

Mechanisms of surface charge development of serpentine mineral

Bo FENG, Yi-ping LU, Qi-ming FENG, Peng DING, Na LUO

School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China

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Abstract: The electrokinetic behavior and surface dissolution of serpentine mineral were studied through Zeta potential measurements, dissolution experiments and X-ray photoelectron spectroscopy. The results show that serpentine has an iso-electric point (IEP) of 11.9, which is higher than that of other phyllosilicate minerals. Dissolution experiments show that the hydroxyl is easy to dissolve with respect to the magnesium cations in the magnesium oxide octahedral sheet. As a result of hydroxyl dissolution, the magnesium ions are left on serpentine surface, which is responsible for serpentine surface charge. The removal of magnesium ions from serpentine surface by acid leaching results in a decrease of serpentine IEP. Therefore, it has been clearly established that the surface charge developed at the serpentine/aqueous electrical interface is a function of the serpentine surface incongruent dissolution.

Key words: serpentine; magnesium ions; hydroxyl; surface charge; incongruent dissolution

1 Introduction

Serpentine is a magnesium-rich phyllosilicate mineral that occurs as a gangue component in many base metal sulfide ore deposits around the world. These ores are generally beneficiated by flotation. In sulfide ore processing, serpentine may report to flotation concentrates through attachment to the valuable minerals as “slime coatings” [1–3]. As a kind of magnesium silicate (MgO) gangue mineral, a large quantity of serpentine in flotation concentrates can cause problems during smelting, often resulting in the imposition of smelter penalties for mineral processing companies [4]. In addition, these hydrophilic serpentine minerals may interfere with the flotation of valuable sulfide minerals, such as pentlandite [1,5]. A coating of hydrophilic slime particles will decrease the hydrophobicity of the sulfide particle and may also reduce collector adsorption [6]. Either of these flotation mechanisms will result in lower recoveries of the valuable sulfide minerals [7,8].

It has been deduced from flotation studies that the formation of slime coatings is directly related to the surface potentials of the sulphide minerals and MgO gangue particles [9,10]. As serpentine has a positive potential at pH values up to 9.5 [1], it is therefore likely that it will attach through electrostatic attraction to the

negatively charged pentlandite surface.

Surface charge is an important factor in controlling particle-particle interactions. All solids immersed in polar media develop a charged surface. The main mechanisms of charging include: 1) The ionization/dissociation of ionogenic groups can take place on the surface of a solid resulting in the development of surface charge; 2) Charge can develop by adsorption of ions; 3) Unequal dissolution of ions in the case of certain ionic substances can lead to a net charge on the substrate; 4) Lattice substitutions and defects can lead to an exchange of one ion for another of similar ionic radius [11].

The aim of this work is to know the mechanisms of surface charge development of serpentine mineral. By knowing the charge development mechanisms of serpentine mineral, it will be easy to regulate the surface charge of serpentine mineral and eliminate the adverse effect of serpentine mineral on sulphide flotation.

2 Experimental

2.1 Samples and reagents

The serpentine used for all experiments was obtained from Donghai, Jiangsu Province, China. Mineralogical and X-ray powder diffraction data confirmed that the serpentine sample was of high purity with trace amounts of chlorite and amphibole (Fig. 1).

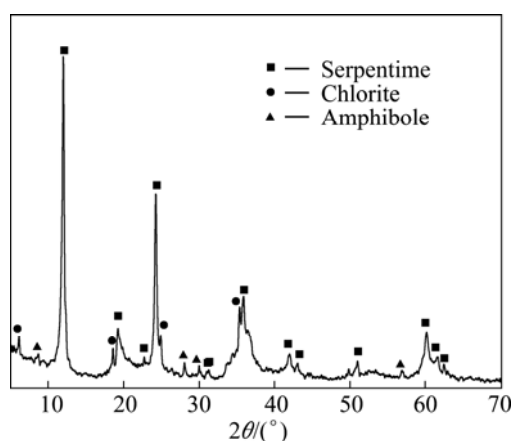


Fig. 1 XRD pattern of serpentine

The sample was dry ground and screened. The particle size distribution determined using a Malvern Instruments Mastersizer was less than 10 μm , with a D_{50} of 3.94 μm , a D_{90} of 9.62 μm and an average diameter of 6.17 μm .

