

Towards nanoparticle flotation collectors for pentlandite separation

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ABSTRACT

Hydrophobic polystyrene nanoparticles (latex) were evaluated as replacement collectors for pentlandite flotation with a view to improving processing of ultramafic ores. Nanoparticles adsorb onto pentlandite particles, rendering them sufficiently hydrophobic to induce flotation. Polystyrene nanoparticles bearing surface imidazole groups specifically bind nickel ions and appear to improve selectivity (i.e. nickel grade), presumably because of chelation interactions between the imidazole groups and the pentlandite surface. Very high nanoparticle concentrations were required for high pentlandite recoveries under the high ionic strength conditions typically used in industry because the nanoparticles were coagulating. The path to commercially relevant nanoparticle flotation collectors involves increasing the colloidal stability of the nanoparticles while minimally impacting hydrophobicity.

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1. Introduction

In Canada and many other countries there is interest and activities aimed at extracting nickel from ultramafic ores. Flotation of pulps with high serpentine contents presents many challenges including: 1) high flotation pulp viscosities (Genc et al., 2012; Patra et al., 2012); and, 2) surface contamination of pentlandite-rich particles (Edwards et al., 1980; Bremmell et al., 2005; Peng and Bradshaw, 2012). Laboratory studies have shown that introduction of 30% serpentine drives pentlandite recovery down from 90% to less than 25% (Mani et al., 1997).

Many studies have revealed the mechanisms of serpentine interference. High viscosity flotation pulps can inhibit or completely prevent bubble transport through the pulp, leading to levitation of the bed of serpentine fibers to the top of the flotation cell. Similar effects have been reported for deinking flotation in wood pulp fiber suspensions (Ajerssch and Pelton, 1996, 1999). If the yield stress of the suspension is greater than the bubble buoyancy force, the bubbles become trapped in the fiber network.

The consequences of serpentine coatings on pentlandite have also been discussed. Pietrobon et al. proposed that slime coatings interfere with collector adsorption (Pietrobon et al., 1997), whereas others have proposed that the slime contamination acts as a surface barrier that interferes with bubble attachment (Mani et al., 1997). Consider a smooth pentlandite surface supporting serpentine fibers and

treated with potassium amyl xanthate (PAX) collector – Fig. 1 shows an example. The diameter of the serpentine fiber, lying on the surface, is typically 20 nm (Yada, 1971) whereas the adsorbed PAX hemi-micelle is approximately equivalent to the extended length of a 5 carbon, hydrocarbon chain which is about 1 nm – Fig. 2 illustrates the range of pertinent size scales. The key point is that an air bubble approaching this surface is most unlikely to contact the conventional collector micelles, which are buried between the much larger serpentine fibers.

There are commercial ultramafic pentlandite processing operations currently running or in the planning stages (Senior and Thomas, 2005; Mani et al., 1997; Dai et al., 2009). The processes employ extensive desliming (grinding fibers and centrifugal separation) and sodium carbonate addition. Other approaches proposed to improving flotation of ultramafic pulps include: dissolving the fibers in acid (Uddin et al., 2012; Feng et al., 2012); copper activation (Peng and Seaman, 2012); and many reports of guar and other depressants. Herein we describe results of a laboratory study in which conventional collectors are replaced with much larger hydrophobic nanoparticles – see Fig. 2. Our hypothesis is that nanoparticle collectors are large enough to reach beyond the adsorbed serpentine fibers to facilitate air bubble attachment in flotation.

