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# Effect and Mechanism of CaO on Iron Recovery and Desulfurization by Reduction Roasting-Magnetic Separation of High-Sulfur Cyanide Tailings

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**Abstract:** The increasing demand for iron ore in the world causes the continuous exhaustion of mineral resources. The utilization of iron in secondary resources has become of focus. The present study was carried out to recover iron from high-sulfur cyanide tailings by coal-based reduction roasting-magnetic separation. The mechanism of CaO to increase iron recovery and reduce sulfur was investigated by observing CO and CO<sub>2</sub> gas composition produced by the reaction, mineral composition and microstructure, distribution characteristics of sulfur, and the intercalation relationship between iron particles and gangue minerals. The results showed that the addition of CaO could increase the gasification rate of the reducing agent, increase the amount of CO<sub>2</sub> gas produced, promote the reduction of iron minerals, and improve the metallization degree of iron. When CaO was not added, sulfur was mainly transformed into troilite, which was closely connected with iron particles and was difficult to remove by grinding and magnetic separation. With the addition of CaO, CaO preferentially formed oldhamite with active sulfur, which reduced the formation of troilite. Oldhamite was basically distributed in an independent gangue structure. There was a clear boundary between iron particles and gangue minerals. Oldhamite could be removed by grinding-magnetic separation.

Keywords: cyanide tailings; reduction roasting-magnetic separation; CaO; troilite; oldhamite

# 1. Introduction

The increasing demand for iron ore in the world causes the continuous exhaustion of mineral resources [1]. High-grade iron ore resources are decreasing [2]. Accordingly, many researchers are focused on the use of secondary sources of iron [3,4].

According to incomplete statistics, the annual discharge of cyanide tailings from Chinese gold smelting enterprises has exceeded 20 million tons [5]. Based on the different cyanide leaching processes, cyanide tailings can be divided into heap leaching tailings, full mud cyanide tailings, concentrate cyanide tailings, oxidation roasting-cyanide tailings, etc. [6]. Cyanide tailings often contain harmful substances such as cyanide and arsenic, which are harmful to the environment [7–9]. Some scholars have conducted research on the harmlessness of cyanide tailings and achieved good results [10–13]. In addition, the proportion of oxidation roasting-cyanide tailings is relatively large, reaching more than 30% of the cyanide tailings. Chemical analysis shows that there is a large quantity of iron minerals in oxidation roasting-cyanide tailings (hereinafter referred to as "cyanide tailings"). The iron grade is often higher than 30%, and some are even higher than 45% [14]. Therefore, cyanide tailings have great potential as an available secondary resource in iron recovery [15,16]. However, for technical and economic reasons, cyanide tailings are still mainly stored and currently only used as ingredients [17,18]. The storage of a large amount of cyanide tailings causes a great waste of resources [19].



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Phase analysis indicated that iron minerals in the cyanide tailings were mainly hematite. There was often more than 0.8% sulfur in the cyanide tailings, and sulfur was mainly in the form of sulfide. Studies have shown that the reduction roasting-magnetic separation technique is an effective method for treating cyanide tailings to recover iron [20–24]. According to the different degree of reduction of iron minerals, the magnetic separation product can be divided into iron concentrate and reduced iron [25,26]. Some researchers have used the reduction roasting-magnetic separation process to treat the cyanide tailings and obtained iron concentrate with higher iron grades under optimal conditions [27–29]. The thermodynamic reaction law of the iron-containing compound in the reduction roasting process of cyanide tailings was also revealed [30]. Some scholars have obtained reduced iron products with an iron grade greater than 90% by the reduction roasting-magnetic separation process [31–35]. However, the common problem is that the reduced iron products often contain higher sulfur. When reduced iron is used as a raw material for blast furnace ironmaking, almost all the sulfur will be concentrated in molten iron. Therefore, desulfurization is important for the effective utilization of high-sulfur cyanide tailings.

Researchers used calcium oxide or calcium carbonate as additives to carry out the study of iron extraction and sulfur reduction in cyanide tailings and found that adding CaO effectively improved iron reduction and decreased the sulfur content in reduced iron products [36–38]. However, how CaO affects the gasification rate of the reducing agent has not been reported yet. Moreover, the phase transition law of sulfur during the reduction roasting of cyanide tailings remains unknown.

