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IMPACT OF PULP RHEOLOGY ON SELECTIVE RECOVERY OF VALUE MINERALS FROM ORES

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ABSTRACT

Rheological behavior of mineral pulps plays a critical role in almost all mineral processing unit operations. Although the impact of rheology in unit operations such as grinding and slurry transport has received much attention in the past, this is not the case for flotation. The pathway by which the pulp rheology influences the flotation performance is not well understood. The aim of this paper is to explore how physical (shape, size and morphology) and surface chemical properties of minerals contribute to pulp rheology and pathways by which rheology can influence selective value mineral recovery and/or concentrate grade. Systematic studies involving spiking experiments (deliberate addition of fibrous minerals and other solids), measurement of pulp viscosity and yield stress, flotation tests, SEM, EDX and XRD were conducted on a Ni ore and a Cu ore. A phenomenological model was developed. The key components of the model are the formation of a macro-network comprising micro-aggregates of fibrous minerals which significantly increases pulp viscosity, and as a result impedes gas dispersion and bubble-particle attachment and influence froth phase properties. Additionally, the role of various reagent types in regulating pulp rheological behavior was explored.

***Keywords**: Flotation, Rheology, Morphology, Fibrous minerals, Macro-network, Reagents.*

INTRODUCTION

In many of the mineral processing operations pulp rheology play a critical role in selective separation of valuable minerals.[1] For example, pasty pulp poses difficulties in grinding and pulp transport operations. These issues have received a considerable attention in the past. But, the role of pulp rheology on value mineral separation in froth flotation has not been considered seriously.

Comminution results in breaking of an ore to varying sizes and shapes of particles (minerals or their composites). Based on the length, width, and depth (thickness) of the particles their shapes can be grouped into three categories. Group one typically includes particles such as sulfides, quartz that has comparable values of length, width and depth. In group two, particles that have comparatively shorter depth can be considered, such as plate/sheet like talc and clay minerals. Group three includes minerals such as attapulgite (needle shaped) and chrysotile[2] that have relatively shorter width and thickness compared to their length. Morphologies of particles, particularly plate type and fibrous types considerably influence the rheological behavior of pulp. For example, pulp becomes increasingly viscous with increase in plate or fibrous type of particles in it. This is because as the ratio of mean length to width/depth of particles varies widely in pulp their effective volume fraction increases.[3]

The aim of this research investigation was to develop a scientific understanding of the pathways by which fibrous/plate type minerals affect beneficiation and further develop technologies for selective value separation. Ultramafic[4] Ni ore at Pipe, Manitoba, Canada was used for this investigation. The ultramafic ore types constituted more that 60% of serpentine type of minerals, and in parts, the ore body contained varying amounts of fibrous serpentines. Historically, the challenges associated with treating these types of ores are well documented. In this regard it is often assumed that heterocoagulation of serpentines with Ni sulfides is the mechanism responsible for poor Ni recovery.[5] Other mechanisms such as impact of pulp rheological behavior owing to fibrous serpentines are rather overlooked. In this research work the role of fibrous serpentines on pulp rheology and the resultant effect on value mineral separation is presented. Furthermore, the pathways and mechanisms by which pulp rheology interfere with the value mineral separation in flotation is proposed.

EXPERIMENTAL

Materials

Ultramafic Ni ore, Birchtree Ni ore, and porphyry copper ore. Ni ores were obtained from Vale Inco, Canada and copper ore was obtained from Kennecott, USA. Table 1 shows brief mineralogical details. According to our SEM analysis fibrous minerals were not present in Birchtree Ni ore and Copper ore. For model system studies nylon fibers of aspect ratio 5000 was used.

Table 1: Brief mineralogy of ore types

Ore type	Ni	Cu	Mg Silicates
Birchtree Ni Ore	0.7	0.02	4.5%
Porphyry Copper Ore	--	0.7%	5%
Ultrmafic ore	0.3%	0.02	70-75%

Reagents and conditions in flotation

The flotation reagents were obtained from Cytec Industries Inc. Ore was ground at 50–60% solids (w/w) in a rod mill to obtain a p80 of ~100 microns. The ground ore was diluted to obtain a pulp density of 22–23% solids (w/w). A mixture of dithiophosphates was used as collector and used at 40g/t. Frother used was MIBC and dosage used was at 50g/t. The airflow rate was set at 3.5 L/min. Concentrates were collected at 0.5, 2, 4, 7 and 12 min during flotation.

