

# THERMODYNAMIC ANALYSIS ON THE REDUCTION OF IRON AND CHROMIUM IN VANADIUM-EXTRACTED WASTE SLAG BY BIOMASS

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In this paper, the feasibility of carbon thermal reduction of vanadium-extracted waste slag with biomass as reducing agent was studied via thermodynamic analysis. The effects of oxygen absorption ratio, temperature and basicity on the reduction results, especially on the recovery of valuable metals (iron and chromium) were discussed emphatically.

*Key words:* vanadium-extracted waste slag; biomass; thermodynamic analysis; reduction

## INTRODUCTION

Vanadium titanomagnetite is one of the main raw materials for smelting valuable metals in metallurgical industry. Vanadium titanomagnetite generates metallurgical slag enriched in vanadium, chromium and iron in smelting process, referred to as vanadium slag. At present, most chemical and metallurgical enterprises only recycle and utilize vanadium from vanadium slag, accounting for 80 % of the global vanadium production [1-2]. The process of nitritization-water leaching-vanadium extraction is mainly adopted, and the solid waste produced after extraction of vanadium is just vanadium-extracted waste slag, containing a large amount of iron and chromium [3]. So, it is not a good choice in the long run to directly use vanadium-extracted waste slag in industrial products, which leads to waste of valuable metal resources and the existence of highly toxic  $\text{Cr}^{6+}$  [4-5]. Although some metal components can be recycled by leaching on some extent, other metal components can't be well utilized and the leaching wastewater needs to be further treated. As a kind of renewable energy, biomass not only has large reserve but also all the carbon elements in it come from the carbon dioxide in the atmosphere absorbed by plant photosynthesis. Therefore, compared with coal, biomass can be used for carbon thermal reduction and is considered to be an ideal reducing agent to replace coal to reduce other metals. In this paper, biomass was used to analyze the equilibrium products of carbon thermal reduction according to Gibbs free energy minimum principle.

## METHODOLOGY

### Raw materials

Vanadium-extracted waste slag selected in this paper is that by water leaching produced from an enter-

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

Name	$\text{Fe}_2\text{O}_3$	$\text{SiO}_2$	$\text{TiO}_2$	MnO	$\text{Cr}_2\text{O}_3$
Content	49,37	14,93	12,17	8,32	7,58
Name	$\text{CrO}_3$	$\text{Al}_2\text{O}_3$	CaO	MgO	$\text{Na}_2\text{O}$
Content	0,60	3,55	1,65	1,09	0,74

prise in Chengde, China and its components are shown in Table 1.

The biomass used in this paper is peanut shell also from Chengde. Its elemental compositions are shown in Table 2, and proximate analysis in Table 3.

Table 2 **Elemental analysis of biomass/%**

	C	H	O	N	S	Total
Biomass	47,22	5,66	46,12	0,93	0,08	100

Table 3 **Proximate analysis of biomass/%**

	Moisture	Ash	Fixed carbon	Volatile	Total
Biomass	5,88	9,32	18,75	66,33	100

## Parameter definition

The oxygen absorption ratio (OAR) is defined as Formula (1), 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 metal oxide in waste slag of vanadium extraction.

$$\text{OAR} = \frac{T_{\text{C}} + 1/2T_{\text{H}} - T_{\text{O}}}{\text{Content of metal oxide in waste slag of vanadium extraction}} \quad (1)$$

