

ENERGY ANALYSIS ON THE REDUCTION OF IRON FROM VANADIUM-EXTRACTED WASTE SLAG: COMPARISON OF BIOMASS AND DIFFERENT COALS

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In this paper, lignite, bituminous coal, anthracite, and biomass were used as reducing agents for carbon thermal reduction of vanadium-extracted waste slag. The energy consumption analysis and environmental impact assessment were carried out on the vanadium-extracted waste slag by reducing with different reducing agents via thermodynamic analysis, providing a reference for energy saving and emission reduction work.

Key words: iron, vanadium-extracted waste slag, reduction, energy consumption, environmental impact

INTRODUCTION

Vanadium titanomagnetite generates metallurgical slag enriched in vanadium, chromium, and iron in the smelting process referred to as vanadium slag [1,2]. Considering the recycling and utilization of valuable metals in vanadium-extracted waste slag, the current mainstream method is to extract valuable metals through reduction reactions of reducing agents and waste residue [3,4]. In this paper, four different reducing agents were selected to conduct the reduction process of vanadium extraction tailings. The thermodynamic reaction equilibrium components of vanadium-extracted waste slag and the differences in energy consumption and environmental pollution of different reductants were discussed.

METHODOLOGY

Raw materials

Vanadium-extracted waste slag in this paper is from an enterprise, Hebei Province, and its components are shown in Table 1.

The biomass used in this paper is a peanut shell from Hebei. Three typical coals (lignite, bituminous coal, and

Table 1 **Constituents of vanadium-extracted waste slag/ %**

Name	Fe ₂ O ₃	SiO ₂	TiO ₂	MnO	Cr ₂ O ₃
Content	49,37	14,93	12,17	8,32	7,58
Name	CrO ₃	Al ₂ O ₃	CaO	MgO	Na ₂ O
Content	0,60	3,55	1,65	1,09	0,74

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Table 2 **Ultimate analysis of biomass and three coals/ %**

	C	H	O	N	S
Biomass	47,22	5,66	46,12	0,93	0,08
Lignite	63,30	5,09	28,82	1,32	1,47
Bituminous coal	84,75	5,06	8,44	0,42	1,34
Anthracite	91,52	3,30	3,26	0,50	1,43

Table 3 **Proximate analysis of biomass and three coals/ %**

	Moisture	Ash	Fixed carbon	Volatile
Biomass	5,88	9,32	18,75	66,33
Lignite	3,13	32,77	49,80	14,30
Bituminous coal	10,72	29,44	51,98	7,86
Anthracite	0,34	5,37	80,95	13,34

anthracite) were also selected as reducing agents. The ultimate and proximate analyses of them are shown in Table 2 and Table 3.

Parameter definition

The oxygen absorption ratio (OAR) is defined as Formula (1) (content in the formula refers to molar amount), which refers to the ratio of the molar amount of carbon and hydrogen in the reducing agent minus the molar amount of oxygen to the molar amount of oxygen in the slag.

$$\text{OAR} = \frac{T_C + 1/2T_H - T_O}{\text{Content of metal oxide in waste slag of vanadium extraction}} \quad (1)$$

T_x is the amount of x element per kg of biomass, and x represents C, H, and O.

The metallization rate of metal, Formula (2) is the ratio of the amount of the metal element in the reduction product to the total amount of the metal element before reduction (mainly metal oxide) in vanadium-extracted waste slag.

$$\text{Metallization rate} = \frac{\text{Metal elemental content in the product}}{\text{Total amount of this metal element in waste slag}} \quad (2)$$

