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## PHASE CHANGE OF CHLORITE IN REDUCING ATMOSPHERE

**Xinghua LIU, Yongfu YU, Wen CHEN, Xiaoyin LIU**

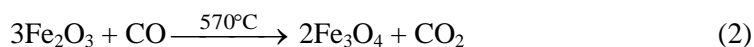
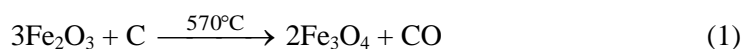
Changsha Research Institute of Mining and Metallurgy, Changsha 410012, Hunan, China  
liu-xinghua0731@163.com

**Abstract.** Magnetizing roasting is an important pre-treatment technique for beneficiation of hematite and limonite ores. Reduction mechanisms of these iron minerals have been fully studied while the mechanism of reduction of chlorite is not well understood. In this study, a reduction roasting study examining the phase change of chlorite with roasting temperature was undertaken. The major finding from this study was that chlorite partially was reduced to magnetite by carbon at 750 °C, and the newly formed magnetite was finely disseminated within quartz and olivine. It was demonstrated that these locked magnetite particles would be reported to iron concentrate by low intensity magnetic separation resulting in high impurity content, especially SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> contents in the concentrate.

**Keywords:** chlorite, phase change, magnetizing, reducing roasting, magnetite

### Introduction

Magnetizing roasting is a very effective process in treatment of iron ores, which are poorly responsive to conventional beneficiation techniques. It involves conversion of weakly magnetic iron minerals in the ore to a strongly magnetic form by subjecting the ore to a reducing atmosphere at elevated temperatures. In most magnetizing reduction systems, the ore is reduced at a particular temperature, and then quenched in water (Svoboda 2004). Hematite and limonite are two most common feebly magnetic iron minerals. They have the main chemical composition of Fe<sub>2</sub>O<sub>3</sub>, and their magnetizing roasting is a process in which Fe<sub>2</sub>O<sub>3</sub> is deoxidized by carbon to yield magnetite Fe<sub>3</sub>O<sub>4</sub>. The reaction formulas are as the following (Zhang 1983):



The resulting magnetite is strongly magnetic and can be recovered by low intensity magnetic separation.

Although the reduction mechanisms of hematite and limonite have been fully understood, the reduced simultaneously associated chlorite has not been found in the literature. Chlorite, as an iron-bearing aluminosilicate mineral, is widely distributed in various rocks, especially in about 70–90% sedimentary rocks (Yang and Zhang 1994). Chlorite also occurs in almost all of the Chinese large iron ore deposits (Wang et al. 2008). Chlorite which in fact is a general term for a group of minerals with a general formula  $(\text{Mg, Al, Fe})_6[(\text{Si, Al})_4\text{O}_{10}](\text{OH})_8$  is 2:1 phyllosilicates with an interlayer sheet. The 2:1 “talc-like” layer has two sheets of  $\text{SiO}_4$  tetrahedron separated by an interlayer “brucite-like” sheet containing Mg, Al and Fe octahedrally coordinated (Silvester et al. 2011).

In our previous work, we have found that chlorite is a refractory gangue mineral in hematite ore just using conventional beneficiation techniques (Chen and Liu 2010). Chlorite has a specific susceptibility similar to that of hematite, and will have a high enrichment in concentrate after a high intensity magnetic separation. Structural iron ions on the surface of chlorite crystals also can cause some difficulties in flotation of chlorite from hematite (Liu et al. 2012; Chen and Liu 2012). Not long ago, another similar phenomenon was observed when we adopted reduction roasting- low intensity magnetic separation technique to beneficiate a high chlorite-containing hematite ore. The roasted chlorite was found to be enriched in magnetic concentrate after low intensity magnetic separation, which caused a large amount of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in the concentrate. The optimum temperature conditions for reduction roasting tests were determined as 750 °C, 10% of coal/sample ratio, and 90 min of the roasting time. In this study, we present an investigation on the phase change of the chlorite mineral in the reducing atmosphere by different roasting temperature tests. The aim was to find out the reason why the roasted chlorite minerals are enriched in iron concentrate and caused contamination.

## Experimental

### Samples

Chlorite with a purity above 90% was prepared for reductive roasting tests. The preparation procedure was as follows. First, high chlorite-containing rocks were selected from a hematite ore, and then crushed, ground, and screened. The undersize of the sample was first subjected to the magnetic separation at 0.4 T for discarding ferromagnetic materials, and second at 0.8 T for rejecting non-magnetic materials, and this separation process was performed repeatedly. Finally, the left material was chlorite concentrate, which was cleaned with distilled water and dried in an oven at 60 °C for 12 h. The size of the chlorite sample was below 30  $\mu\text{m}$ , and a specific surface area of the sample was found to be as 3.8609  $\text{m}^2\cdot\text{g}^{-1}$ . Its chemical composition and X-ray diffraction pattern are shown in Table 1 and Figure 1, respectively.