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

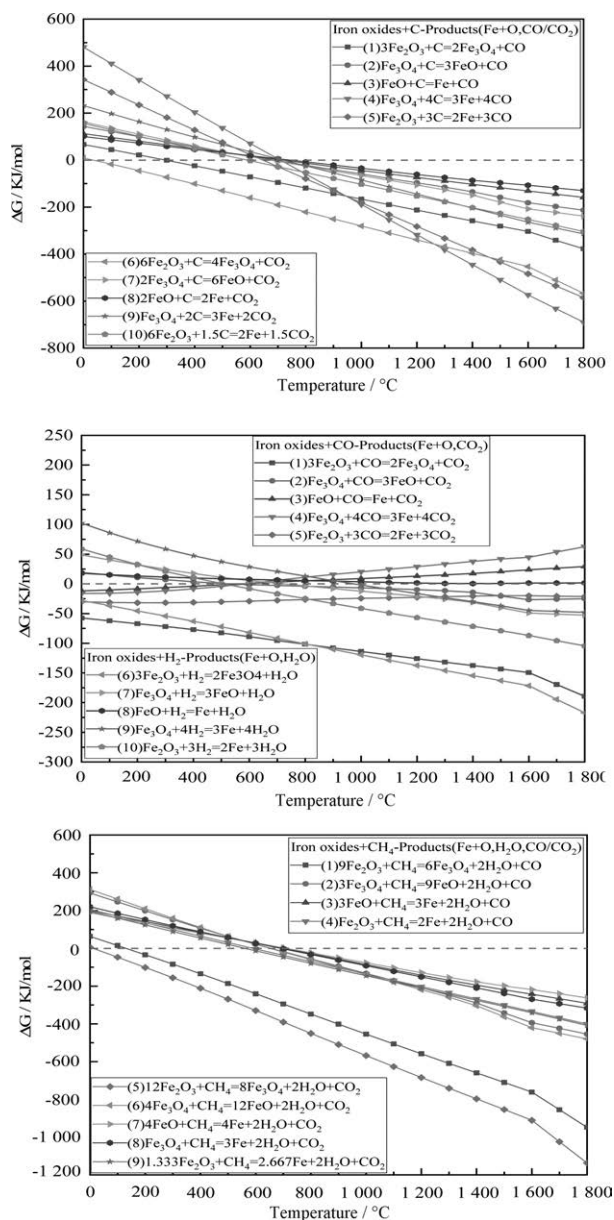
The metallization rate of a metal, Formula (2) is the ratio of the amount of the metal elemental in the reduction product to the total amount of the metal element before reduction (mainly metal oxide) in vanadium-extracted waste slag.

