001
128 129 130 131 132 133	Bai Xiaojun, Guo Junwei, Liu Yuejian (2020) Test and effect analysis of steam jet on sintered material surface. Henan Metallurgy 28(03):4-7 (in chinese) Buhre BJP, Elliott LK, Sheng CD, Gupta RP, Wall TF (2005) Oxy-fuel combustion technology for coal-fired power generation. Progress in Energy and Combustion Science 31:283-307 http://doi.org/10.1016/j.pecs.2005.07.001 Cai, Lijun; Firdousi, Saba Fazal; Li, Cai; Luo, Yusen (2021) Inward foreign direct investment, outward
128 129 130 131 132 133 134	Bai Xiaojun, Guo Junwei, Liu Yuejian (2020) Test and effect analysis of steam jet on sintered material surface. Henan Metallurgy 28(03):4-7 (in chinese) Buhre BJP, Elliott LK, Sheng CD, Gupta RP, Wall TF (2005) Oxy-fuel combustion technology for coal-fired power generation. Progress in Energy and Combustion Science 31:283-307 http://doi.org/10.1016/j.pecs.2005.07.001 Cai, Lijun; Firdousi, Saba Fazal; Li, Cai; Luo, Yusen (2021) Inward foreign direct investment, outward foreign direct investment, and carbon dioxide emission intensity-threshold regression analysis based on
128 129 130 131 132 133	Bai Xiaojun, Guo Junwei, Liu Yuejian (2020) Test and effect analysis of steam jet on sintered material surface. Henan Metallurgy 28(03):4-7 (in chinese) Buhre BJP, Elliott LK, Sheng CD, Gupta RP, Wall TF (2005) Oxy-fuel combustion technology for coal-fired power generation. Progress in Energy and Combustion Science 31:283-307 http://doi.org/10.1016/j.pecs.2005.07.001 Cai, Lijun; Firdousi, Saba Fazal; Li, Cai; Luo, Yusen (2021) Inward foreign direct investment, outward

- 438 Chaoqun Li, Qingzhen Han, Tingyu Zhu, and Wenqing Xu (2020) Catalytic NO Reduction by CO over
- 439 Ca-Fe Oxides in the Presence of O₂ with Sintering Flue Gas Circulation. Industrial & Engineering
- 440 Chemistry Research 59 (47), 20624-20629 http://doi.org/10.1021/acs.iecr.0c03843
- Chen, Wenying, Yin, Xiang, Ma, Ding (2014) A bottom-up analysis of China's iron and steel industrial
- 442 energy consumption and CO₂ emissions. Appl Energ 136: 1174-1183
- 443 <u>http://doi.org/10.1016/j.apenergy.2014.06.002</u>
- 444 Cheng, Zhilong, Wang, Jingyu, Wei, Shangshang, Guo, Zhigang, Yang, Jian, Wang, Qiuwang (2017)
- Optimization of gaseous fuel injection for saving energy consumption and improving imbalance of heat
- 446 distribution in iron ore sintering. Appl Energ 207: 230–242
- 447 http://doi.org/10.1016/j.apenergy.2017.06.024
- Denton, Chad B (2014) Steel of Victory, Scrap of Defeat: Mobilizing the French Home Front,1939-40
- 449 WAR & SOCIETY 33: 130 http://doi.org/10.1179/0729247314Z.000000000034
- 450 Escudero, Ana, I; Aznar, Maria; Diez, Luis, I (2021) Oxy-steam combustion: The effect of coal rank and
- 451 steam concentration on combustion characteristics. FUEL 285 http://doi.org/10.1016/j.fuel.2020.119218
- 452 Fan, Xiaohui, Zhao, Yuanjie, Ji, Zhiyun, Li, Haorui, Gan, Min, Zhou, Haoyu, Chen, Xuling, Huang,
- 453 Xiaoxian (2021) New understanding about the relationship between surface ignition and low-carbon iron
- 454 ore sintering performance. PROCESS SAFETY AND ENVIRONMENTAL PROTECTION 146: 267-
- 455 275 http://doi.org/10.1016/j.psep.2020.09.004
- 456 Fan, Xiaohui; Wong, Guojing; Gan, Min; Chen, Xuling; Yu, Zhiyuan; Ji, Zhiyun (2019) Establishment
- of refined sintering flue gas recirculation patterns for gas pollutant reduction and waste heat recycling.