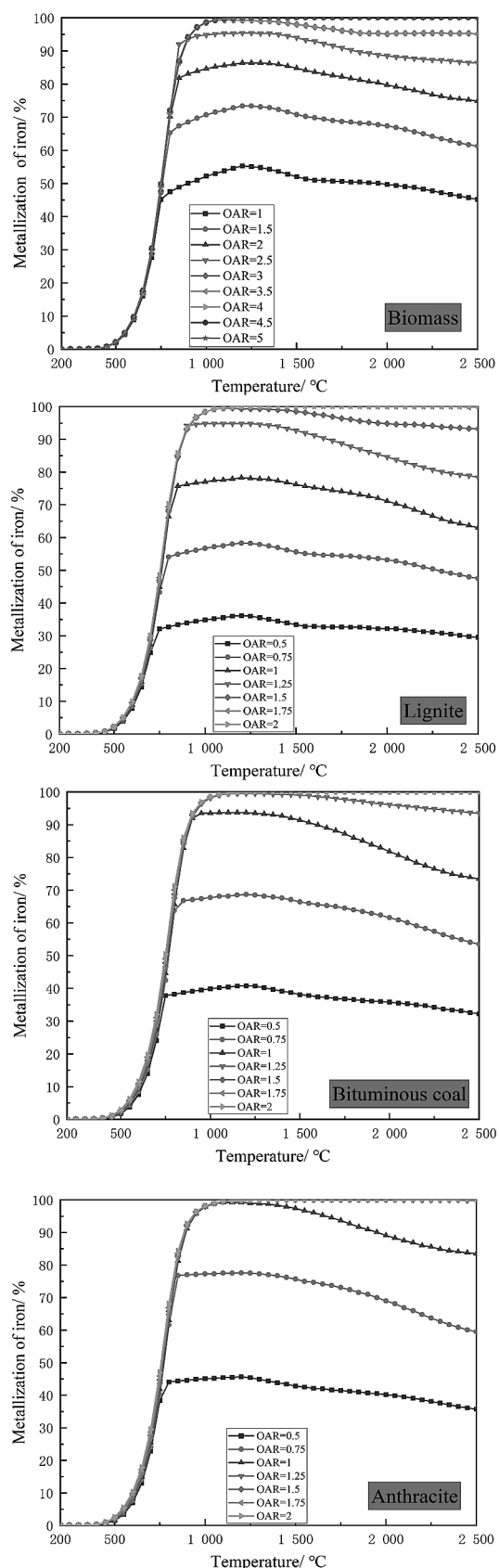


Figure 1 Variation of the iron metallization rate with the temperature at different OAR

Energy parameters

Q_1 , the physical heat of reaction, is defined as the heat required to raise the reactants from 25 °C to the reaction temperature.

Q_2 , the enthalpy change of reaction, is defined as the heat released by the reduction reaction of biomass and three coals with vanadium-extracted waste slag at the reaction temperature.

Q_3 , the heat generated by the combustion of reducing gas and air, is under the assumption of complete combustion and no loss of energy with the excess air consumption coefficient of 1,05.

Q_4 , the sum of physical heat of reaction (Q_1), the enthalpy change of reduction reaction (Q_2), and heat release from reduced gas and air combustion (Q_3) involved in the process of vanadium extraction from waste residue reduced by biomass.

COMPARATIVE ANALYSIS OF THE REDUCTION RESULTS

Figure 1 shows the variation of the iron metallization rate with the temperature at different OAR. For biomass, when the oxygen absorption ratio is 3, the reduction effect of iron reaches saturation, and then increasing OAR has almost no effect on the reduction rate of iron. For coals: when the OAR is less than 2, the iron metallization rate can be increased by increasing the OAR. When the OAR is 2, the reduction effect has reached a state of saturation, and a further increase of the OAR has almost no effect on the reduction rate of iron. According to the calculation results, the optimal OAR of biomass, lignite, bituminous coal, and anthracite is 3, 1,5, 1,25, and 1,25 respectively. In addition, with the increase in temperature, the iron metallization rate gradually increases and then decreases, reaching the maximum value at about 1 050 °C.

ENERGY CONSUMPTION ANALYSIS AND ENVIRONMENTAL IMPACT

Energy consumption analysis

Figure 2 shows the reduction process and the energy recovery and utilization scheme. It can be seen that after reduction, not only iron, chromium, and slag are produced, but also gas products are produced. The reducing gas is then mixed with air and burned to provide heat for the reduction reaction.

Assuming that the reducing gas and air are completely burned, the net energy consumption of the whole

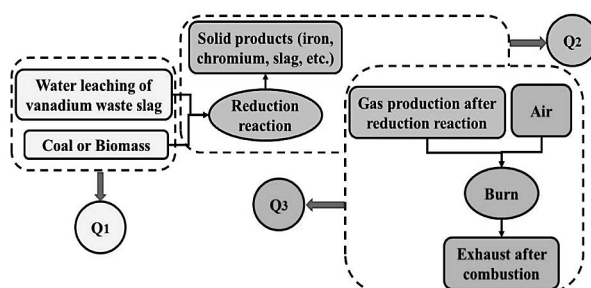


Figure 2 Recovery and utilization scheme of produced gas

Table 4 Energy budget of reduction reaction (KJ/mol)

Part	Q ₁	Q ₂	Q ₃	Q ₄	Mass(g)
Biomass	337,91	-74,12	1163,47	-899,68	93,50
Lignite	171,14	94,70	421,39	-155,55	60,31
Bituminous coal	137,97	139,44	256,06	21,35	40,1
Anthracite	132,34	139,08	239,74	31,68	40,2

reduction process is estimated with no loss of energy, which is denoted by Q_4 . $Q_4 = Q_1$ (Physical heat of reaction) + Q_2 (Enthalpy change of reaction) + Q_3 (Heat generation by combustion of reducing gas). The energy calculation results are shown in Table 4.

