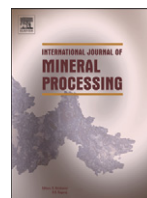




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## Sulfuric acid leaching of South African chromite. Part 1: Study on leaching behavior

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## ABSTRACT

The leaching behavior of chromite by sulfuric acid in the presence of oxidant was studied experimentally in this work, where most tests were carried out at 160 °C. The results indicated that magnesium and aluminum were leached out together from the silicate phase and porous amorphous silica was produced as a product layer, while the spinel phase gradually shrank with the duration of leaching. The separation of silicate and spinel phases had an influence both on the extraction yield of chromium and the leaching reaction rate by reducing the resistance presented by the silicon-rich phase. It was found that the erosion along the phase boundary was more severe than in other areas, and it can be speculated that groovy corrosion in the spinel phase occurred and developed at the grain boundary. The precipitation behavior of sulfate during the leaching process was also investigated at different temperatures up to 200 °C, showing that the sulfate precipitated in the silicon-rich phase at higher temperatures, while the main phase of the sulfate was chromium sulfate, coinciding with results reported by other researchers. All considered metal elements in the spinel phase leached out together in the experiments of this study.

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### 1. Introduction

Chromium salts and other chromium compounds are significant chemical products that serve as tanning agent, pigments, catalyst, preservative, oxidant etc. in various fields. The manufacturing of chromium salt from chromite, the only natural raw material, has been studied for hundreds of years, but the chromium (VI) formation during traditional oxidation roasting processes at 1100 °C cannot be prevented (Li et al., 2011; Sampath et al., 1990). It is widely recognized that the presence of chromium (VI), even in trace quantities, can act as a strong oxidant, mutagen and even carcinogen, which have a negative impact on human health and may poison other living creatures (Aynur, 2004). Thus, suppression of pollution caused by chromium (VI) to protect the environment has become a vital consideration for the chromium salt industry. China has for more than a decade been the principal producer of chromium salt and today contributes by more than 40% of the world production (Ji, 2010). Therefore, the exploration for cleaner production of chromium salt has lately received increased attention from authorities and researchers in China.

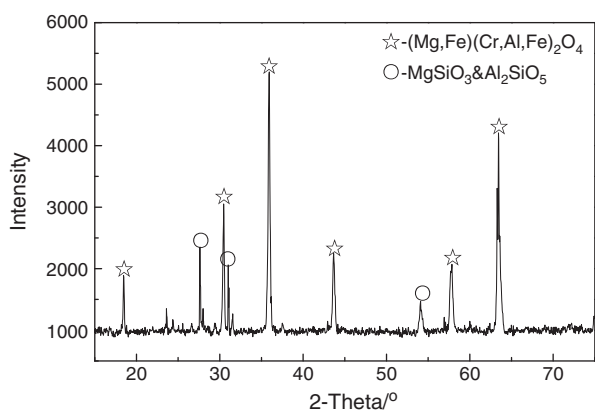
A cleaner production for preparing chromium salt by alkali leaching at 300 °C was extensively studied by the Institute of Process Engineering, Chinese Academy of Sciences (Liu et al., 2013; Zhang et al., 2010; Zheng et al., 2006), showing that the amount of chromium (VI)-bearing slag could be reduced to a low level. Another cleaner process beyond the proof of concept stage for processing chromite and other refractory ores (Bayca, 2013; Li et al., 2008) is the acid leaching process. It shows that chromite dissolves in concentrated sulfuric acid below 200 °C in the presence of oxidant without generating any chromium (VI)-bearing substance (Ji, 2012). Geveci et al. (2002) reported that the maximum extraction yield of chromium was 83%, all in the form of chromium (III), when chromite was leached by 70% sulfuric acid and perchloric acid at 175 °C. Furthermore, the investigators pointed out that sulfate precipitate was obtained as a cover coating on the chromite particle surface, obstructing the leaching reaction, a phenomenon earlier mentioned by Vardar et al. (1994). The latter authors attributed the precipitation of sulfates, including chromium sulfate, iron sulfate, aluminum sulfate and magnesium sulfate, to the increase of the amount of metal present in the solid–liquid interface boundary layer, while Amer (1992) suggested that the decrease of solubility of metal sulfate with increasing temperature was the primary cause. With the aim to elucidate the reaction mechanism of leaching, the main focus of the present study is on the leaching behavior of chromite by sulfuric acid using lump-size chromite, although some results from

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**Table 1**  
Chemical composition of South African chromite (wt.%).

$\Sigma$ FeO	Cr <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	CaO	Other
23.91	45.18	6.79	13.25	8.87	1.82	0.18