Therefore, in this work, the mechanism of CaO in reduction roasting was investigated using the CO and CO<sub>2</sub> gas composition produced by the reaction, total reaction gasification rate, mineral composition and microstructure, distribution characteristics of sulfur, and intercalation relationship between iron particles and gangue minerals, for which the roasting temperature and time were 1150 °C and 40 min, and bituminous coal was 20 wt%. It is expected that the present research will provide theoretical guidance for desulfurization in treating high-sulfur cyanide tailings.

## 2. Materials and Methods

# 2.1. Cyanide Tailings

The cyanide tailings used in this study were sampled from a gold smelter (Shandong Province, China). The results of main chemical element/oxide analysis are shown in Table 1. The total iron grade and sulfur grade of cyanide tailings are 48.05% and 1.05%, respectively. Cyanide tailings contain SiO<sub>2</sub> (20%), Al<sub>2</sub>O<sub>3</sub> (5.38%), and Na<sub>2</sub>O (3.48%), respectively. Iron is the main recycling valuable element. Sulfur may affect the quality of iron products. The results of X-ray diffraction (XRD) analysis (Rigaku Corporation, Akishima-shi, Japan) are presented in Figure 1. Combined with microscope observation results and Figure 1, cyanide tailings were mainly composed of hematite, magnetite, quartz, albite, potassium feldspar, and pyrite.

Table 1. Results of main chemical element/oxide analysis on cyanide tailings.

Element/Oxide	TFe	S	Р	SiO <sub>2</sub>	$Al_2O_3$	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O
Content (wt%)	48.05	1.05	0.02	20.00	5.38	0.78	0.69	3.48	0.73

The results of a chemical-phase analysis of iron are shown in Table 2. From Table 2, iron mainly existed in the form of hematite and magnetite, with distributions of 92.48% and 3.27%, respectively. Iron in iron oxide was mainly recovered by reduction roasting-magnetic separation. The results of chemical-phase analysis of sulfur are shown in Table 3. As shown in Table 3, sulfur mainly existed in the form of pyrite, with a distribution of 96.23%.



Figure 1. Results of XRD analysis of cyanide tailings.

Distribution Phase	Iron in Magnetite	Iron in Hematite	Iron in Pyrite	Other Iron	Total
Content (wt%)	1.57	44.40	0.89	1.15	48.01
Distribution (%)	3.27	92.48	1.85	2.40	100.00

Table 2. Results of iron phase analysis on cyanide tailings.

Table 3. Results of sulfur phase analysis on cyanide tailings.

Distribution Phase	Sulfur in Pyrite	Sulfur in Sulfate	Total
Content (wt%)	1.02	0.04	1.06
Distribution (%)	96.23	3.77	100.00

# 2.2. Reductant and Additive

Bituminous coal was chosen as the reductant. The results of a bituminous coal industry analysis are presented in Table 4. The additive calcium oxide (CaO) is chemically reagent grade from Sinopharm Group Chemical Reagent Co., Ltd (Shanghai, China).

Table 4. Results of industry analysis on bituminous coal (wt%).

Moisture	Ash	Volatile Component	Fixed Carbon
1.42	9.17	33.68	55.73

# 2.3. Testing Method

The steps of reduction roasting-magnetic separation tests of cyanide tailings were as follows: (1) mixing; (2) reduction roasting; (3) grinding and magnetic separation; and (4) analysis. The process flowsheet is shown in Figure 2. The specific operation process was as follows.



Figure 2. Experimental procedure for reduction roasting-magnetic separation process of cyanide tailings.

(1) Mixing. Cyanide tailings (40 g), bituminous coal (20 wt%), and a certain proportion of CaO were accurately weighed. The samples were fully mixed.

