Research on Utilization of Flue Gas From Titanium Slag Smelting in the Closed Electric Arc Furnace

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Abstract. According to the nature of the tail gas produced from titanium slag smelting process in the closed electric arc furnace, the feasibility of the tail gas utilization scheme is discussed for the titanium slag smelting environment, and the purification process and utilization scheme of the tail gas from titanium slag smelting are introduced. The purified electric furnace tail gas is used for preheating the titanium concentrate raw materials, which can save 15-20% of electric energy and reduce production costs.

1. Introduction
Titanium slag is a high-quality raw material for the production of titanium dioxide and titanium sponge. In the smelting process of a closed DC electric furnace, titanium slag produces a large amount of flue gas. Its main components are CO, CO₂, N₂, H₂ and SO₂. The volume content of CO is 60-90%, which is toxic, flammable and explosive. The flue gas also contains a large amount of soot, and the soot is mainly oxides of titanium and iron. The random discharge of electric furnace exhaust gas will pollute the environment and so to be treated. Due to the high content of CO in the exhaust gas, the combustion heat of CO is 283.0kJ/mol. Most companies use combustion exhaust gas, which not only wastes energy but also pollutes the environment. The world's total anthropogenic carbon monoxide CO emissions are 300 to 400 million tons per year, and China’s total anthropogenic CO emissions have shown a continuous growth trend, with an average annual growth rate of 3.53%, of which industrial process sources are the main source of emissions. Its emissions account for about 42% of the total emissions [1]. It’s a lot of waste. A 250 KVA electric furnace loses 270 tons of standard coal every year. In recent years, the loss of standard coal due to exhaust emissions and combustion is about 2 million tons in China [2]. Therefore, looking for economically reasonable and technically feasible ways to utilize the tail gas of the closed electric furnace of titanium slag is not only beneficial to the safe production of the titanium smelting process, but also has a good energy saving and emission reduction significance.
2. The gas properties of titanium smelting in a closed electric arc furnace

The process of producing titanium slag by the electric furnace method is: ilmenite and anthracite or petroleum coke and other reducing substances are added to the electric furnace for reduction smelting. The main oxides in the ilmenite are selectively reduced to metallic iron, the oxides of titanium concentrated in the slag, two stages in the reduction of ilmenite. The first is Fe$^{+3}$$\rightarrow$Fe$^{+2}$, that is, the pseudo rutile in the mine (Fe$_2$Ti$_3$O$_9$ or Fe$_2$O$_3$$\cdot$3TiO$_2$) is reduced to ilmenite and rutile:

$$Fe_2TiO_3O_9 + C = 2FeTiO_3 + TiO_2 + CO$$

(1)

The first stage of reduction is easy to proceed, and it can be completed in a short time even at low temperatures, such as 900°C.

The second stage of reduction is Fe$^{+2}$$\rightarrow$Fe$^{0}$, and this stage of reduction is more complicated. Although at a lower temperature, FeTiO$_3$ can be reduced to rutile or metal iron, but when the temperature is higher than 1100°C, FeTiO$_3$ is reduced to produce ferrous brookite (FeTi$_2$O$_5$) to precipitate metal iron:

$$2(FeTiO_3) + C = FeTi_2O_5 + Fe + CO$$

(2)

The stable temperature of ferrous brookite is higher than 1150°C, but the solid solution of MgO and MO in the ore increases the stability of FeTi$_2$O$_5$. If the FeTiO$_3$ in the ore is completely reduced to FeTi$_2$O$_5$ according to the reaction formula (2), a partial reduction of TiO$_2$ occurs, that is, reaction (2) is carried out at the same time as reaction (3).

$$\frac{x}{2}Fe_2TiO_5 + 5(\frac{x}{2} - 1) = Fe_3-xTi_xO_5 + 3(\frac{x}{2} - 1)Fe + 5(\frac{x}{2} - 1)CO$$

(3)

Due to the gasification reaction of carbon, part of the reducing agent added to the electric furnace will also produce CO, and CO will also participate in the reduction reaction. Due to the higher temperature in the furnace, the reduction effect of CO will be strengthened [3], the closed electric furnace is conducive to the reduction reaction, but also brings the problem of a large amount of CO emissions in the tail gas. The flow chart of titanium slag production process is shown in Figure 1.

