Influence of Carbothermal Reduction Process on the Microscopic Properties of Lime-Free Roasting Chromite Ore Processing Residue (COPR)

Geng CHENG¹, Xuejun QUAN¹, Huazheng LUO¹, Weiyang BAI¹, Cunfang LU¹*

¹ School of Chemistry and Chemical Engineering, Chongqing University of Technology, Chongqing, 400050, China
*Corresponding author’s e-mail: lucunfang@cqut.edu.cn

Abstract: The lime-free roasting chromite ore processing residue (COPR) was more environmentally friendly than the lime-based COPR. And its components in lime-free COPR should be reused as secondary resource. The process of carbothermal reduction associated with magnetic separation was adopted in this study to reclaim the iron oxide in lime free roasting COPR. The microscopic properties of COPR samples treated by carbothermal reduction were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), etc. The effects of process parameters on iron recovery rate were studied by single-factor experiments. The results indicated that the carbothermal reduction roasting process was beneficial to the destruction of the iron-rich spinel in the original lime-free roasting COPR and the enrichment of iron metal in lime-free roasting COPR. The optimal conditions were obtained as follows: reduction calcination temperature of 1100 ℃, reduction time of 2 hours, coke ration of 3.5 times of theoretical content. The main components of the separated fraction were iron particles and some magnesium aluminum spinel.

1. Introduction
The heavy metal contamination is a serious problem to the environment, because the anthropogenic activities from mining, processing and applications of these metals have increased enormously during the past few decades and have become a challenge for life on earth[1-2]. Chromium was widely used in many industrial processes such as electroplating, leather tanning and mineral extraction, and as a common ingredient used in protective coatings, pigments, and stainless steel[3-7].

Chromite ore processing residue (COPR) is a by-product generated from the extraction process of chromium (Cr) from chromite ore. The total Cr concentration in COPR was up to 5%, including the hexavalent chromium Cr(VI) concentration up to 2% on dry weight basis[8-10].

According to the flux used in the roasting process, the chromium salt manufacturing process could be divided into the lime-based roasting process and the lime-free roasting process[11-12]. The lime-based COPR were more toxic than the lime-free COPR, for the hexavalent chromium Cr (VI) in COPR was mainly existed in the form of calcium chromate, CaCrO₄. The leaching of Cr(VI) in CaCrO₄ was a slow dissolution process for the solubility of Cr(VI) was poor[13-15].

So far there are still millions of metric tons of lime based chromite ore processing residue (COPR) were deposited in urban areas around the world in Europe and the US such as Glasgow, U.K., and Jersey City, as well as at chromite ore processing plants operating in Japan, India, Pakistan and the former Soviet Union[16-17].
Comparing with the lime-based COPR, the lime-free COPR were much more environmentally friendly. The main components of the lime-free roasting COPR were iron oxide, chromite oxide and etc. For lime-free COPR, the iron oxide content was about 40%, which is similar to the iron content of some lean iron ore mines\cite{18}. Magnetized roasting is one of the most effective methods for the treatment of the lean iron ore\cite{19-20}. Therefore, the magnetization roasting method was adopted to in this study to investigate the iron separation of iron metal from lime-free COPR.

2. Materials and methods

2.1. Materials

The lime-free roasting COPR samples used in the experiments were supplied by a chromium salt manufacturer in the southwest of China. Reduction agents used in the carbonthermal experimental were industrial coke. The components of COPR were shown in Table 1.

| Component | Composition (%) |
|-----------|----------------|
| Al₂O₃     | 20.90          |
| CaO       | 0.15           |
| Cr₂O₃     | 14.76          |
| Fe₂O₃     | 41.87          |
| MgO       | 12.62          |
| SiO₂      | 1.18           |

Figure1. XRD results of the original COPR

2.2. Methods and procedure

COPR and the coke powder were uniformly grounded and mixed to place in a crucible after they were dried at 105 °C for 24 hours. The carbon content required for calcination was calculated according to the stoichiometry of equation (1).

\[
\text{MgO·Fe₂O₃ + 3C = MgO + 2Fe + 3CO}\]

Mixtures of COPR and coke were roasted in muffle furnace at certain temperatures. When the calcination was completed, the samples were taken out and immersed into water to avoid the oxidation of by oxygen in air during the cooling time. The magnetic separation process was carried out by Ø50 magnetic tube. The magnetic fraction ratios were calculated by the magnetic weight divided by the weight of the original COPR.