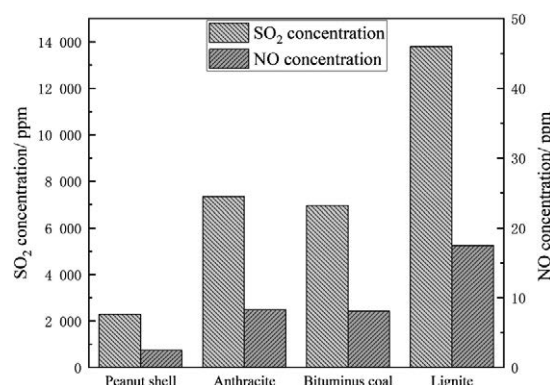
At the same time, the quality of the reducing agent required for reducing 100 g waste slag of vanadium extraction under the optimal working conditions is calculated according to the oxygen absorption ratio.

As can be seen from Table 4, without considering the heat loss and combustion efficiency was 100 %, the reduction of 100 g vanadium-extracted waste slag by biomass and lignite as reductants is exothermic as a whole, that is, there is no need to add extra heat. This means that the process can be realized without additional heat if the gas production is fully utilized. However, the reduction of 100 g vanadium-extracted waste slag by bituminous coal and anthracite requires 21,35 kJ and 31,68 kJ, respectively.

The heat released by the reaction of biomass and vanadium-extracted waste slag emits the most heat. Analyze the causes of this phenomenon: the biomass mass required for reducing 100 g of vanadium-extracted waste slag is 93,5 g, which is more than twice as much as 40,0 g of bituminous coal and anthracite. This makes the physical heat (heating biomass and waste residue of vanadium extraction to 1 050 °C) needed by reducing 100 g vanadium-extracted waste slag by biomass more than coal. This also makes the overall reduction enthalpy change negative, the reaction is exothermic. At the same time, biomass contains less carbon and more hydrogen, and the resulting gas contains more methane, and the calorific value of methane is high, which makes the combustion heat of the gas produced by biomass higher than that of coal.

Comparison of pollution emission

The reducing gas contains a large amount of CO, H₂, and other reducing gases, which can be recycled for heating the reduction process. It achieves the purpose of saving energy and reducing consumption, but the additional sulfur oxides and nitrogen oxides cause pollution to the environment. Therefore, it is necessary to compare the pollution gas generated after the complete combustion of the reducing gas. Assuming that the reducing gas can be completely burned at a high temperature (1 500 °C), the concentration of NO and SO₂ are mainly considered in this paper, as shown in Figure 3. The contents of SO₂ and NO generated by the combustion of the reductive gas produced by biomass are the lowest, indicating that biomass has advantages in re-

Figure 3 The concentration of NO & SO₂ in combustion tail gas

ducing sulfur oxide gas emissions compared with coal as a reducing agent.

CONCLUSION

In this paper, carbon thermal reduction of vanadium-extracted waste slag was conducted, through the comparison of three kinds of coals and a kind of biomass as reducing agents.

(1) The net energy consumption of the reduction process was estimated, and the results showed that without considering the energy loss, the reaction of vanadium-extracted waste slag reduced by biomass did not need to supplement the extra heat.

(2) The reducing gas produced in the reduction process was combusted to supply energy for the reduction process. For the produced flue gas, using biomass as a reducing agent has a relatively small environmental impact with less sulfur gas and nitrogen gas emissions, compared to those using coals.

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REFERENCES

- [1] P. Weber, R. Hurman Eric. The reduction of chromite in the presence of silica flux. *Minerals Engineering* 19(2006)3, 318-324.
- [2] X.S. Li, B. Xie, G.E. Wang, X.J. Li. Oxidation process of low-grade vanadium slag in presence of Na₂CO₃. *Transactions of Nonferrous Metals Society of China* 21(2011)8, 1860-1867.
- [3] H.F. Yang, L.L. Jing, B.G. Zhang. Recovery of iron from vanadium tailings with coal-based direct reduction followed by magnetic separation. *Journal of hazardous materials* 185(2011)2/3, 1405-1411.
- [4] H. Yang, L.L. Jing, J.J. Wang. Experiment of direct reduction iron with carbon from vanadium tailings. *Journal of vanadium and titanium steel* 34(2013)05,28-32.

Note: The responsible for English language is Z. Y. Wang.