Gas-phase reduction of iron and chrome from chromites

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Abstract. This paper focuses on studies of iron and partially chromium gas-phase reduction from chrome ore raw material of the Kempirsay Massif. The studies were carried out using a thermogravimetric method in a CO flow followed by chemical analysis of the samples. It is shown that: depending on the time of the samples exposure at the CO consumption rate 75 m³/h and the temperature of 1200 °С, basic reduction processes take place in the first 20 minutes of exposure; with temperature growth from 1000 to 1400 °С and an exposure time of 20 minutes, the degree of Fe and Cr reduction from the considered samples increases from 13 to 37%. Gaseous reducing agent and low temperatures contribute to a greater reduction of iron rather than chromium. Gaseous CO is a good iron reducing agent (with a small excess it allows to obtain a high degree of iron reduction) and a weak chromium reducing agent (the degree of chromium reduction is 14% with the multiple excess of CO and on condition of the chromium carbides formation).

1. Introduction
Gaseous-phase reduction of chromite ore elements can be considered as one of components preliminary reduction methods - metallization of charge materials. The issues of obtaining and using metallized chrome materials (pellets, briquettes) are considered in a number of works [1-4]. The firm “Outokumpu” in Finland carried out industrial research on the chromium ores preparation. According to the Daavittila J. data (Outotec Oyj, Finland), selective reduction of iron (more than 80%) and chromium (10%) was performed, however, technological difficulties were noted in the process for the chromium ores of the Kemi deposit, which contain a large number of silicates with a low melting point. Nevertheless, it is known that preliminary reduction and heating of chrome-ore materials allow to save 10-20% of electric power and to substantially increase the productivity of ore-reduction electric furnaces.

2. The materials studied
In this paper during studying the preliminary reduction of iron and partially chromium from chromium ore, CO was used as the gaseous reducing agent. According to the reaction:

\[ \text{MeO}(s) + \text{CO} (s) \rightarrow \text{Me} (s) + \text{CO}_2 \ (\text{gas}) \]

reduction process is accompanied by samples mass decrease due to the transition of oxygen from the solid (iron and chromium oxides) to the gas phase, therefore a thermogravimetric method was used to study the kinetics of gas-phase reduction. Chemical composition of the initial chromic ore materials is presented in table 1.
Table 1. Chemical composition of chromium ore materials

| No. | Origin of chromium ore materials | Cr$_2$O$_3$ | FeO  | Al$_2$O$_3$ | SiO$_2$ | MgO  | CaO  |
|-----|---------------------------------|-------------|------|-------------|--------|------|------|
| 1   | Kazakhstan, Kempirsay Massif     | 52.0        | 13.3 | 8.2         | 5.3    | 18.3 | 1.4  |
| 2   | Russia, Saranovskoye field      | 40.9        | 29.0 | 19.8        | 3.1    | 15.5 | -    |

3. Experiment and discussion

Influence of the exposure time from 0 to 40 min on the sample mass loss of 1.5-2.0 mm Kempirsay Massif chromium ore fraction during CO gas-phase reduction with a flow rate of 75 m$^3$/h and a temperature of 1200° C was studied. Results of the experiments are presented in figure 1. It is shown that main mass change in the sample, and, consequently, the reduction processes, takes place in the first 20 minutes of exposure. With subsequent exposure to 40 minutes, the mass of the sample remains almost unchanged.

![Figure 1](image-url)

**Figure 1.** Influence of the exposure time on the mass loss of chromium ore sample from the Kempirsay Massif at CO consumption rate 75 m$^3$/h and temperature 1200 ° C.

Under similar conditions, the temperature effect on the mass loss of a chromium ore sample with an exposure time of 20 min was studied at each temperature. The results of experiments are shown in figure 2. Total reducibility of Fe and Cr is calculated from the mass loss. It was found that temperature growth from 1000 to 1400 °C, with CO consumption of 75 m$^3$/h and an exposure of 20 minutes, increases the reducibility of Fe and Cr samples from Kempirsai massif from 13 to 37%.

Similar studies on the components reducibility of the Saranovskoye deposit chromium ore samples were carried out in [5] under comparable conditions. In the high-temperature region (≥ 1200 °C), experimental data on Fe and Cr reducibility from Kempirsay ore samples are consistent with literature data on the reducibility of the same elements from Saranovo ore. In the low temperature range (1000-1200 °C), Fe and Cr reducibility of the Saranovo ore is much higher, which can be justified by the low ratio of Cr / Fe (1.2) in the Saranov ore, compared to the Kempirsai massif sample (Cr / Fe = 3, 4). Gaseous reducing agent and low temperatures contribute to a better reduction of iron than chromium. Gaseous CO is a good iron reducing agent from FeO (with a slight excess allows to completely reduce iron) and a weak chromium reducing agent (the degree of chromium reduction is 14% with a multiple excess of CO and the condition of the carbide Cr$_7$C$_3$ formation).
Figure 2. Temperature effect on the mass loss of chromium ore sample from the Kempirsay Massif at CO consumption rate 75 m$^3$/h and at 20 min exposure time.

The influence of atmosphere (reducing, weakly reducing and oxidizing) on the reducibility of chromium ore elements by a solid carbon reductant at 1000-1400 °C with a calculated amount of reducing agent on obtaining metal with 20% Cr was studied. A coke with 73% of C content was used as a solid reducing agent. It is shown that during the transition from reducing to oxidizing atmosphere, the rate and completeness of the elements reduction from chromium ore decreases. Thus, at 1400 °C and 60 min exposure during the transition from oxidizing atmosphere to the reducing, the loss of the sample mass increases by 25% (rel.).

4. Conclusion

Thus, when considering the processes of chromium and iron gas-phase reduction from chromium ore materials:

- the effect of temperature and exposure time on the mass loss of samples and the degree of iron and chromium reduction have been studied;
- it is shown that temperature growth from 1000 to 1400 °C, at CO consumption rate of 75 m$^3$/h and an exposure of 20 minutes, increases Fe and Cr reducibility of Kempirsai massif samples from 13 to 37%;
- it was found that, depending on the time of samples exposure there is a significant change in the mass of the samples at the 75 m$^3$/h CO consumption rate and 1200 °C, and therefore basic reduction processes occur in the first 20 minutes of exposure.

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