- 458 JOURNAL OF CLEANER PRODUCTION 235, 1549-1558
- 459 <u>http://doi.org/10.1016/j.jclepro.2019.07.003</u>
- 460 Fernandez-Gonzalez, D. Ruiz-Bustinza, I. Mochon, J. Gonzalez-Gasca, C. Verdeja, L.F (2017) Iron Ore
- 461 Sintering: Quality . MINERAL PROCESSING AND EXTRACTIVE METALLURGY REVIEW 38(4):
- 462 254-264 http://doi.org/10.1080/08827508.2017.1323744
- 463 Gan min; Xiaohui Fan; Wei Lv; Xuling Chen; Zhiyun Ji; Tao Jiang; Zhiyuan Yu; Yang Zhou (2016) Fuel
- 464 pre-granulation for reducing NOx emissions from the iron ore sintering process. Powder Technology
- 465 301: 478-485 http://doi.org/10.1016/j.powtec.2016.05.043
- 466 Haider, Salman.; Mishra, Prajna Paramita (2021) Does innovative capability enhance the energy
- 467 efficiency of Indian Iron and Steel firms? A Bayesian stochastic frontier analysis. ENERGY
- 468 ECONOMICS 95: 105-128 http://doi.org/10.1016/j.eneco.2021.105128
- 469 He, Jiankun (2018) Situation and measures of China's CO₂ emission mitigation after the Paris Agreement.
- 470 FRONTIERS IN ENERGY 12: 353-361 http://doi.org/10.1007/s11708-018-0564-0
- 471 Hideo TODA, Kimio KATO (1984) Theoretical Investigation of Sintering Process. ISIJ international
- 472 24(3): 178-186 http://doi.org/10.2355/isijinternational1966.24.178
- Hobbs M.L.; Radulovic P.T.; Smoot L.D.(1993) Combustion and gasification of coals in fixed-beds.
- 474 Progress in Energy and Combustion Science 19(6): 505-586. http://doi.org/10.1016/0360-
- 475 <u>1285(93)90003-W</u>
- 476 HUANG Jianping (2019) Application Effect of Spraying Steam Technology on Sintered Surface.
- 477 Ferroalloy 50(06):22-25 (in chinese)
- 478 Jongsup Hong, Gunaranjan Chaudhry; J.G. Brisson; Randall Field; Marco Gazzino; Ahmed F (2009)
- 479 Ghoniem. Analysis of oxy-fuel combustion power cycle utilizing a pressurized coal combustor. Energy
- 480 34(9): 1332-1340 <u>http://doi.org/10.1016/j.energy.2009.05.015</u>

- 481 Kristin Onarheim; Anette Mathisen; Antti Arasto (2015) Barriers and opportunities for application of
- 482 CCS in Nordic industry—A sectorial approach. International Journal of Greenhouse Gas Control 36: 93-
- 483 105 http://doi.org/10.1016/j.ijggc.2015.02.009
- 484 Letter for Soliciting Comments on the Revised List of 20 National Pollutant Emission Standards (Draft
- 485 for Soliciting Comments) for Iron and Steel Sintering and Pelletization Industrial Air Pollutant Emission
- 486 Standards. Brick and tile:7: 45-48 http://doi.org/10.16001/j.cnki.1001-6945.2017.07.010
- 487 Li, Guanghui; Liu, Chen; Rao, Mingjun; Fan, Zhenyu; You, Zhixiong; Zhang, Yuanbo; Jiang, Tao (2014)
- 488 Behavior of SO₂ in the Process of Flue Gas Circulation Sintering (FGCS) for Iron Ores. ISIJ
- 489 INTERNATIONAL 54(1), 37~42 http://doi.org/10.2355/isijinternational.54.37
- 490 Li, Sen; Wei, Xiaolin; Guo, Xiaofeng (2012) Effect of H₂O Vapor on NO Reduction by CO: Experimental
- 491 and Kinetic Modeling Study. ENERGY & FUELS 26(7), 4277-4683 http://doi.org/10.1021/ef300580y
- 492 Li, Zehua; Zou, Renjie; Hong, Dikun; Ouyang, Juncheng; Jiang, Liangkui; Liu, Huan; Luo, Guangqian;
- 493 Yao, Hong (2020) Effect of CO₂ and H₂O on Char Properties. Part 2: In Situ and Ex Situ Char in Oxy-
- 494 Steam Combustion. ENERGY & FUELS 34(6) http://doi.org/10.1021/acs.energyfuels.0c00845
- 495 Mao, Jia; Sun, Qi; Ma, Changhai; Tang, Ming (2021) Site selection of straw collection and storage
- 496 facilities considering carbon emission reduction. ENVIRONMENTAL SCIENCE AND POLLUTION
- 497 RESEARCH 35 https://doi.org/10.1007/s11356-021-15581-z
- 498 Pal,J (2019) Innovative Development on Agglomeration of Iron Ore Fines and Iron Oxide Wastes.