(2) Reduction roasting. The samples were loaded into the corundum crucibles (height of 80 mm and internal diameter of 77mm). The reduction roasting tests were carried out in the shaft furnace. When the furnace temperature rose to the preset reduction temperature of 1150 °C, 5 L·min<sup>-1</sup> of N<sub>2</sub> was introduced to remove the air in the shaft furnace. When the flue gas analyzer showed that the O<sub>2</sub> in the furnace was zero, the corundum crucible was hung into the shaft furnace. Then, the N<sub>2</sub> flow rate was reduced to 3 L·min<sup>-1</sup>. The volumetric concentration of CO and CO<sub>2</sub> gas produced by the reaction was measured and recorded in real time by the flue gas analyzer. When the set reduction time was reached, the hanging corundum crucible was taken out, and the roasted products were cooled to room temperature.

(3) Grinding and magnetic separation. The grinding and magnetic separation process was two-stage grinding and two-stage magnetic separation. The first-stage grinding fineness was -0.074 mm 85% and the strength of magnetic field was  $112 \text{ kA} \cdot \text{m}^{-1}$ . The second-stage grinding fineness was -0.043 mm 80%, and the magnetic field strength was 96 kA·m<sup>-1</sup>. The main grinding and magnetic separation equipment used were a RK/BK three-roll four-tube smart rod mill and a CXG-99 magnetic separator (Tianjin Hualian Mining Instrument Co. Ltd., Tianjin, China). The resulting magnetic product was called powder direct reduced iron product, or "reduced iron" for short.

(4) Analyses. S and Fe grade in the roasted products and the reduced irons were examined by infrared absorption method and titrimetric method, respectively. The iron metallization degree was calculated according to Equation (1):

$$\eta = \frac{MFe}{TFe} \times 100\% \tag{1}$$

where  $\eta$  is the iron metallization degree (%), MFe is the mass content of metallic iron of the roasted products (%), and TFe is the total iron grade of the roasted products (%). A part of the roasted products was pulverized to -0.074 mm and analyzed by XRD (Rigaku D/Max 2500, Rigaku Corporation, Akishima-shi, Japan) and phase analysis of sulfur. The other part of the roasted products was made into polished sections for observing microstructure by SEM-EDS (Vega 3 XHU, Tescan Co. Ltd., Brno, Czech Republic). The microstructure of the reduced irons was also observed by SEM.

# 3. Results and Discussion

#### 3.1. The Influence of CaO on Reducing Atmosphere

It is generally accepted that the reduction effect in the direct reduction of materials is mainly the CO gas produced by the gasification reaction of fixed carbon. At the same time, there is a partial pressure balance of CO and  $CO_2$  in the reaction system. When the partial pressure of  $CO_2$  generated by the reduction reaction exceeds the equilibrium partial pressure of  $CO_2$  of the Boudouad reaction, the  $CO_2$  in the system will react with the fixed carbon to generate CO, and then the generated CO will further react with  $Fe_xO_y$ , and the cycle is repeated [39–41]. When the mass fraction of CaO was 0, 5 wt%, 10 wt%, and 15 wt%, the gas composition of CO and  $CO_2$  produced by direct reduction roasting of cyanide as a function of roasting time were studied.

It can be seen from Figure 3 that the CO and CO<sub>2</sub> generated by the reduction roasting reaction of cyanide tailings had the same changing law when the mass fraction of CaO was different. CO<sub>2</sub> gas was produced first, and then CO started to be produced. With the acceleration of the gasification reaction, the amount of CO produced was much greater than the amount of CO<sub>2</sub> produced. When the mass fraction of CaO was 5 wt%, 10 wt%, and 15 wt%, the amount of CO<sub>2</sub> produced was higher than that when CaO was not added. The results show that adding CaO in the reduction roasting of cyanide tailings could promote the production of CO<sub>2</sub> gas.



**Figure 3.** Effect of the added amount of CaO on the gas composition of CO<sub>2</sub> and CO. (**a**) 0 wt% CaO; (**b**) 5 wt% CaO; (**c**) 10 wt% CaO; (**d**) 15 wt% CaO.

Figure 4 shows that as the added amount of CaO increased, the gasification rate of the total reaction gradually increased in the early stage of the reduction reaction of cyanide tailings (0–10 min). It shows that adding CaO could increase the gasification rate of the reducing agent bituminous coal; that is, reaction (2) increased the amount of CO gas produced. It was beneficial to reaction (3) (T represents the sample), resulting in an increase in the amount of CO<sub>2</sub> gas produced. In the late stage of the cyanide tailings reduction reaction (10–40 min), the gasification promotion effect of CaO on bituminous coal was

weak. This may be due to the gradual reduction in bituminous coal consumption as the reduction reaction progresses.