Leached serpentine was prepared by leaching pure serpentine sample in solution under strong acid condition (pH 3) at constant ionic strength (0.1 mol/L KNO_3) for a period of 24 h. The pH was kept constant by using a titrator and the suspension was mechanically stirred throughout the experiment. Samples were filtered to obtain the supernatant. The concentration of ions was measured using ICP (inductively coupled plasma) and the result is shown in Table 1.

Table 1 Concentration of ions dissolved from serpentine by acid leaching

Element	Mg	Si	Fe	Ni	Cu	P	Mn
Concentration/ ($\text{mg}\cdot\text{L}^{-1}$)	14.63	2.01	1.10	0.18	0.13	0.07	0.04

One of the shortcomings of the filtrate analysis is that it only highlights the net dissolution chemical species. There is no tracking of the amount or identity of species that may have initially dissolved but subsequently re-adsorbed back onto the mineral surface. To overcome this shortcoming and further characterize the leached samples, the surface of each serpentine sample was analyzed using X-ray photoelectron spectroscopy (XPS). The atomic concentrations of the different elements present on the surface of the serpentine were determined based on the intensities of the C 1s, O 1s, Mg 1s, Fe 2p, Si 2p signals produced. The results of this surface analysis are summarized in Table 2. Analysis of chemical species present on the surface of each sample by XPS indicated that the surface of the leached sample contained less magnesium and slightly more silicon.

Table 2 Mole fraction of elements on surface of serpentine samples by XPS

Sample	$x(\text{C})/\%$	$x(\text{O})/\%$	$x(\text{Si})/\%$	$x(\text{Mg})/\%$	$x(\text{Fe})/\%$
Serpentine	13.4	53.1	9.1	23.8	0.6
Leached serpentine	5.2	63.7	11.8	18.8	0.5

The characterization of surface properties of original and leached serpentine mineral was also carried out with the SEM images (Fig. 2). The surface morphologies of original serpentine and leached serpentine are different, confirming the result that acid leaching dissolved ions from serpentine surface.

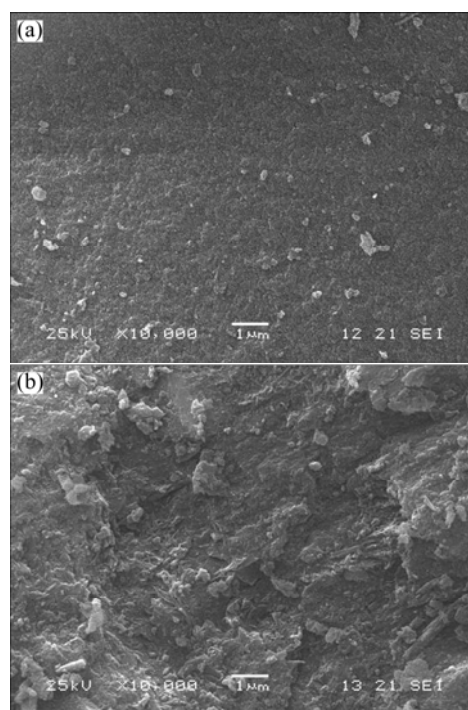


Fig. 2 SEM images of serpentine sample: (a) Original serpentine; (b) Leached serpentine

Potassium nitrate was used to maintain the ionic strength and hydrochloric acid and potassium hydroxide were used as pH modifiers. All the reagents used in this study were of analytical grade. Deionized double distilled water was used for all tests.

2.2 Methods

2.2.1 Dissolution experiment

The dissolution experiments of serpentine aqueous suspension were carried out at constant ionic strength (0.1 mol/L KNO_3). Serpentine powder was taken and made up to 40 mL in 100 mL Erlenmeyer flask. The suspension was then agitated with a magnetic stirrer. The sample was then centrifuged and the concentration of ions left in solution was analyzed using the ICP. The concentration of hydroxyl ion dissolved from serpentine

surface was measured by pH, and the increase of solution pH illustrated the increase of hydroxyl concentration. Five different runs were accomplished for each experiment, and the average was taken as the amount of ions present in the liquid.

2.2.2 Zeta potential measurements

Isoelectric point (IEP) values of serpentine samples were determined by measuring the electrophoretic mobility of aqueous dispersions as a function of pH in a zeta potentiometer. For these measurements, 30 mg of serpentine sample was added to desired amount of 1 mmol/L KNO_3 solution and ultrasonicated for 30 min, magnetically stirred for 10 min and the pH was adjusted using HCl or KOH. To check the effect of magnesium on the serpentine/water electrical interface, MgCl_2 was also used as electrolyte, adding the appropriate amount of KNO_3 to keep the ionic strength a constant.