3. Results and discussion

3.1. Morphology and microscopic characteristic of lime free COPR
The surface morphology and Fe distribution of COPR was shown in Fig 2. It can be seen from Figure 2 a) and b) that the original lime free COPR had a rough surface. There was a disorderly grass like layer on the top of the residue, and encapsulated are some little tone particles. Figure 2 c) showed that the COPR surface morphology of after carbonthermal reduction became compact and smooth. It seemed that the rough surface of the original COPR was burn-off during the calcination process. Little iron metals could be observed through EDS in with an average particle size less than 1 µm, also crystals of regular shape could be observed Figre 2 d). It may be the crystals of magnesium aluminate spinel according to the XRD results. Figure 2 e) and f) were the magnetic fraction of COPR. There were plenty of magnesium aluminum spinel crystals still in the magnetic part. In addition, the particles sizes of the enrichment iron metal were significantly increased with an average size at about 2-3µm.
3.2. Carbonthermal reduction process results

Single-factor experiments were conducted to study the effects of carbonthermal reduction parameters on the magnetic separation process, including carbon addition amount, reduction temperature and reduction time. During the experiments, the magnetic field intensity of the separation process changed from zero to 500 mT (micro Tesla).

3.2.1. Effect of carbon content on the magnetic separation results

To investigate the effect of coke amount addition on the iron oxide reduction reactions, different times of stoichiometric ratio amount of coke ranging from 1.5 to 3.5 was added roasted at 1100 ℃ for 2 hours. The results were shown in Fig. 3.

It can be seen that with the increase of the coke addition, the magnetic fraction ratio increased from 10 % to 70 % when the magnetic intensity was about 100-150mT. For samples times of stoichiometric ratio amount of coke were 3.0 and 3.5, the magnetic mass separation reached 70 % under the condition that the magnetic intensity was 150 mT. And the corresponding magnetic intensity was about 350 mT when the times of stoichiometric ratio amount of coke were 1.5, 2.0 and 2.5.

Besides, the increase of coke amount was helpful to enhance the reduction reaction of the iron oxides in COPR. From Fig. 3 b), there were obvious iron metal peak in the XRD pattern. The peak corresponding to iron metal was become higher and sharper with the increase of coke amount.

3.2.2. Effect of reduction temperature on the magnetic separation results

Influence of roasting temperatures from 800 ℃ to 1200 ℃ was investigated under condition that times of stoichiometric ratio amount of coke was 3.5 and roasting time was 2 hours. Fig.4 (a) and (b) show the results of magnetic mass fraction and XRD. It can be observed that high temperature was benefit to the improvement of the magnetic mass fraction, with an average ratio of 30 %, when the roasting temperature increased from 800 ℃ to 1100 ℃. However, the magnetic mass fraction was only 40% at the temperature of 1200 ℃. It may be caused by the burning of coke at high temperature or the formation of iron compounds, such as carbide.
3.2.3. Effect of reduction time on the magnetic separation results

![Graph showing magnetic mass fraction under various magnetic field intensities](image1)

![XRD results for roasted COPR, A - MgFeAlO4, B - FeO, C - Fe](image2)

Figure 4. Effects of temperature on the magnetic part ratio

![Graph showing magnetic mass fraction under various magnetic field intensities](image3)

![XRD results for roasted COPR from 1.0 h to 3.0 h; A - MgFeAlO4, B - FeO, C - Fe](image4)

Figure 5. Effects of roasting time on the magnetic part ratio

Influence of roasting time ranging from 1.0 hour to 3.0 hours were investigated under conditions that times of stoichiometric ratio amount of coke was 3.5 and roasting temperature was 1100 °C. With the magnetic field intensity increased from 50 mT to 400 mT, the magnetic fraction mass ratio reached about 70-80 % for all the samples. However, it is about 150 mT for samples roasted for 2 hours. And the metal iron of the corresponding sample had the comparable peak in Fig. 3b) with samples roasted for longer times. Thus, the optimal roasting time was 2 hours.

4. Conclusions

Carbothermal reduction method was adopted to treat the lime-free COPR in this study. The experiment results indicated that the carbothermal reduction and magnetic separation process was effective to reclaim the iron metals in lime-free COPR. Under the conditions that of the times of theoretical carbon content, calcination temperature and calcination times were 3.5, 1100 °C and 2 hours, particles of iron metal with a particle size of 1 µm about were enriched. After the magnetic separation treatment, the particle sizes of the enrichment iron were significantly increased with an average size at of about 2-3µm. Due to the size of the iron particles has a large influence on the magnetic properties, the iron
particles of the smaller particles not existed in the magnetic part. The magnetic magnesium aluminate spinel in the COPR was not destroyed during the carbothermal reduction process.

Acknowledgement
Supported by the Science and Technology Research Program of Chongqing Municipal Education Commission (Grant No. KJQN201801140).