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

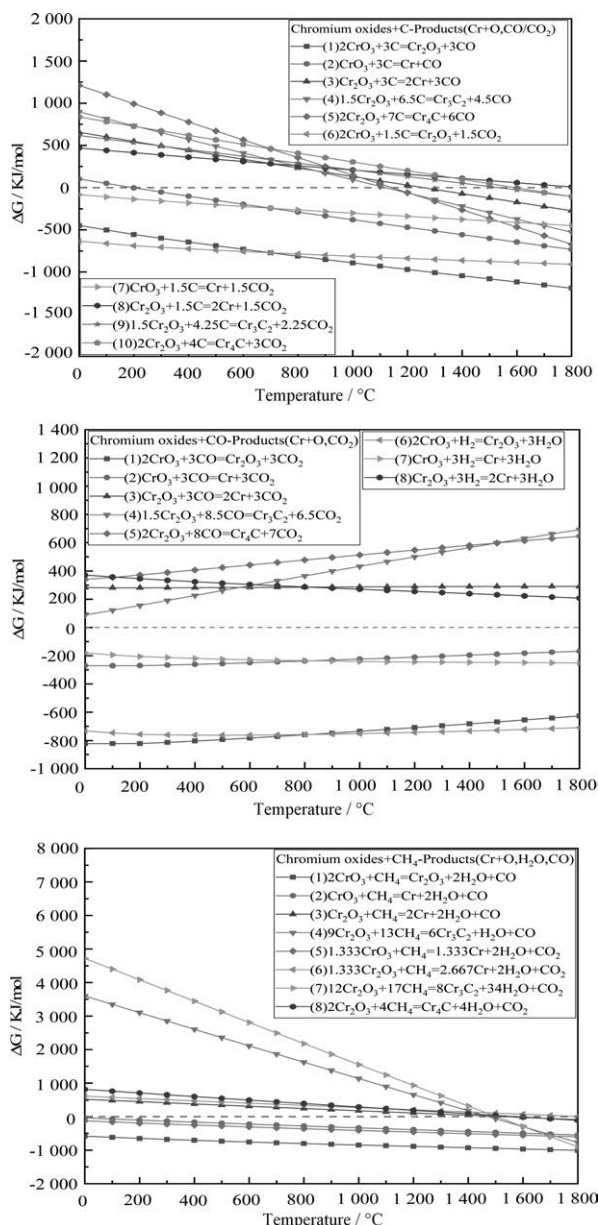
## GIBBS FREE ENERGY CHANGE OF MAIN REDUCTION REACTIONS

Under heating conditions, biomass is easily decomposed into solid carbon C and reducing gases such as CO, H<sub>2</sub> and CH<sub>4</sub>. Gibbs free energy change ( $\Delta G$ ) diagram of iron oxides reaction with these reductants are shown in Figure 1. When the temperature is lower than 700 °C, iron oxides mainly react with CO to produce lower iron components, and Fe<sub>2</sub>O<sub>3</sub> is mainly reduced to Fe<sub>3</sub>O<sub>4</sub> by CO. When the temperature is higher than 700 °C, C can reduce all the high-valence iron oxides to Fe, while Fe<sub>2</sub>O<sub>3</sub> and FeO cannot be reduced to Fe by CO. When the temperature is higher than 1 000 °C, the reduction of H<sub>2</sub> with high iron oxides can basically occur, except that the reduction of FeO to Fe is relatively difficult. All the reduction reactions by CH<sub>4</sub> can occur at about 700 °C, not to mention higher temperature.

Gibbs free energy change diagram of chromium oxides reaction are shown in Figure 2. When the tempera-



Figures 1  $\Delta G$  of iron oxide reduction reaction



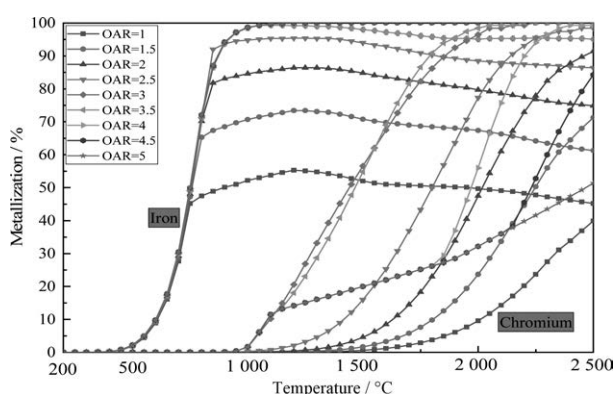
Figures 2  $\Delta G$  of chromium oxide reduction reaction

ture is higher than 200 °C, high-valence chromium oxides CrO<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> can be reduced to low-priced chromium oxides and Cr by C, in which the reduction of Cr<sub>2</sub>O<sub>3</sub> to Cr requires a high temperature above 1 200 °C. At 0~1 800 °C, CO can reduce CrO<sub>3</sub> to Cr, and other reduction reactions cannot occur. H<sub>2</sub> can reduce CrO<sub>3</sub> to low-valence chromium oxides, but Cr<sub>2</sub>O<sub>3</sub> cannot be reduced to low-valence chromium oxides by H<sub>2</sub>. CH<sub>4</sub> can reduce CrO<sub>3</sub> to low-valence chromium oxides, and Cr<sub>2</sub>O<sub>3</sub> can be reduced to low-valence chromium oxides by CH<sub>4</sub> at a high temperature of 1 400 °C.

## ANALYSIS OF EQUILIBRIUM PRODUCTS

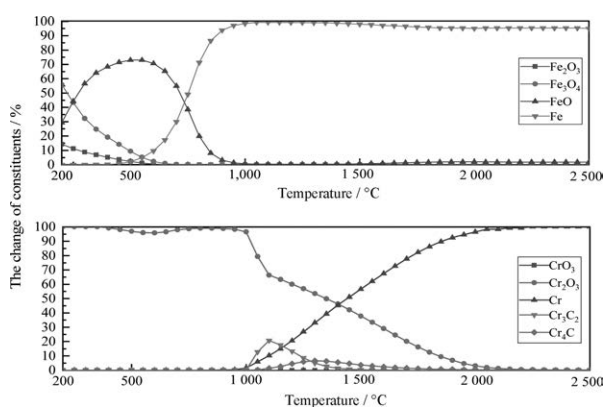
Figure 3 show the change of reduction rates of iron and chromium with temperature under different OAR of vanadium-extracted waste slag from peanut shell. When the temperature is between 1 000 °C and 1 300 °C, the iron metallization rate reaches the maximum. As