Figure 4. Effect of the added amount of CaO on the gasification rate.

Figure 5 shows that the addition of CaO increased the metallization degree of iron. The metallization degree of iron was 89.79%, 91.90%, 93.25%, and 94.12%, respectively. This also further confirmed that adding CaO promoted the reduction of iron oxides and generated more  $CO_2$  gas.

$$C + CO_2 \rightarrow 2CO$$
 (2)

$$T + CO \rightarrow reducedT + CO_2$$
 (3)



Figure 5. Effect of the added amount of CaO on the metallization degree of the reduced samples.

## 3.2. The Influence of CaO on the Mineral Compositions of the Roasted Products

Under the conditions of different CaO dosage, 20 wt% bituminous coal addition, roasting temperature of 1150 °C, and roasting time of 40 min, the roasted products were obtained. The phase transition behavior of the roasted products was analyzed by XRD. The results are presented in Figure 6.



**Figure 6.** XRD patterns of roasted products under the different added amounts of CaO. 1—Metal iron (Fe); 2—Quartz (SiO<sub>2</sub>); 3—Oldhamite (CaS); 4—Troilite (FeS); 5—Wollastonite (Ca<sub>3</sub>Si<sub>3</sub>O<sub>9</sub>); 6—CaO.

Figure 6 shows that when CaO was not added, the roasted product was mainly composed of metallic iron and quartz and a small amount of troilite. The results indicate that hematite and magnetite were reduced to metallic iron.

The high-temperature reducing atmosphere converted pyrite into troilite, volatilized gaseous elemental sulfur ( $S_2$ ), and gaseous carbonyl sulfide (COS), as in Equations (4) and (5) [42]:

$$2FeS_2 = 2FeS + S_2(g) \tag{4}$$

$$FeS_2 + CO = FeS + COS(g)$$
(5)

The reduced metallic iron reacted with gaseous elemental sulfur  $(S_2)$  to form troilite, as in Equation (6):

$$2Fe + S_2(g) = 2FeS \tag{6}$$

When the amount of CaO was 5 wt%, the roasted product mainly consisted of metallic iron and quartz, as well as a small amount of troilite and oldhamite. Compared with no CaO, the diffraction peak intensity of metallic iron was enhanced, the diffraction peak intensity of troilite was weakened, and oldhamite appeared newly. This shows that CaO promoted the transformation of iron oxide to metallic iron. In a reducing atmosphere, CaO reacted with the active sulfur [S] generated in the roasting process to form the oldhamite (CaS), which reduced the formation of troilite, as in Equations (7) and (8) [43]. However, in the literature [37], in addition to the formation of oldhamite, there was also a formation of jasmundite (Ca<sub>11</sub>(SiO<sub>4</sub>)<sub>4</sub>O<sub>2</sub>S), which was mainly due to the different types of coal.

$$CaO(s) + [S] = CaS(s) + [O]$$
(7)

$$CaO(s) + [S] + C(s) = CaS(s) + CO(g)$$
(8)

When the amount of CaO was increased to 10 wt%, the roasted product was mainly composed of metallic iron and quartz, as well as a small amount of troilite, oldhamite, and wollastonite. Compared with the addition of 5 wt% CaO, the diffraction peaks of metallic iron and oldhamite were further enhanced, the diffraction peaks of quartz and troilite were further weakened, and wollastonite appeared newly. It shows that in addition to the

reaction of CaO with active sulfur [S] to form oldhamite, CaO also reacted with quartz to form wollastonite, as Equation (9):

$$CaO + SiO_2 = CaSiO_3 \tag{9}$$

When the amount of CaO was increased to 15 wt%, the roasted product was mainly composed of metallic iron and quartz, a small amount of troilite, oldhamite, wollastonite, and calcium oxide. Compared with the 10 wt% CaO dosage, the diffraction peak of oldhamite was further enhanced, and the intensity of the diffraction peak of troilite was further weakened. The results show that reactions (7) and (8) were further enhanced, while suppressing the occurrence of reaction (6). The appearance of CaO indicated that calcium oxide remained.