2.2.3 X-ray photoelectron spectroscopy (XPS)

X-ray Photoelectron spectroscopy, also known as electron spectroscopy for chemical analysis (ESCA), is an ex-situ technique used to analyze the surface layers of solids. It provides information about the chemical composition of species detect on the mineral surface. The X-ray photoelectron spectra of the samples were recorded using the ESCALAB MK-II instrument.

2.2.4 Scanning electron microscopy

A CAMSCAN CS44FE scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDXS) was used to produce images and characterize the elemental composition of the serpentine particles.

3 Results and discussion

3.1 Determination of dissolution of hydroxyl from serpentine surface

Serpentine is a layered silicate mineral that is made of a stacking of layers: each layer being constituted of one magnesium oxide octahedral sheet and one silicate tetrahedral sheet [12]. Two crystallographic distinct O—H groups occur in serpentine minerals (Fig. 3). Inner O4—H4 bonds point towards the center of the hexagonal rings inside the layer thickness while surface O3—H3 lies within the interlayer space between two layers. The latter are considered to be responsible for the cohesion between two successive layers by forming hydrogen bonds [14]. Within the tetrahedral and the octahedral sheets, the structure is held by ionic-covalent bonds while the sheets are usually linked by the weak hydrogen bonding interactions [15]. As a result, crystal cleavage along these layers is easy to occur and electrically neutral faces will form on the surface. Any charge on these faces is developed by lattice defects or incongruent dissolution [16].

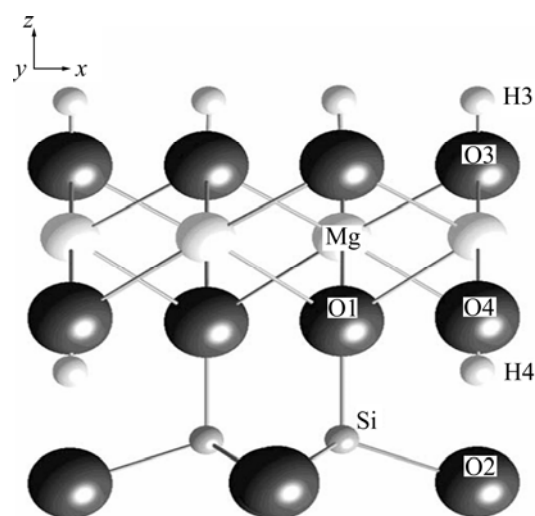


Fig. 3 Crystal structure of lizardite along (010) [13]

In serpentine minerals the lateral dimensions of the Si tetrahedral layer are smaller than those of the Mg octahedral layer which forces the mineral to adopt different strategies to solve the mismatch [17]. The isomorphous substitutions of trivalent cations (Al^{3+} and Fe^{3+}) in the tetrahedral sheets can solve this mismatch, preserving the ideal topological layer of the serpentine structure [12]. For the samples used here, Al element exists in a small quantity and so iron must be the element that plays the main role in stabilizing the serpentine structure. The substitution of Fe^{3+} for Si^{4+} in the silica tetrahedral will cause a proton deficiency in outer tetrahedral layers, which results in the presence of a negative charge on surface of serpentine. However, from the result in Fig. 4, we can see that the serpentine surface is positively charged at an extensive pH range, having an IEP value of 11.9. So the incongruent dissolution of ions from serpentine surface may be the main mechanism of surface charge development of serpentine minerals.

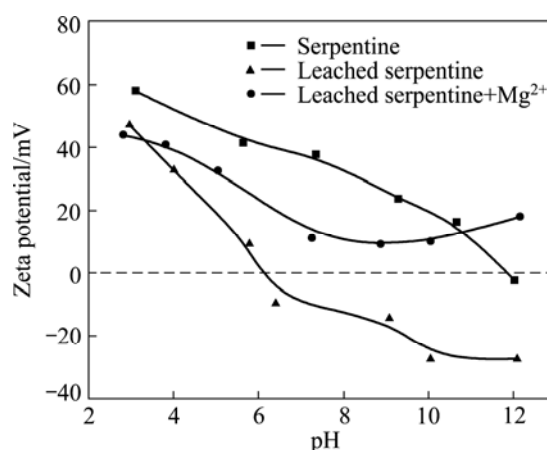


Fig. 4 Electrophoretic mobility curves as function of pH for different samples

MARTINEZ and ZUCKER [18] measured the zeta potentials of lizardite and chrysotile and suggested that the greater the exposure of magnesium in the outer layer, the higher the positive charge and that reducing this exposure decreases the magnitude of the positive. In the magnesium oxide octahedral sheet, each magnesium atom is coordinated to six oxygen atoms. The magnesium atom lies at the centre of the oxygen atoms, forming an octahedron. The majority of the oxygen atoms are bonded to hydrogen atoms, creating hydroxyl groups [19]. So, the exposure of magnesium in the outer layer could be explained by a surface preferential dissolution of the hydroxyl with respect to the magnesium cation in the magnesium oxide octahedral sheet.