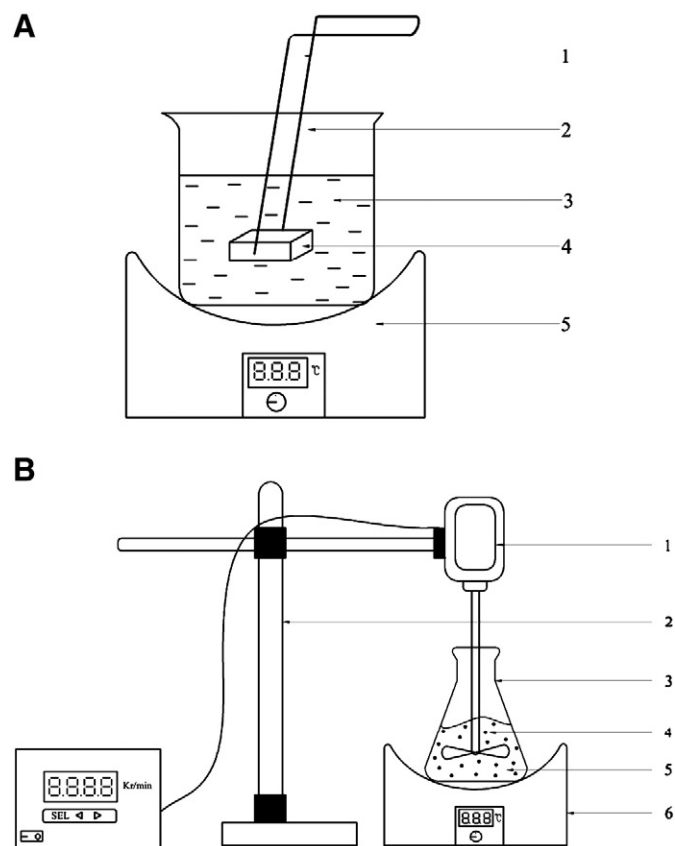
**Fig. 1.** XRD pattern of South African chromite.

leaching of powder material are reported as well. In part 2 of this study (Jiang et al., submitted for publication), the effect of the leaching conditions on the results is presented in more detail, and conclusions are drawn on how the conditions could be optimized.

## 2. Material and methods

### 2.1. Materials

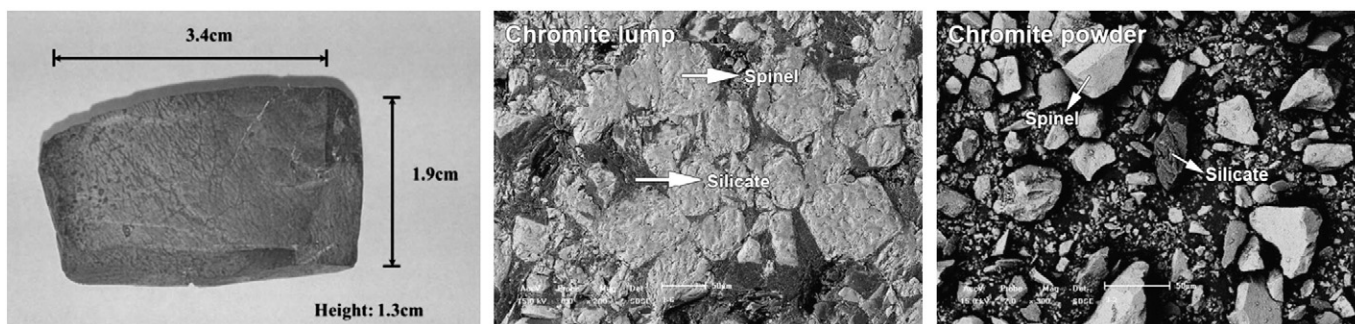
South African chromite used in the experimental investigation has the chemical composition given in Table 1. Fig. 1 presents the X-ray diffraction (XRD) pattern of South African chromite, which as expected (Sanchez et al., 2008) shows the major phases of the ore to be (Mg,Fe)(Cr,Al,Fe)<sub>2</sub>O<sub>4</sub> and silicate. (Mg,Fe)(Cr,Al,Fe)<sub>2</sub>O<sub>4</sub> as the chromium-bearing phase is a kind of isomorphous spinel, in which Mg<sup>2+</sup> and Fe<sup>2+</sup> occupy the tetrahedral sites of the lattice, while Cr<sup>3+</sup>, Al<sup>3+</sup> and Fe<sup>3+</sup> occupy the octahedral sites. A photograph of the chromite lump and scanning electron microscopy (SEM) images of the ore in lump and powder were shown in Fig. 2. The distinct boundary between spinel and silicate phases can be seen in the SEM image of chromite lump with centimeter-sized, ensuring the exclusive study for each phase. Chromite powder in micrometer-sized ascertained an adequate separation of the two phases, which favored the leaching efficiency study regardless the influence from silicon-rich phase.



**Fig. 3.** Schematic illustration of the experimental apparatus used in this study. (A) For leaching chromite lump. 1-Teflon holder; 2-Glass beaker; 3-Sulfuric acid and oxidant; 4-Chromite lump; 5-Automatic temperature-controlled electric heater. (B) For leaching chromite powder. 1-Variable speed blender; 2-Retort stand; 3-Erlenmeyer flask; 4-Chromite powder; 5-Sulfuric acid and oxidant; 6-Automatic temperature-controlled electric heater.

### 2.2. Methods

The leaching behavior of both the silicate and the spinel phases was investigated in the current study. Before the test, a chromite lump was polished by polisher and several types of abrasive paper to get two smooth flat surfaces. 100 mL 80 wt.% sulfuric acid and 1 g oxidant were mixed in a glass beaker on an automatic temperature-controlled electric heater, and the heating of the solution was started. When the temperature reached the set point, the chromite lump held by a Teflon holder was immersed in the solution, which was agitated (cf. Fig. 3(A)). After a certain period of time, the chromite lump was taken out of the vessel followed by quenching with deionized water, which was performed carefully to avoid any significant change of the surface eroded by the solution.



**Fig. 2.** Photograph (left) and SEM images (center and right) of South African chromite.

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