- 499 MINERAL PROCESSING AND EXTRACTIVE METALLURGY REVIEW 40(4): 248-264
- 500 https://doi.org/10.1080/08827508.2018.1518222
- 501 Pei, Yuandong; Xiong, Jun; Wu, Shengli; Ou, Shuhai; Ma, Huaiying; Zhao, Zhixing; Shi, Jiangshan
- 502 (2018) Research and Application of Sintering Surface Steam Spraying Technology for Energy Saving
- and Quality Improvement. 9TH INTERNATIONAL SYMPOSIUM ON HIGH-TEMPERATURE
- 504 METALLURGICAL PROCESSING, Minerals Metals & Materials Series 785-796
- 505 http://doi.org/10.1007/978-3-319-72138-5 75
- 506 Pugh, D-G, Bowen, P-J, Marsh, R, Crayford, A-P, Runyon, J, Morris, S, Valera-Medina, A, Giles, A,
- 507 (2017) Dissociative influence of H₂O vapour/spray on lean blowoff and NOx reduction for heavily
- 508 carbonaceous syngas swirling flames. Combust Flame 177: 37-48
- 509 <u>http://doi.org/10.1016/j.combustflame.2016.11.010</u>
- 510 Ryan, Nicole A.; Miller, Shelie A.; Skerlos, Steven J.; Cooper, Daniel R (2020) Reducing CO₂ Emissions
- from US Steel Consumption by 70% by 2050. ENVIRONMENTAL SCIENCE & TECHNOLOGY
- 512 54(22): 14598-14608 <u>http://doi.org/10.1021/acs.est.0c04321</u>
- Wang, Hui, Zhang, Pu (2020) Emission characteristics of PM, heavy metals, and dioxins in flue gases
- from sintering machines with wet and semi-dry flue gas desulfurization systems. ENVIRONMENTAL
- 515 SCIENCE AND POLLUTION RESEARCH 28: 46089–46099 https://doi.org/10.1007/s11356-020-
- 516 <u>11500-w</u>
- 517 Wang, Lin, Liu, Zhaohui, Chen, Sheng, Zheng, Chuguang, Li, Jun (2013) Physical and Chemical Effects
- of CO₂ and H₂O Additives on Counterflow Diffusion Flame Burning Methane. Energ Fuel. 27, 7602-
- 519 7611 <u>http://doi.org/10.1021/ef401559r</u>
- World Bank open data. https://data.worldbank.org/
- Yang, Boyu; Bai, Zhongke; Zhang, Junjie (2021) Environmental impact of mining-associated carbon
- 522 emissions and analysis of cleaner production strategies in China.ENVIRONMENTAL SCIENCE AND
- 523 POLLUTION RESEARCH 28: 13649–13659 https://doi.org/10.1007/s11356-020-11551-z

524	Yukihiro, HIDA, Minoru, SASAKI, Kaoru, ITO (1980) Consideration on the CO and NO Formation
525	around the Coke Specimen during Combustion. Tetsu-to-Hagane 66
526	http://doi.org/10.2355/tetsutohagane1955.66.13_1801
527	Zhang, Liang, Zou, Chun, Wu, Di, Liu, Yang, Zheng, Chuguang (2016) A study of coal chars combustion
528	in O-2/H2O mixtures by thermogravimetric analysis. J Therm Anal Calorim 126: 995-1005
529	http://doi.org/10.1007/s10973-016-5536-1
530	Zhu Deqing, He Aoping, Pan Jian, Mu Xiao (2006) Study on the emission of greenhouse gas COx in the
531	sintering process of iron ore. Iron and Steel 2: 76-80 http://doi.org/10.13228/j.boyuan.issn0449-
532	749x.2006.02.019
533	Zhuozhi Wang; Rui Sun; Yaying Zhao; Yupeng Li; Xiaohan Ren (2019) Effect of steam concentration on
534	demineralized coal char surface behaviors and structural characteristics during the oxy-steam combustion
535	process. Energy 174: 339-349 http://doi.org/10.1016/j.energy.2019.02.187
536	Zhang, Shu, Min, Zhenhua, Tay, Hui-Ling, Asadullah, Mohammad, Li, Chun-Zhu (2010) Effects of
537	volatile-char interactions on the evolution of char structure during the gasification of Victorian brown
538	coal in steam. FUEL 90(4): 1529-1535 http://doi.org/10.1016/j.fuel.2010.11.010
539	
540	