Table 1. Chemical composition of the chlorite sample

Component	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	FeO	Fe <sub>2</sub> O <sub>3</sub>	CaO	TiO <sub>2</sub>	MnO	K <sub>2</sub> O	Na <sub>2</sub> O
Content (%)	27.24	18.35	7.11	25.36	11.21	0.55	0.50	0.12	0.086	0.025

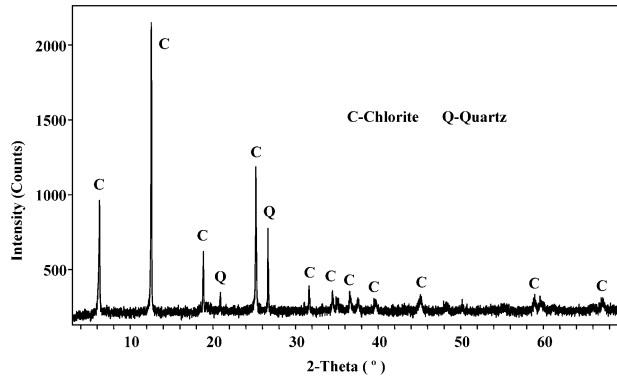


Fig. 1. X-ray diffraction pattern of the chlorite sample

Table 1 shows that the chlorite is a high iron-bearing aluminosilicate, which contains 25.36% FeO, 11.21% Fe<sub>2</sub>O<sub>3</sub>, 18.35% Al<sub>2</sub>O<sub>3</sub>, and 27.24% SiO<sub>2</sub>. Figure 1 indicates that the chlorite sample was relatively pure, besides a small amount of quartz, and there are no iron mineral peaks.

## Methods

The reduction roasting tests were conducted in a SX-8-10 type muffle roaster. Firstly, 10 g of chlorite sample and 1 g coal powder were weighed and blended each time. Secondly, the mixture was packed into a 30 cm<sup>3</sup> ceramic crucible. Thirdly, the crucible was sealed and placed in the heating muffle roaster which had reached a desired temperature. Finally, after a certain time, the roasted crucible was taken out from the roaster and quenched in cool water. In the roasting process, duration time and coal/chlorite sample ratio were held constant at 90 min and 10%, respectively. Meanwhile, the roasting temperatures were examined ranging from 500 °C to 750 °C. The roasted products were analyzed, and identified by X-ray diffraction and an electronic microscope.

## Results and discussions

### Phase change of chlorite at different roasting temperatures

Figure 2 plots the X-ray diffraction pattern of the roasted product at 500 °C. Compared with Figure 1, the diffraction pattern showed no big difference while the chlorite diffraction peaks are still there, and no other new phase appeared. When the roasting temperature increased to 600 °C, the diffraction peaks of chlorite disappeared and an

intermediate phase appeared as seen in Figure 3. With the roasting temperature continuing to increase up to 750 °C, the intermediate phase disappeared, while magnetite and olivine were newly formed, and their diffraction peaks are displayed in Figure 4. This clearly indicates that chlorite is partially reduced to magnetite by carbon at 750 °C, and the rest is turned into olivine which still has a complex chemical composition. According to the electron probe microanalysis (EPMA), olivine has a general formula of  $(\text{Fe}_{1-a}\text{X}_a)_2\text{SiO}_4$ , where  $\text{X} = \text{Al}, \text{Mg}$  and other isomorphous cations, which shows that this newly formed olivine is also, like chlorite, an iron-bearing aluminosilicate mineral.

In the past decades, different investigators have studied the differential thermal analysis (DTA) of chlorite (Martin 1955; Yang 1991; Yang and Zhang 1994), for relatively pure chlorite samples. Variations in chemical composition are reflected in the differential thermal curves, and their thermal behaviors mainly depend on the type of cation in octahedral sites. Chlorites high in ferrous iron lose most of their hydroxyl water at a lower temperature than do the magnesian and aluminous chlorites, which indicates iron atoms produce a marked change in the thermal behavior of chlorite because (a) the Fe-OH bond is weaker than the Al-OH or Mg-OH bond, (b) Fe atoms are larger than Al or Mg atoms, and therefore, do not fit into the structure as well, and (c) ferrous ions are subject to oxidation. From Table 1, the chlorite sample used in this study also contains Fe, Al, and Mg atoms, and among the three atoms, Fe atoms are the majority. According to the DTA results of chlorite, as the roasting temperature increases, Fe-OH bond is easier to be broken and ferrous ions in octahedral sites are also more appropriate to react with atmosphere than that of Al and Mg ions. Therefore, the reduction products of Fe atoms (magnetite) were first produced at 750 °C, as shown in Figure 4.