In the early stages of this project we were surprised to learn that colloidal or nanoparticles had never been employed as collectors. Thus we did not know if nanoparticles could serve as collectors for any type of mineral or mineral model. Furthermore, we had no idea of the potential roles of nanoparticle size, hydrophobicity and coverage (i.e. the fraction of the mineral surface coated with nanoparticle). Coverage is a particularly important parameter because completely

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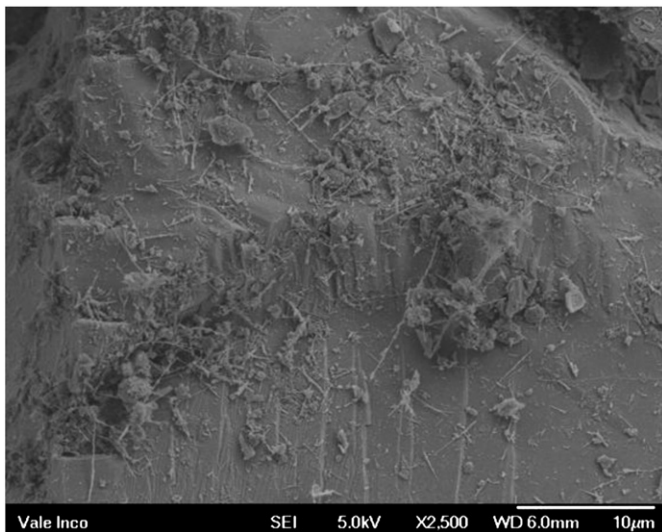


Fig. 1. An electron micrograph showing serpentine fibers on pentlandite surfaces (Xu et al., 2010).

coating mineral particles with what is essentially a latex paint would be too expensive. Our initial work addressed these issues and the key findings were: 1) nanoparticles based on polystyrene (polystyrene latex) are sufficiently hydrophobic to promote flotation when adsorbed onto hydrophilic glass beads; coverage of as little as 5% of the glass bead area was sufficient to give good recoveries (Yang et al., 2011); 2) nanoparticle surface chemistry is important – if the nanoparticles are too hydrophilic, recovery is low (Yang and Pelton, 2011); 3) for smooth, uncontaminated glass beads, smaller nanoparticles are more efficient than larger ones at the same coverage; and, finally nanoparticle adsorption kinetics is slower than that of conventional molecular collectors (Yang et al., 2012). Herein we report the performance of nanoparticle flotation collectors specifically designed for ultramafic pentlandite. Although we do not yet have a commercially feasible product, we do show that the nanoparticles

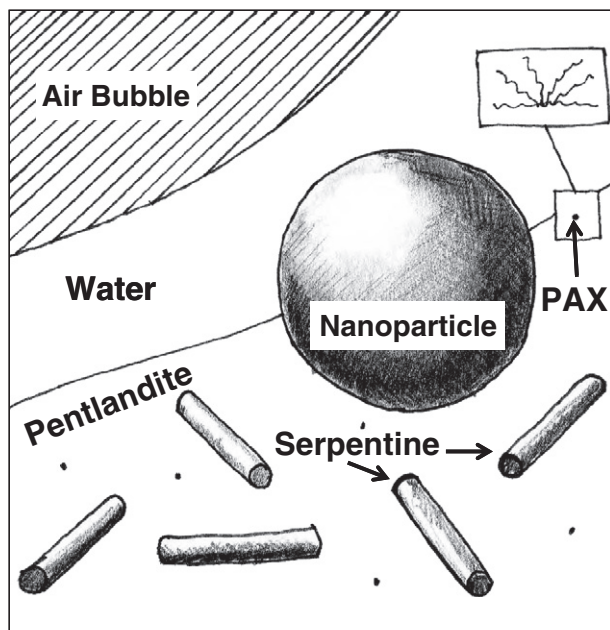


Fig. 2. Illustrating the nanoparticle collector hypothesis – nanoparticles larger than the diameter of serpentine fibers can contact and adhere to air bubbles, whereas conventional collector hemi-micelles are too small to contact bubbles when surfaces are contaminated with serpentine fibers.

can give both high recoveries and nickel grades. Furthermore our experiments point to the issues that need to be resolved as we move towards commercially significant nanoparticle flotation collectors.