# 3.3. The Influence of CaO on the Distribution of Sulfur in the Roasted Products

In order to reveal the law of sulfur conversion during the roasting process, the roasted products under different CaO dosage were analyzed for sulfur phases. The results are shown in Figure 7.



Figure 7. Sulfur phase composition of roasted products under different CaO dosage.

Figure 7 presents that when no CaO was added for roasting, the sulfur in the roasted product mainly occurred in the form of troilite and sulfate, and the distribution ratio of sulfur was 95.15% and 4.85%, respectively. It shows that the sulfur in the pyrite after reduction roasting mainly produced troilite; that is, reactions (4)–(6) occurred. When the amount of CaO was 5 wt%, the distribution ratio of sulfur in oldhamite and troilite was 68.27% and 26.92%, respectively. This was because CaO and gaseous sulfur reacted (7) and (8) to produce oldhamite, which inhibited the progress of the reaction (6) between gaseous sulfur and metallic iron. As the amount of CaO continued to increase, the sulfur in the oldhamite gradually increased, and the sulfur in the troilite gradually decreased. When the amount of CaO was 15 wt%, the distribution ratio of sulfur in oldhamite rose to 91.27%, and the distribution ratio of sulfur in troilite decreased to 4.85%. The results revealed that reactions (7) and (8) were further enhanced, and reaction (6) was further suppressed.

#### 3.4. The Influence of CaO on the Microstructure of the Roasted Products

The SEM images of the roasted products with additive CaO dosages of 0, 5 wt%, 10 wt%, and 15 wt% are shown in Figure 8. The SEM-EDS images and elemental surface scanning images of the roasted products without CaO and with 15 wt% CaO are shown in Figure 9 and Table 5.

**Figure 8.** SEM images of roasted products under different CaO dosage. (**a**) 0 wt% CaO; (**b**) 5 wt% CaO; (**c**) 10 wt% CaO; (**d**) 15 wt% CaO.

Point	С	S	Ca	Fe	Phase
1	0.27	36.17	0.25	63.31	Troilite
2	0.18	44.10	54.97	0.75	Oldhamite

Table 5. Chemical composition of points indicated in Figure 9 (wt%).

It can be seen from Figures 8 and 9 and Table 5 that the sulfur-containing minerals in the roasted products were mainly troilite in the absence of CaO. These troilite were closely connected with iron particles and were difficult to effectively remove by grinding and magnetic separation, resulting in high sulfur content in reduced iron products. The sulfur-containing minerals in the roasted products after adding CaO were mainly oldhamite. This oldhamite was distributed in independent gangue structures, and the amount closely connected with metallic iron particles was very small. It was easy to remove in the grinding and magnetic separation process, thereby reducing the sulfur content in the reduced iron product. The iron particles when CaO was not added were larger than those after CaO was added, indicating that the addition of CaO was not conducive to the melting and aggregation of iron particles.

When the amount of CaO was 15 wt%, the inclusion structure of some gangue minerals can be clearly seen in the roasted products, as shown in Figure 10 and Table 6. Figure 10 and Table 6 showed that the thin layer outside of the package was mainly gangue minerals such as wollastonite, and the middle package was mainly oldhamite. These inclusions and iron particles were not intercalated with each other. So, they were easily removed through the grinding and magnetic separation process.



**Figure 9.** SEM-EDS images and elemental surface scanning images of roasted products without CaO and with 15 wt% CaO. (**a**) SEM-EDS images without CaO, "+" refers to analyzed point by EDS, numbers refer to composition data in Table 5; (**b**) SEM-EDS images with 15 wt% CaO; (**c**) elemental surface scanning images of (**a**); (**d**) elemental surface scanning images of (**b**).



**Figure 10.** SEM-EDS images and elemental surface scanning images of roasted products with 15 wt% CaO. (a) SEM-EDS images with 15 wt% CaO; (b) the structure of magnified inclusion, "+" refer to analyzed point by EDS, numbers refer to composition data in Table 6; (c) elemental surface scanning images of (a).