Many researches (Caillere and Henin 1951; Phillips 1963; Schneider et al. 2008) also showed that the major endothermic peak is controlled by ferrous iron in chlorite structure depending on iron content. The dehydroxylation and the mineral reactions occur at different temperatures. And chlorites, high in ferrous iron, begin their initial dehydration at appreciably lower temperatures than low-iron chlorites. For chlorites very high in ferrous iron ( $\geq 18.7\%$  FeO), oxidation of ferrous to ferric iron occurs during the first dehydration stage at 450 °C. The second dehydration occurs between 500 °C and 600 °C, and the oxidation reaction within chlorite structure may be in accordance with conversion of one OH species to  $\text{O}^{2-}$  for each conversion of  $\text{Fe}^{2+}$  ion to  $\text{Fe}^{3+}$ .

With the continuing heating, the recrystallization products are finally formed depending on the type of chlorite. Magnesian chlorite is turned into forsterite and enstatite, aluminous chlorite is converted into mullite, and chlorite high in ferrous iron is oxidized into hematite and hercynite (Yang 1991). These reactions take place in vacuum or in a flow of  $\text{N}_2$  or in air, but no references to chlorite reactions in reducing atmosphere have been found in the literature. In fact, the thermal behaviour of a high FeO content chlorite is markedly influenced by the nature of the furnace atmosphere (Martin 1955). Therefore, one possible reduction mechanism is that the high iron

content chlorite is first oxidized into hematite with the increasing temperature, and hematite is next reduced quickly to magnetite by burning carbon or CO. It can also be inferred that the olivine formed at 750 °C is still an intermediate phase, not the final reduction product. Further work on this will need to be undertaken.

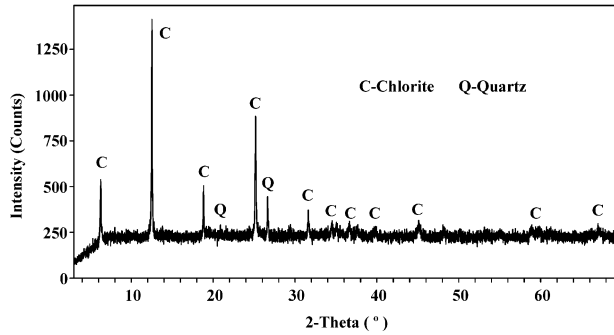


Fig. 2. X-ray diffraction pattern of the roasted product at 500 °C

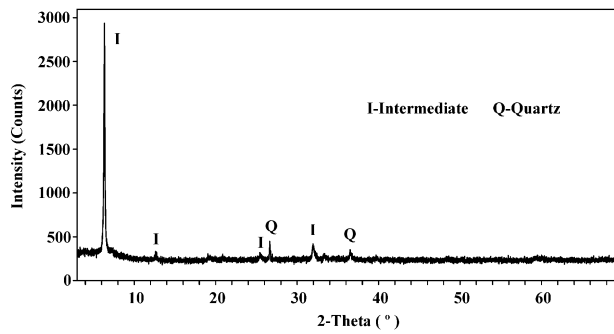


Fig. 3. X-ray diffraction pattern of the roasted product at 600 °C

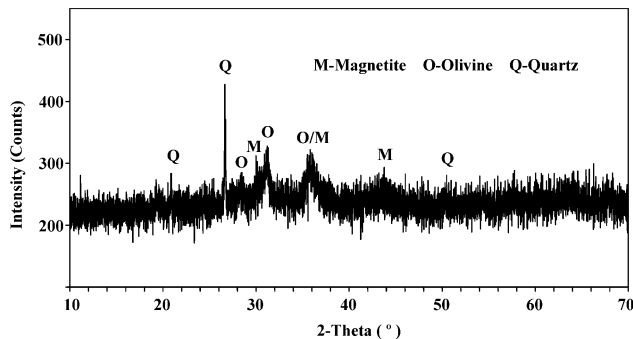


Fig. 4. X-ray diffraction pattern of the roasted product at 750 °C

### Characteristics of the chlorite reduction product

Figure 5 shows the photomicrographs of the chlorite reduction product at 750 °C. Although the reduction product is no longer for the former chlorite, they still retain in the shape of chlorite crystal structure as seen in Figures 5 a and b. Additionally, Figures 5 c and d indicate that the newly formed magnetite particles are very fine and mostly below 10 μm, which are all locked with gangues (quartz and olivine) closely.