Spiking experiments

Spiking experiments involved adding calculated weights (0%–10%, w/w) of Ultramafic ore/nylon fibers to the both Ni ore (Birchtree) and Cu ore (Porphyry) in separate set of experiments. 1 kg of the Cu and Ni ore was spiked with Ultramafic ore with calculated weight of Ultramafic ore/nylon fibers and feed to the grinding mill. The mill discharge was collected for either rheology or froth flotation experiments.

Rheology

Rheological measurements were carried out using Anton Paar DSR 301 rheometer. 100ml of the grind discharge was poured into a sample holder. A vane geometry was used to measure the yield stress of the pulp.[6] The rheometer was calibrated with standard Cannon viscosity standards. The yield stress value was obtained using Hershel Bulkley model.[7] Yield stress measurements were repeated twice and average values are reported.

Scanning Electron Microscopy

The SEM micrographs were obtained using the Zeiss DSH 982 Gemini SEM. A drop of pulp sample was mounted on an SEM stub. To restore the structure of solids in pulp[8] we adopted an acetone drying. To obtain high resolution images low electron beam voltage (3KeV) was used.

RESULTS AND DISCUSSION

A widely acknowledged problem in processing of ultramafic Ni ore types is slime coating, which is due to opposite surface charge difference between serpentines (positive) and Ni sulfides (negative). An approach to minimize surface charge difference includes processing at highly alkaline conditions, e.g. pH 10. But in many cases processing at alkaline pH has limited success. Thus the goal of this investigation was to find out other pathways by which serpentines affect selective Ni minerals separation. Our research approach includes investigation on a model system. In the model system serpentines were deliberately added (spiking) to a “good” (containing no serpentine type Mg silicates) ore. A serpentine rich (70%) ore was used for spiking in the model system, and the ore contained around 15% of plate type lizardite and 55% of fibrous chrysotile minerals. A schematic of the model system is shown in Fig. 1.

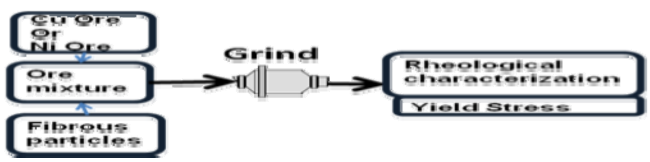


Fig. 1: Schematic of the Spiking experiment design.

Flotation studies were carried out using the model system. In the model system Birchtree Ni ore was spiked with varying amounts of serpentine rich ore. Fig. 2 shows a decrease in Ni recovery with increase in spiking level of serpentine ore in the model system. Slimecoating of serpentines on Ni minerals is a reasonable explanation to justify the decrease in Ni recovery. However, during the tests, the pulp was observed to be increasingly viscous with the level of spiking. Thus, it was not clear as to which one of the two i.e. slime coating or pulp rheology is the responsible factor for decrease in Ni recovery.

In order to minimize slime coating effect deliberately the model system components and the flotation conditions were manipulated accordingly. Thus, in the changed model system Birchtree Ni ore was replaced with a copper ore and the flotation conditions included alkaline conditions with pH value around 10–10.5. Ideally, this would eliminate slimecoating issue as the surface charge of copper mineral (predominantly chalcopyrite) around and above this pH value is negative and that of serpentines are near to zero or negative.[9] Fig. 3a shows copper recovery vs. concentration of the serpentine ore. Decrease in copper recovery was observed with increase in spiking level of serpentine ore. A similar trend was also observed with the model system that included Birchtree ore. Additionally, similar to the studies carried out with Birchtree ore, the pulp was observed to be increasingly viscous with level of spiking. Other observations include, pulp containing 5–6% of fibrous serpentines lead to (1) difficulty in processing due to immovable pulp, (2) absence of a typical froth phase and bubbles bursting as volcanoes at the pulp surface. This indicated that pulp rheology plays an important role in froth flotation.