![Flow chart of ilmenite smelting in high-power large-closed DC arc furnace.](image-url)

According to the process conditions, the main component of the flue gas of the electric furnace is CO gas, the dust concentration is 5-15g/Nm$^3$, the flue gas temperature is 1775°C, the average gas volume at the furnace outlet is 5723Nm$^3$/h, and the flue gas composition is shown in Table 1.
Table 1. Electric furnace flue gas composition table

| Composition | CO  | CO₂ | O₂ | H₂ | H₂O | SO₂ | N₂ | Total |
|-------------|-----|-----|----|----|-----|-----|----|-------|
| % (v/v)     | 89.42 | 7.4 | 0.00 | 1.78 | 0.00 | 1.00 | 0.4 | 100   |

CO is the main component of the flue gas of the closed electric furnace, the content can reach 84-96%, and it has a high combustion calorific value. After purification, it is burned and utilized at the terminal of use and converted to CO₂. According to production experience, the feed ratio is 0.14, that is, 0.14t anthracite to 1t of ilmenite. After calculation, the amount of CO produced is about 17.7% of the total amount of anthracite and ilmenite. Considering that due to the presence of volatile matter in anthracite coal and the presence of moisture in anthracite and ilmenite, the final flue gas still contains a certain amount of H₂. The charging process of the electric arc furnace is through the hollow electrode under nitrogen protection, so the final flue gas also contains a small amount of N₂. After fully considering the above factors, the final flue gas quality is about 20% of the total mass of the added materials. The flow diagram of flue gas emissions is shown in Figure 2. A gas storage tank is required to ensure the stable output and utilization of furnace gas.

Figure 2. Flue gas flow diagram

3. Main utilization methods and conditions of tail gas from titanium slag smelting in electric furnace

The calorific value of the tail gas of the titanium slag by the enclosed electric furnace is generally 800-12000 kJ/m³, which can generally be used as fuel or chemical raw material. As a fuel, it can be mainly input into a waste heat boiler to generate electricity after combustion, or input into an internal combustion engine to generate electricity. It can also be used in the drying process of raw and auxiliary materials in the production of titanium slag by the electric furnace method. As a raw material, CO is a widely used chemical raw material, which can produce important one-carbon chemical products such as CH₃O, CH₂O₂, C₂H₂O₂, C₃H₄O₃, CH₂O and (CH₂O)n.

According to the summary of Zhang Shaobo and others, the current utilization of tail gas from titanium slag smelting mainly includes:

3.1 Used as fuel for power generation

1) Power generation through waste heat boiler. This method makes full use of the sensible heat of the exhaust gas, the combustion heat of combustible gas and the combustion heat of some dust in the exhaust gas. The heat energy of the exhaust gas is converted into steam through the tube bundle in the
boiler to produce steam. The steam is used to drive the steam turbine and then drive the generator to generate electricity. This method is widely used in coke oven gas. This method has certain shortcomings and limitations: First, the operation of the boiler is completely affected by the operation of the electric furnace, and the boiler has many start and stop times, the operation rate is limited, and the steam supply cannot be stabilized; the second is that to have steam users, the supporting system is complicated, and the investment Large, thermal efficiency is only 20% to 25% [4-7].

2） Power generation by gas turbine. The method uses exhaust gas as the working medium, expands in the inner cavity after compression and heating, and converts part of the thermal energy into mechanical energy. Gas turbines are suitable for fuels with high hydrogen content, low heating value and gas containing more impurities. The power generation efficiency is generally 30% to 35%, and the generated waste heat flue gas temperature is as high as 450 to 550℃ [8-10].

The main problem with this method is that the gas turbine fuel intake pressure is relatively large. The more efficient the power generation unit, the higher the fuel intake pressure. The tail gas pressure from the closed electric furnace by smelting titanium slag is not high, which requires gas compressor and gas booster regulating delivery system. This method has higher requirements on the technical quality of the operators and requires more spare parts.

3） Power generation by gas internal combustion engine. This method is a new technology developed and applied in recent years. Its working principle is similar to that of a car engine. The exhaust gas is ignited by a spark plug to drive the piston to move. The working temperature of the core area in the cylinder of the internal combustion engine can reach 1400 ℃, making it more efficient than steam. The power generation efficiency of a gas internal combustion engine is usually between 30% and 40%. Its equipment is highly integrated and quick to install, low requirements for dust in the gas, basically no need for water, and the cost per kilowatt is relatively low of equipment. However, the one-time investment of gas internal combustion engines is very high, and the maintenance costs are also expensive. After being put into use, the oil and spark plugs need to be replaced frequently. In addition, for low-calorific value fuels, the output of internal combustion engine units is significantly reduced. At the same time, the incoming gas must not contain corrosive components to avoid corrosion of equipment [11-12].

3.2 Used as a heat source for titanium slag production
The production of titanium slag is a process of high energy consumption, and the drying of titanium concentrates, anthracite and other raw materials and titanium slag products in the production process requires a large amount of heat source. The exhaust gas of the electric furnace is used as the heat source fuel, which can be used nearby, directly reducing the energy consumption of the electric furnace. The exhaust gas of the electric furnace used for drying energy needs to be dedusted and purified first. At present, there are still some problems in the transportation process, there are also safety risks, and corresponding special equipment is required.