In order to determine whether or not the incongruent dissolution of hydroxyl with respect to the magnesium cation is the main reason of surface charge development of serpentine mineral, solubility studies were carried out at different serpentine concentration and conditioning time (Fig. 5) to study the dissolution of hydroxyl from serpentine surface. The concentration of hydroxyl dissolved from serpentine surface was determined by solution pH. The pH of deionized water used in this study was 6.45; upon serpentine addition, the

solution pH increased significantly with the increase of serpentine concentration, illustrating that more hydroxyl dissolved from serpentine surface when the concentration of serpentine increased. Conditioning time also had an important effect on the dissolution of hydroxyl from serpentine surface. The pH of solution markedly increased up to a conditioning time of 5 min, with further conditioning time producing little increase in pH.

For this system, as no pH modifiers were presented, the change of solution pH was mainly the result of dissolution of hydroxyl from serpentine surface. When the conditioning time reaches 5 min, the pH of serpentine solution (10 g/L) increases from 6.45 to 9.46, corresponding to an increase in the concentration of hydroxyl from 2.82×10^{-8} mol/L to 2.82×10^{-5} mol/L. The concentration of cations dissolved from serpentine surface was also measured under the same condition. The result is shown in Table 3. Neither silicon nor aluminum was detected; however, serpentine released 0.24 mg/L of magnesium and 0.031 mg/L of iron. The total concentration of cations released from serpentine surface is 1.055×10^{-5} mol/L. This result shows that the ions are incongruently dissolved as hydroxyl was more easily dissolved from serpentine surface than cations.

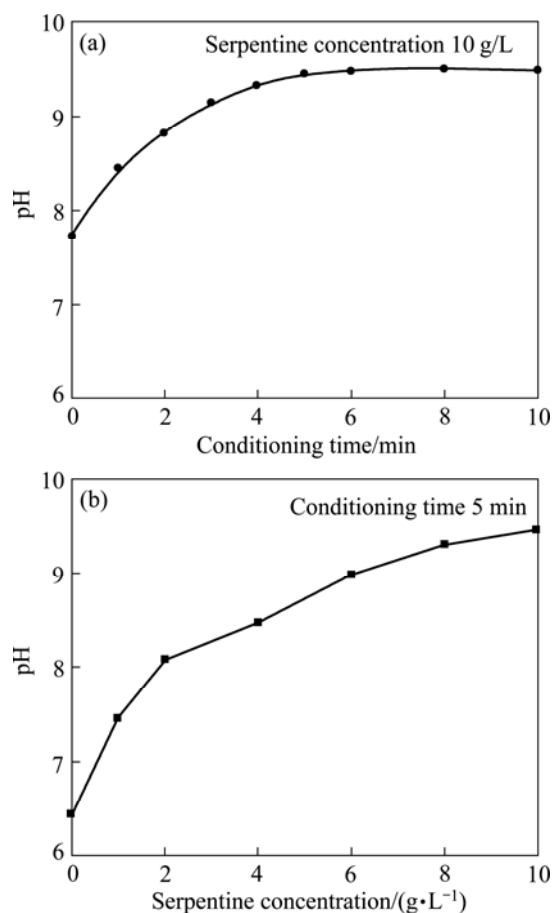


Fig. 5 Dissolution of hydroxyl from serpentine surface as a function of conditioning time (a), serpentine concentration (b)

Table 3 Concentration of ions dissolved from serpentine

Element	Mg	Fe	Si	Al
Concentration/(mg·L ⁻¹)	0.240	0.031	—	—

3.2 Effect of magnesium ions on serpentine surface charge

The dissolution of hydroxyl ions has a strong effect at the water/serpentine electrical interface. In our opinion, as a result of hydroxyl dissolution, the magnesium ions are left on serpentine surface, which are responsible for serpentine surface charge. To determine this conclusion, the zeta potential of leached serpentine was measured and compared with the original serpentine and the result is shown in Fig. 4. The XPS results have shown that the leached serpentine sample contains less magnesium and slightly more silicon on its surface. From Fig. 4, we can see that acid leaching results in a significant change in IEP for serpentine, and the IEP decreases from pH 11.9 for the original sample to pH 6.2 for the leached serpentine. These differences suggest that the electrokinetic properties of serpentine minerals are strongly dependent on their surface dissolution behaviour.