References
[1] A. Benedetti, Defining soil quality: introduction to round table, in: S. deBertoldi, F. Pinzari(Eds.), COST Actions 831, JointWCs Meeting, Biotechnology of soil: monitoring conservation and remediation, 1998, pp 29–33.
[2] M. Wazne, S.C. Jagupilla, D.H. Moon, S.C. Jagupilla, C. Christodoulatos, M.G. Kim, Assessment of calcium polysulfide for the remediation of hexavalent chromium in chromite ore processing residue (COPR), J. Hazard. Mater. 143 (2007) 620–628.
[3] D.H. Moon, M. Wazne, D. Dermatas, C. Christodoulatos, A.M. Sanchez, D.G. Grubb, M. Chrysochoou, M.G. Kim, Long-term treatment issues with chrome ore processing residue (COPR): Cr6+ reduction and heave, J. Hazard. Mater. 143 (2007) 629–635.
[4] Weng CH, Huang CP, Allen HE, Cheng AHD, Sanders PF. Chromium leaching behaviour in soil derived from chrome ore processing waste. Sci Total Environ 1994; 154:71–86.
[5] James BR. The challenge of remediating chromium-contaminated soil. Environ Sci Technol 1996;30:248A–51A.
[6] Chrysochoou M, Moon DH, Dermatas D, Wazne M, Christodoulatos C, Meng X, et al. Mineralogical analysis of chromite ore processing residue by X-ray powder diffraction. In: Allenman BC, Kelley ME, editors. 8th international in situ and on-site bioremediation symposium, 6–9 June. Baltimore, Maryland: Battelle Press; 2005.
[7] Dermatas D, Chrysochoou M, Moon DH, Pardali S, Christodoulatos C, Lazarte CA, et al. Mineralogical characterization of chromite ore processing residue at Dundalk Marine Terminal Area 1800. In: Allenman BC, Kelley ME, editors. 8th international in situ and on-site bioremediation symposium, 6–9 June. Baltimore, Maryland: Battelle Press; 2005.
[8] Chrysochoou M, Dermatas D, Moon DH, Christodoulatos C, Wazne M, French C, et al. Investigation of barium treatment of chromite ore processing residue. J ASTM Int 2006;3(6). doi:10.1520/JAI13314.
[9] Moon DH, Chrysochoou M, Dermatas D, Christodoulatos C, Kaouris M, Morris J. Investigation of ettringite formation in chromite ore processing residue. In: Allenman BC, Kelley ME, editors. 8th international in situ and on-site bioremediation symposium, 6–9 June. Baltimore, Maryland: Battelle Press; 2005.
[10] Moon DH, Dermatas D, Chrysochoou M, Shen G. An investigation of the heaving mechanism related to chromite ore processing residue. J ASTM Int 2006;3(6). doi:10.1520/JAI13309.
[11] T. Burke, J. Fagliano, M. Goldoft, R.E. Hazen, R. Iglewicz, T. McKee, Chromite ore processing residue in Hudson County, New Jersey, Environ. Health Perspect. 92 (1991) 131–137.
[12] G. Darrie, Commercial extraction technology and process waste disposal in the manufacture of chromium chemicals from ore, Environ. Geochem. Health 23 (2001) 187–193.
[13] J.G. Farmer, R.P. Thomas, M.C. Graham, J.S. Geelhoed, D.G. Lumsdon, E. Paterson, Chromium speciation and fractionation in ground and surface waters in the vicinity of chromite ore processing residue disposal sites, J. Environ. Monit. 4 (2002) 235–243.
[14] M. Chrysochoou, D. Dermatas, M. Asce, D.G. Grubb, M. Asce, D.H. Moon, C. Christodoulatos, Importance of mineralogy in the environmental characterization and treatment of chromite ore processing residue, J. Geotech. Geoenviron. Eng. 36 (2010) 510–521.
[15] Arndt, U., Batz, M., Bellinghausen, R., Hans-Dieter, B., Heinrich, H., Norbert, L., HansHeinrich, M., Hans-Georg, N., Hans, R., Bernhard, S., 1996. Method for manufacturing alkali chromates from chromite ore. US Patent Application, US 5505918.
[16] YANG Yang. It is very serious of chromium salts waste slag pollution in China [J]. Chemical Industry Management, 2003(1): 4−6. (in Chinese)

[17] ZHU Ji. The two key factors for disposal of chrome residue [J]. Inorganic Chemicals Industry, 2004, 36(5): 1−4. (in Chinese)

[18] Zhang Min. Experimental study on ore dressing in an iron ore mine in Panxi [J]. Mining and Metallurgical Engineering, 2017, 37(1): 57-59.

[19] Zhu Deqing, Zhao Qiang, Qiu Guanzhou. Magnetization roasting-magnetic separation process of Anhui limonite [J]. Journal of University of Science and Technology Beijing 2010,

[20] Chen G, Wang J, Wang X H, et al. An investigation on the kinetics of chromium dissolution from Philippine chromite ore at high oxygen pressure in KOH sub-molten salt solution[J]. Hydrometallurgy, 2013, 139(3): 46-53.