Point	0	S	Ca	Si	Fe	Phase
1	-	44.69	54.92	0.39	-	Oldhamite
2	41.02	-	34.40	24.21	0.37	Wollastonite

**Table 6.** Chemical composition of points indicated in Figure 10 (wt%).

# 3.5. The Influence CaO on Iron Recovery and Sulfur Reduction

To observe the influence of CaO on the reduction roasting-magnetic separation of cyanide tailings, reduction roasting-grinding-magnetic separation tests were carried out. Figure 11 shows that, under the conditions of 20 wt% bituminous coal, 1150 °C reduction temperature, and 40 min reduction time, with the increase in CaO addition, the iron grade of reduced iron gradually decreased, the iron recovery gradually increased, and the grade of sulfur greatly decreased. When CaO was not added, the sulfur grade in reduced iron was as high as 0.49%, and the iron grade and iron recovery were 92.64% and 88.73%, respectively. When CaO was added at 5 wt%, the sulfur grade dropped to 0.21%, and the iron grade and iron recovery were 91.59% and 90.80%, respectively. When the amount of CaO added was 15 wt%, the sulfur grade dropped to 0.06%, and the iron grade and iron recovery were 90.68% and 92.71%, respectively. The above results show that the addition of CaO promoted iron reduction, increased iron recovery, and decreased sulfur grade in reduced iron products. The quality of reduced iron met steelmaking requirements.



Figure 11. Effect of the different added amounts of CaO on reduction iron product index.

SEM analysis was performed on the reduced iron products obtained without CaO and 15 wt% CaO, as shown in Figures 12 and 13 and Tables 7 and 8. Figure 12 and Table 7 show that, after grinding and magnetic separation, the reduced iron product without CaO contained more sulfur (troilite). The troilite and metallic iron particles were densely embedded, and it was not easy to realize the monomer dissociation through the grinding process. The troilite could not be effectively removed by the magnetic separation process, which affected the quality of the reduced iron. Figure 13 and Table 8 show that there was almost no sulfur content in the reduced iron product after adding 15 wt% CaO. The results revealed that the oldhamite was easily removed by grinding and magnetic separation, which greatly reduced the sulfur content of the reduced iron product.



**Figure 12.** SEM-EDS images and elemental surface scanning images of reduced iron products without CaO. (a) SEM-EDS images, "+" refer to analyzed point by EDS, numbers refer to composition data in Table 7; (b) elemental surface scanning images of (a).



**Figure 13.** SEM-EDS images and elemental surface scanning images of reduced iron products with 15 wt% CaO. (**a**) SEM-EDS images, "+" refer to analyzed point by EDS, numbers refer to composition data in Table 8; (**b**) elemental surface scanning images of (**a**).

Point	С	S	Ca	Si	Fe	Phase
1	6.60	-	-	0.92	92.48	Iron
2	0.44	36.42	0.03	-	63.11	Troilite

**Table 7.** Chemical composition of points indicated in Figure 12 (wt%).

Table 8. Chemical composition of points indicated in Figure 13 (wt%).

Point	С	Si	Fe	Phase
1	6.11	0.84	93.05	Iron
2	6.53	0.71	92.76	Iron

# 4. Conclusions

(1) The direct reduction reaction of cyanide tailings first produced  $CO_2$  gas and then started to produce CO. With the acceleration of the gasification reaction, the amount of CO produced was much greater than that of  $CO_2$ . CaO increased the gasification rate of bituminous coal and promoted the reduction of iron minerals as well as the metallization rate of iron.

(2) In the absence of CaO, the sulfur minerals in the cyanide tailings were transformed into troilite, which were closely connected with iron particles and were difficult to remove by grinding and magnetic separation. With the addition of CaO, CaO preferentially reacted with active sulfur to form oldhamite, which inhibited the formation of troilite. There was a clear boundary between oldhamite and iron particles. Oldhamite was removed by grinding and magnetic separation.

(3) The addition of CaO improved the effect of reduction roasting-magnetic separation of cyanide tailings. Under the conditions of 20 wt% bituminous coal, 15 wt% CaO, 1150 °C reduction temperature, and 40 min reduction time, the reduced iron index of 90.68% iron grade, 0.06% sulfur grade, and 92.71% iron recovery rate was obtained. The reduced iron product can be used for subsequent steelmaking.

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