3.3 Used as a chemical raw material
The tail gas from the smelting of titanium slag in a closed electric furnace is used as a chemical raw material, and it first needs to be cleaned and purified. As a raw material for chemical production of synthetic ammonia and methanol, catalysts are needed. Even with trace impurities, catalyst poisoning may cause production stagnation. Purification and purification of tail gas from titanium slag smelting in a closed electric furnace is currently the biggest technical obstacle to chemical utilization.

The chemical production process of this technology is long and difficult, the investment is large, and the amount is large, so there are few examples of successfully using the tail gas of a closed electric furnace as a chemical raw material.

Considering the requirements of exhaust gas purification, exhaust gas utilization efficiency, technological maturity, investment situation and other advantages and disadvantages of the above schemes, combined with the production needs of titanium slag plants, it is a more feasible scheme to use as a heat source for the titanium slag production process.
4. Purification process of electric furnace flue gas

4.1 Selection of purification process for electric furnace flue gas

The tail gas produced by electric furnace titanium smelting slag contains more dust particles and SO₂, so it is generally subjected to dust removal and desulfurization treatment before use, there are mainly wet and dry treatments. At present, the most widely used and mature process in China is the wet purification process, and the representative wet processes are: two-tower one-stage process, two-stage one-tower process, washing machine process, etc. The purpose of flue gas purification can also be achieved by adopting the double-tower one-text process and the double-text one-tower process. From the use effect, these two methods require a large amount of equipment maintenance work, low operation efficiency, and poor performance reliability of supporting facilities.⁷¹³,¹⁴ A titanium industry company uses wet process technology to process flue gas. The washing machine process combines flue gas washing and flue gas pressurization. A washing machine is used to complete the pressurization and washing of furnace gas. It can guarantee safe and stable operation for more than ten years, with stable technology and simple equipment maintenance. The process has mature auxiliary equipment. The disadvantage is that the sewage treatment volume is large, but the sewage can be recycled.

4.2 Brief description of the purification scheme of electric furnace flue gas

Tyson washing machine process adopts wet purification technology to recover waste gas. The recovered waste gas is used for drying of anthracite and ilmenite, drying of titanium slag, baking of slag bag, etc. In order to meet the use requirements, a gas storage and distribution station needs to be configured for gas pressurization and transmission and distribution.

Brief description of the process flow: the high-temperature flue gas sent from the outlet of the electric furnace enters the quench cooler and the temperature is cooled to about 70°C; the cooled furnace gas enters the flue gas purification tower, and the purification tower washes the flue gas with water; the washed furnace gas Enter the Tyson washing machine to wash and pressurize the furnace gas twice, and the outlet is qualified gas. The air leakage rate of the entire system is 10%. The clean gas is sent to a gas storage tank, and then sent to users in each workshop with a pressurizer. The system is equipped with a safety relief valve and a gas relief tower, and uses meters to detect and control the CO and O₂ content. The gas tower is used to burn excess furnace gas. The flow chart of Flue gas treatment and use are shown in Figure 3.

The purified flue gas contains less than 30mg/Nm³ of dust and less than 300mg/Nm³ of sulfur dioxide, which meets the fuel gas requirements. The waste water produced in the purification process
is sent to the sewage treatment station, and the treated waste water is returned to the washing process for recycling.

The average gas supply of the furnace: 5900Nm3/h, and the gas consumption is shown in Table 2.

Table 2. Gas consumption balance sheet (Nm3/h)

| User unit               | Ilmenite drying | Anthracite drying | Slag bag preheating | Slag drying | Gas dispersal tower and others |
|-------------------------|-----------------|-------------------|---------------------|-------------|-------------------------------|
| Average gas consumption | 2470            | 210               | 690                 | 790         | 1740                          |

The purified electric furnace tail gas is mainly used for preheating titanium concentrate raw materials, which reduces the electricity consumption of electric furnace smelting. Using electric furnace tail gas as a heat source, preheating titanium concentrate raw materials to a temperature above 800°C, and then entering the electric furnace for smelting, which can save 15-20% of electric energy and reduce production costs.

5. Conclusion

CO is the main component of the flue gas of the closed electric furnace, and it has a high combustion calorific value. Considering the requirements of exhaust gas purification, exhaust gas utilization efficiency, technological maturity, investment situation and other advantages and disadvantages, combined with the production needs of titanium slag plants, it is a more feasible scheme to use as a heat source for the titanium slag production process. The tail gas produced by electric furnace titanium smelting slag contains more dust particles and SO2, there are safety risks, and corresponding special equipment must be used. The exhaust gas of the electric furnace used for drying energy needs to be dedusted and purified. The purification system of the flue gas of a company's DC electric arc furnace for titanium slag smelting adopts a spray cooling and dust scrubber system to reduce safety risks.

The flue gas after treatment and purification can be reused for raw materials drying, Slag bag preheating, which can save 15-20% of electric energy and reduce production costs.

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