Acid leaching dissolved magnesium ions from serpentine surface and influenced water/serpentine electrical interface. Experiments were also conducted to determine the effect of the addition of magnesium on the electrophoretic mobility curves of leached serpentine.

For an MgCl_2 concentration of 10^{-4} mol/L, large variations in the mobility values were observed with respect to the experiment only with the non adsorbing electrolyte (KNO_3). The adsorption of Mg cations promoted a shift of the mobility from negative to positive values, which was more significant for the basic pH region where leached serpentine particles were more negatively charged. The adsorption of Mg^{2+} on serpentine surface was associated with the cation hydrolyzing to $\text{Mg}(\text{OH})^+$ and surface precipitation of metal hydroxide, which occurred at pH values just below those for bulk precipitation [20,21]. For magnesium under current conditions, bulk precipitation would start at pH 10 (Fig. 6).

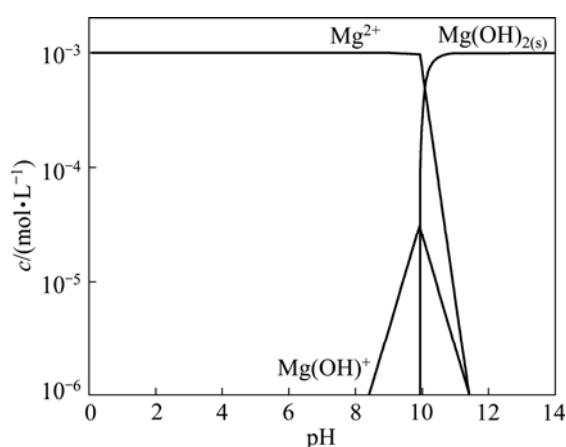


Fig. 6 Species distribution diagram for 1×10^{-4} mol/L Mg^{2+}

Based on the observations made in this work, it is proposed that the surface of serpentine carries a positive charge over a wide pH range as a result of preferential dissolution of the hydroxyl with respect to the magnesium cation in the magnesium oxide octahedral sheet. It is also proposed that the surface of serpentine undergoes a change from positive to negative at pH above 6.2, after treating the serpentine sample by HCl. This finding gives us an inspiration on how to regulate the surface charge of serpentine mineral, which will be researched in the future.

4 Conclusions

1) Serpentine is a layered silicate mineral that is made of a stacking of layers: each layer being constituted of one magnesium oxide octahedral sheet and one silicate tetrahedral sheet. Within the tetrahedral and the octahedral sheets, the structure is held by ionic-covalent bonds while the sheets are usually linked by the weak hydrogen bonding interactions. As a result, crystal cleavage along these layers is easy to occur.

2) Dissolution experiments have determined that the preferential dissolution of the hydroxyl with respect to

the magnesium cation causes an increase of solution pH and makes the magnesium ions left in serpentine surface. The removal of magnesium ions from the serpentine surface by acid leaching results in a decrease of serpentine IEP.

3) The incongruent dissolution of hydroxyl with respect to magnesium ions is the main mechanism of surface charge development of serpentine mineral.

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蛇纹石表面电荷的形成机理

冯 博, 卢毅屏, 冯其明, 丁 鹏, 罗 娜

中南大学 资源加工与生物工程学院, 长沙 410083

摘 要: 通过 zeta 电位测试、溶解试验以及 X 射线光电子能谱测试研究了蛇纹石矿物的动电行为和表面溶解行为。结果表明, 蛇纹石的等电点为 11.9, 比其它的镁硅酸盐矿物的高。溶解试验表明蛇纹石结构中的镁氧八面体层中的羟基比镁离子容易溶出, 羟基的溶出使镁离子留在蛇纹石表面, 这是蛇纹石等电点较高的原因。移除表面的镁离子可以降低蛇纹石的等电点。因此, 可以推断蛇纹石等电点较高的原因在于蛇纹石表面羟基和镁离子的不等量溶解。

关键词: 蛇纹石; 镁离子; 羟基; 表面电荷; 不等量溶解

(Edited by Hua YANG)