



Selective surface magnetization of pentlandite with magnetite and magnetic separation



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ABSTRACT

In this work, selective surface magnetization technology was employed to separate pentlandite from serpentine by adding fine magnetite coating on pentlandite surfaces, which was different from the conventional flotation. EDLVO (Extended Derjaguin-Landau-Verwey-Overbeek) theory calculations indicate that under a weak external magnetic field of 4.77 kA m^{-1} . Interactions between magnetite and pentlandite were obviously stronger than that between magnetite and serpentine. Therefore, fine magnetite fractions selectively adhered to pentlandite surfaces and enhanced its surfaces' magnetism. The above prediction was well confirmed by the magnetic coating and magnetic separation tests with adding 3% magnetite fines, at a magnetic field intensity of 200 kA m^{-1} . SEM-EDS analyses show that magnetite particles were preferentially adsorbed onto pentlandite instead of serpentine. VSM (vibrating sample magnetometer) measurements further confirm that the magnetism of magnetic products (pentlandite) was strongly enhanced.

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1. Introduction

In nature, sulphide ores and laterites are the major sources of Ni metal. Although about 70% of nickel resources are contained in laterites, only 40% of the world's nickel production comes from these ores. This is because nickel in laterites is often finely disseminated in various minerals (goethite, garnierite, serpentine, cronstedtite, limonite, harzburgite, and dunite and so on) in very fine size (about $\sim 38 \mu\text{m}$). Therefore, laterite ores are usually characterized by complex mineralogy and low grade which leads to compromise any significant upgrading in Ni values, including conventional physical methods (sink-float or dense media separation, gravity separation, magnetic separation, electrostatic separation, reduction roasting and flotation) and chemical methods (conventional smelting process: hydrometallurgical or pyrometallurgical processing, high temperature and/or high pressure autoclave methods) [1–3]. Therefore the sulphide ores are still the main source of Ni (pentlandite) worldwide, which is typically floated by adopting combinations of xanthate collector, MIBC frother, soda ash or acid pH modifier, and carboxymethyl-cellulose (CMC) or sodium hexametaphosphate (SHMP) dispersant [4,5]. In sulphide nickel or nickel-copper ores, the predominant sulphide minerals are pentlandite, chalcopyrite, and pyrrhotite. Gangue minerals are mainly composed of MgO silicates, such as serpentine, pyroxene, lizardite, chlorite, and talc and so on. Relatively high levels of

MgO silicates often report to the froth phase resulting in Ni grade dilution during flotation, affecting the smelter efficiency and lifetime. A great number of researchers have revealed mechanisms of magnesium silicates interference as follows: 1) entrainment or entrapment of fine MgO silicates liberated particles or poor liberation of sulphide minerals locked with them [6,7]; 2) heterocoagulation or slime coating due to the attachment of MgO silicates to surfaces of the Ni minerals [8]; 3) transport of MgO silicates via composite particles having hydrophobic sites [9]; and 4) inadvertent activation of these MgO silicate minerals by Cu^{2+} or Ni^{2+} species dissolved from chalcopyrite or pentlandite [10].

In the past 10 years, many measures have been conducted to reject MgO minerals and Ni recovery has been improved. A new process, a combination of a two-stage cyclone classification and column flotation, was implemented at Mt. Keith to raise Ni recovery [11]. Saline water was reported to improve pentlandite flotation due to electrolytes in saline water, though compressing the electrical double layer, reducing the coating of MgO silicates on pentlandite surfaces [12]. Other approaches proposed to improve pentlandite floatability include: high intensity conditioning (HIC) that especially increases the flotation rate of pentlandite contained in the 8 to $75 \mu\text{m}$ particle size range [13]; thermal pretreatment with microwave radiation to convert serpentine into olivine, reducing the hetero-aggregation [14]; and disintegrating the fibers by chemical dissolution (H_2SO_4) and mechanical attack (grinding) [15]. This paper proposes a new technology, called selective magnetic coating, to enhance the pentlandite surface magnetization through adding fine magnetite, and then separating pentlandite from serpentine through magnetic separation.

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At present, the magnetic coating technology has been used widely in many fields of the treatment of effluent, the separation of biological cells, coal desulphurization, and mineral processing [16]. The principle of this technology is to incorporate a discrete magnetic phase (mainly fine magnetite) into the weakly or non-magnetic target particles to increase their magnetism and to recover these agglomerates by magnetic separation [17]. By means of this approach, Nott et al. could remove TiO₂ from clay or kaolin [18]. The separation of calcite and dolomite from phosphate minerals was described both experimentally and theoretically by Parsonage [19]. Prakash et al. discussed the selective magnetic separation of hematite from quartz and corundum using a magnetic coating method, in which the hematite was coated by the magnetite particles and separated at a magnetic field of 620 kA m⁻¹ [20]. Singh et al. adopted this process to recovery iron minerals from Indian iron ore slimes containing 56% Fe, 4.8% SiO₂, and 7.2% Al₂O₃. By adding oleate colloidal magnetite of 10–40 g/t, an iron concentrate of 62.6% Fe, 2.0% SiO₂, and 3.5% Al₂O₃, 72% recovery of Fe was achieved [21]. Other minerals such as chromite/serpentine, quartz/magnesite, and calcite/quartz and so on were also separated using this magnetic coating technology by different scholars [22–24]. In spite of the fact that many minerals have been successfully separated, very few studies have been published to process sulphide ores, particularly, the separation of pentlandite from serpentine using the selective magnetic coating method. Thus, the paper discusses the application of magnetic coating process for the separation of pentlandite from serpentine minerals and aimed to demonstrate the possibility of sorting copper-nickel sulphide ores with this technology.