Furthermore, specific susceptibilities of chlorite sample and its reduction product were determined through the Gouy method. The specific magnetic susceptibility of chlorite sample is  $41.46 \cdot 10^{-6} \text{ cm}^3 \cdot \text{g}^{-1}$  and its reduction product is  $476.45 \cdot 10^{-6} \text{ cm}^3 \cdot \text{g}^{-1}$  which shows that the specific susceptibility increased nine-fold after the reduction roasting. Using a magnet with a field intensity of 0.2T to attract the chlorite reduction product, a small amount of magnetic particles was picked up. It can be inferred from this phenomenon that these intergrown magnetite particles will report to the iron concentrate during the low intensity magnetic separation. As a result, the quality of iron concentrate will be deteriorated.

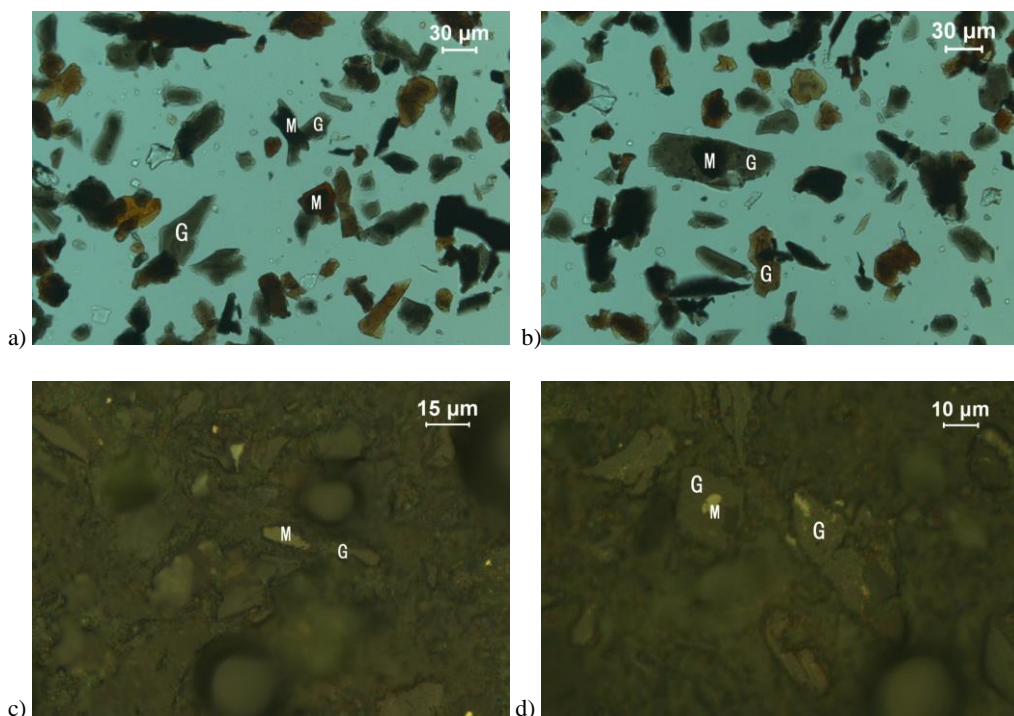


Fig. 5. Photomicrographs of the chlorite reduction product at 750 °C (M - magnetite, G - gangue minerals including quartz and olivine)

## Conclusions

Above 90% pure chlorite was used for the reduction roasting tests in a muffle roaster. The chlorite sample was a high iron-bearing aluminosilicate mineral which assayed 25.36% FeO, 11.21% Fe<sub>2</sub>O<sub>3</sub>, 18.35% Al<sub>2</sub>O<sub>3</sub>, and 27.24% SiO<sub>2</sub>. At the coal/chlorite sample ratio of 10% and the roasting time of 90 min, chlorite showed no big phase change at 500 °C, and then the chlorite phase disappeared and an intermediate phase appeared at 600 °C, and then the intermediate phase changed into magnetite and olivine at 750 °C. Obviously chlorite is partially reduced to magnetite by carbon.

The photomicrographs of the chlorite reduction product at 750 °C showed that they still retain the shape of chlorite crystal structure, though the former chlorite no longer exists. All the newly formed magnetite particles were very fine and also associated with gangues (quartz and olivine). These intergrown magnetite particles will report to the iron concentrate during low intensity magnetic separation, which can lead to a high impurity content of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in the magnetic concentrate.

Olivine formed at 750 °C is still an intermediate phase, which can be further reduced to magnetite in the reducing atmosphere by extending the roasting time or improving the roasting temperature. More work and further study on detailed reduction mechanism of chlorite need to be carried out in future.

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