the temperature continues to rise, the metallization rate of iron decreases gradually. This is because in this temperature range, iron oxides mainly exist in the form of FeO, and the reduction of FeO by CO is an exothermic reaction. Reduction was inhibited by high temperature, resulting in the reduction rate of iron decreasing. With the increase of OAR (the amount of biomass added increases), the iron metallization rate will gradually increase. When the OAR is 3, the reduction effect of biomass reaches a state of saturation, and the continuous increase of OAR will increase the CO produced by biomass pyrolysis, resulting in the decline of iron metallization rate at high temperature. Considering the economic cost, when the temperature is 1 050 °C and the OAR is 3, the iron metallization rate is 99,3 %, which can be considered as an ideal working condition.



**Figure 3** Metallization rates of Iron and chromium

For chromium, the metallization rate increases with the increase of the reduction temperature. However, the chromium metallization rate can't reach 99 % at the OAR of 3~3,5 until the temperature is over 2 000 °C. So, it is not economical to pursue a higher chromium metallization rate while obtaining a higher iron metallization rate. Therefore, the metal reduction rate of iron is mainly considered.



**Figure 4** Variation of Fe and Cr components

Figure 4 shows the variation curves of different valence Fe and Cr with temperature. At 200 °C, the iron containing components are mainly FeO, Fe<sub>3</sub>O<sub>4</sub> and FeO. With the temperature rising to 550 °C, Fe<sub>3</sub>O<sub>4</sub> is reduced

to FeO. When the temperature is between 550 °C and 900 °C, the content of FeO decreases, and that of Fe increases. And, as the temperature rises further, the Fe content can gradually increase to more than 99 %. Thus, it can be roughly judged that the reduction process of Fe<sub>2</sub>O<sub>3</sub> is as follows: T<550 °C, Fe<sub>2</sub>O<sub>3</sub>-Fe<sub>3</sub>O<sub>4</sub>-FeO; T≥550°C, Fe<sub>2</sub>O<sub>3</sub>-Fe<sub>3</sub>O<sub>4</sub>-FeO-Fe. When the temperature is below 1 000 °C, most chromium exists in the form of Cr<sub>2</sub>O<sub>3</sub>, because CrO<sub>3</sub> is easily decomposed into Cr<sub>2</sub>O<sub>3</sub> when heated, but Cr<sub>2</sub>O<sub>3</sub> is reduced at a higher temperature. When the temperature is higher than 1 000 °C, Cr<sub>2</sub>O<sub>3</sub> is gradually reduced to Cr. In addition, a small amount of Cr<sub>4</sub>C and Cr<sub>3</sub>C<sub>2</sub> will appear at the temperature of 1 000 °C~2 000 °C, but their content is not high, so the chromium reduction process can be roughly considered as: T<1 000 °C, CrO<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>; T≥1 000 °C, CrO<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr.

## CONCLUSION

In this paper, the thermodynamic analysis of vanadium-extracted waste slag reduced by biomass was discussed.

(1) When the temperature is 1 050 °C, the oxygen absorption ratio is 3, the reduction rate of iron is more than 99 %. When the temperature is 2 200 °C, oxygen absorption ratio is 3,5, the chromium reduction rate is above 99 %.

(2) The reduction path of iron and chromium was preliminarily explored. For iron-containing components, T<550 °C: Fe<sub>2</sub>O<sub>3</sub>-Fe<sub>3</sub>O<sub>4</sub>-FeO; T≥550 °C: Fe<sub>2</sub>O<sub>3</sub>-Fe<sub>3</sub>O<sub>4</sub>-FeO-Fe. For chromium-containing components, T<1 000 °C: CrO<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>; T≥1 000 °C: CrO<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr.

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**Note:** The responsible for english language is H. Q. Xie – China.