2. Theoretical bases

The selective adsorption of fine magnetic fractions on surfaces of minerals are controlled by the total interaction energy between the particles of the suspension. In case of a net repulsive interaction, the particles will tend to be prevented from absorbing and hence no magnetic coating occurs. In contrast, a net attractive interaction between minerals and magnetite will favor conglutination and produce a coating of the magnetite on the mineral surface. The dominating interactions between particles are mainly determined by the Van-Der-Waals interactions (U_A) and electrical interactions (U_E) in the deionized water. While the external magnetic field is added, there also exist magnetic interactions (U_M) between two magnetic particles. In this case, the total interaction (U_T) is given by Lu [25]:

$$U_T = U_A + U_E + U_M$$

The magnitude of the above interactions (U_A , U_E , U_M) is calculated according to the following expressions.

2.1. Van-der-Waals interaction, U_A

- 1) The interaction between spherical mineral particles is calculated according to the following expression.

$$U_A = -\frac{A_{132}}{6} \left[\frac{2R_1R_2}{H^2 - (R_1 + R_2)^2} + \frac{2R_1R_2}{H^2 - (R_1 - R_2)^2} + \ln \frac{H^2 - (R_1 + R_2)^2}{H^2 - (R_1 - R_2)^2} \right] \tag{1}$$

where, for $H \ll \min(R_1, R_2)$

$$U_A = -\frac{A_{132}R_1R_2}{6H(R_1 + R_2)} \tag{2}$$

The critical parameter determining the value of the Van-Der-Waals interaction is the Hamaker constant. For mineral particles in the

deionized water, the calculation formula is as follows:

$$A_{132} = (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}}) \tag{3}$$

where A_{11} and A_{33} are the Hamaker constant of mineral 1 and mineral 2, respectively; A_{22} is the Hamaker constant of water in the vacuum (3.68×10^{-20} J).

- 2) The interaction between a spherical particle and a layered particle is usually determined by the following equation:

$$U_A = -\frac{A_{132}}{6} \left[\frac{2R}{H} + \frac{2R}{H + 4R} + \ln \left(\frac{2R}{H + 4R} \right) \right] \tag{4}$$

where H is the distance between two mineral particles; R is the radius of the spherical particle.

It is must be noted that the particle size of magnetite mineral is extremely fine (less than 10 μm), while the serpentine belongs to phyllosilicates. Therefore, the magnetite and serpentine are assumed into a sphere and a layer, respectively, and the interaction between them should be calculated by the Eq. (4). The Hamaker constant of pentlandite, serpentine and magnetite here are 22.8×10^{-20} J, 10.6×10^{-20} J, and 24.0×10^{-20} J, respectively. The radius of magnetite and pentlandite are 2.0 μm and 28 μm, respectively, which were from the median diameter D_{50} (D_{50} of magnetite: 4.01 μm, D_{50} of pentlandite: 56.1 μm) directly measured by the Malvern-2000 particle size analyzer.

2.2. Electrical interaction under constant potential, U_E

- 1) The interaction between two different spherical particles has been described by Hogg et al. as follows:

$$U_E = \frac{\pi\epsilon_0\epsilon R_1R_2}{R_1 + R_2} (\varphi_1^2 + \varphi_2^2) \left[\frac{2\varphi_1\varphi_2}{\varphi_1^2 + \varphi_2^2} \ln \frac{1 + e^{-\kappa H}}{1 - e^{-\kappa H}} + \ln(1 - e^{-2\kappa H}) \right] \tag{5}$$

where ϵ_0 and ϵ are the permittivity of vacuum and solution ($\epsilon_0\epsilon = 7.17 \times 10^{-20}$ F·m⁻¹), respectively; φ_1 and φ_2 are the Zeta potential of minerals 1 and 2, respectively; κ^{-1} is the Deby-Huckel parameter of 10.4×10^{-20} m⁻¹; R is ditto.

- 2) The interaction between a spherical particle and a platelike particle is usually determined by the following equation:

$$U_E = \pi\epsilon_0\epsilon R (\varphi_1^2 + \varphi_2^2) \left[\frac{2\varphi_1\varphi_2}{\varphi_1^2 + \varphi_2^2} \ln \frac{1 + e^{-\kappa H}}{1 - e^{-\kappa H}} + \ln(1 - e^{-2\kappa H}) \right] \tag{6}$$

The above Eqs. (5) and (6) hold exactly for φ_1 or φ_2 of less than 25 mV and the particle radius should be greater than $10/\kappa$. The Zeta potential of magnetite, serpentine and pentlandite was -4.21 mV, 8.08 mV and -18.01 mV, respectively, measured by the Nano-ZS900 Zeta Plus potential meter, at pH = 7 ± 0.5.

2.3. Magnetic interaction of two magnetic mineral particles, U_M

- 1) Wang et al. proposed the following equation for the magnetic interaction between magnetite and weakly magnetic minerals (such as hematite, pentlandite) due to the remanent magnetization of magnetite, which is originated by the ambient geomagnetic field, when there is no external magnetic field [26].

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