2. Materials and methods

2.1. Materials

Chemicals: styrene (99%, Sigma-Aldrich) and 1-vinylimidazole (VI, $\geq 99\%$, Sigma-Aldrich) were purified by vacuum distillation. 3-(Methacryloylamino)propyl trimethyl ammonium chloride solution (MAPTAC, 50 wt.% in H_2O , Sigma-Aldrich) was passed through an inhibitor-removing column. 2,2'-Azobis(2-methylpropionamide) dihydrochloride (V50, 97%) and cetyltrimethylammonium bromide (CTAB, 95%) were purchased from Sigma-Aldrich and used as supplied. Potassium amyl xanthate (PAX), a molecular collector and UNIFROTHER 250C were donated by Vale Base Metals Technology Development (VBMTD, Mississauga, ON). For nanoparticle preparation and characterization and small-scale laboratory flotation tests, all solutions were made with Type 1 water (18.2 $M\Omega$ cm, Barnstead Nanopure Diamond System). Soda ash (Na_2CO_3) was used to adjust the pH of the flotation slurry.

Glass beads ($\leq 106 \mu m$, -140 U.S. sieve, unwashed) were purchased from Sigma-Aldrich. The particle size distributions of the glass beads were measured with a Malvern Mastersizer 2000. The particle size distribution was approximately log normal with an area averaged mean diameter of $66 \mu m$, and a corresponding specific surface area of $0.037 m^2/g$. The electrophoretic mobility of the beads in 5 mM NaCl at ambient pH was $-2.33 (\pm 0.22) \times 10^{-8} m^2 s^{-1} V^{-1}$.

Synthetic ore: A purified high-grade pentlandite (Pn) sample, provided by Vale, was blended with a model slime sample to give a model synthetic ultramafic ore. The Pn sample had a nickel content of $27 \pm 2\%$. Note that the Ni grade of 100% pure pentlandite, $Ni_{4.5}Fe_{4.5}S_8$, is about 34%. The particle size distribution was measured with a Malvern Mastersizer 2000 giving a $12 \mu m$ mean particle size with a standard deviation of $15 \mu m$.

The model slime sample was taken from scavenger flotation tails of a Pipe drill ore sample. Vale's flotation procedures for acquiring tails included grinding, hydrocyclone desliming followed by rougher and scavenger flotation – details have been published elsewhere (Dai et al., 2009).

Both Pn and slime samples were chemically cleaned to remove residual xanthate and oxidation products from particle surfaces. 5 g Pn and 50 mL of deoxygenated 0.1 M HCl were charged into a three-necked 100 mL flask equipped with a sealable condenser, a rubber stopper with a needle valve for N_2 purging, and a magnetic stirring bar. The mixtures were mixed for 1 h followed by settling and decanting the supernatant. The sediment was twice rinsed with 50–80 mL deoxygenated

Table 1

Recipes for preparation of functionalized nanoparticle collectors, where the final number in the nanoparticle designation is the average particle diameter.

Nanoparticle designation	Initial reactor charge (g)				Starved-feed charge (g)		
	Water	St	MAPTAC or CTAB	V50	St	MAPTAC or VI	Water
St-46	100	0.5	0.10 CTAB	0.10	4.5	–	–
St-56	250	1.0	0.15 CTAB	0.15	9.0	–	–
St-MAPTAC-79	250	0.5	0.125 MAPTAC	0.06	4.5	0.125 MAPTAC	4.7
St-VI-52	100	0.5	0.10 CTAB	0.10	4.5	0.125 VI	4.9
St-VI-MAPTAC-68	100	0.5	0.125 MAPTAC	0.06	4.5	0.125 VI	4.9
St-VI-MAPTAC-92	250	0.5	0.125 MAPTAC	0.10	4.5	0.25 VI	4.7
St-VI-MAPTAC-121	500	1.0	0.50 MAPTAC	0.15	9.0	0.25 VI	9.7
St-VI-MAPTAC-158	100	0.5	0.125 MAPTAC	0.10	4.5	0.25 VI	4.7

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