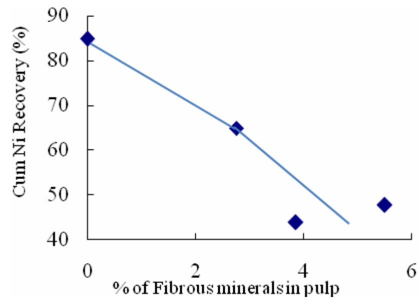
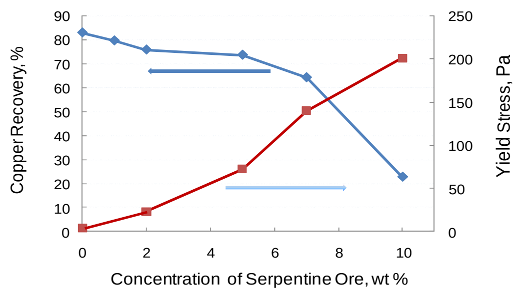


Fig. 2: Effect of HF ore concentration on cumulative Ni Recovery.



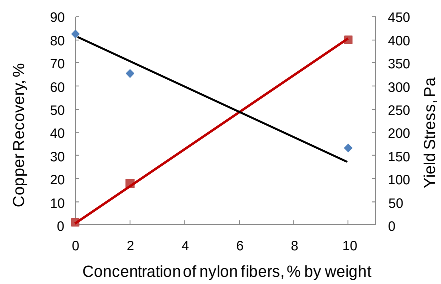


Fig. 3: Effect of (a) serpentines and nylon fibers (b) on copper recovery and yield stress

Our thought was that what would be the contribution of pulp rheogical behavior alone on the froth flotation process. Thus we aim to deliberately negate all the chemical factors of fibrous minerals that would contribute to value mineral separation. Thus to minimize effects due to the chemical factors the model system constituents were further manipulated. Thus the model system included copper ore spiked with surface chemically inert fibers. Surface chemically inert fibers, such as nylon fibers were used for spiking instead of serpentine ore. Nylon fibers used in this investigation were similar in dimensions compared to the fibers in serpentines which were spiked with the copper ore. Flotation results showed a decrease in copper recovery with increase in level of spiking (Fig. 3b). This indicated that fibrous particles in the pulp contribute to increase in viscosity and as a result lead to poor recovery. However, the pathways and mechanisms by which pulp rheology affect value mineral separation was not understood. Thus impact of rheological properties on the fundamental pathways responsible for selective value separation in flotation was further investigated. This includes two steps

1. Investigation on the contributions of fibrous particles to pulp rheological behavior
2. Inference on the possible pathways and mechanism and their contribution to factors responsible for value mineral separation.

Contribution of fibrous and plate type minerals to pulp rheological behavior

Pulp rheological properties were correlated to the level of spiking of serpentine ore model system. Yield stress values of pulp obtained from grind mill were measured. An increase in yield stress values was observed (Figs. 3 and 4) with increase in level of spiking. It is to be noted here that plate type (lizardite, 15% w/w) and fibrous (chrysotile, 55% w/w) of minerals were the majority of the minerals present in the serpentine ore. These types of minerals typically contribute to increase in yield stress of pulp.[3] Plate like particles tumbles in suspension leads to increase in the effective volume fraction.[3] It is rather intuitive that increase in volume fraction will lead to increases the yield stress of pulp. However, a difference phenomenon is responsible with respect to fibrous particles in suspension. Fibers occupy a volume equivalent to a sphere drawn along the length of the particle in suspension.[10] Besides this, the fibers often entangle to form network/flocs in pulp. Fibers entangle even at very low (<1% v/v) concentration.[10] In this regard, the extent of network formation by nylon fibers (700–800 microns in length and 15–20 microns thick) at varying concentration is shown in a series of optical microscopic images in Fig. 5. Network formation by fibrous minerals was investigated using SEM studies. Fig. 4, a SEM micrograph of serpentine ore sample shows that fibers are grouped in bubbles. Fig. 4 b shows SEM micrograph of pulp sample which constituted fibrous minerals only. This clearly indicated that the fibers in serpentine ore form network in suspension. Furthermore, based on optical micrograph analysis of serpentine ore pulp, uniform size (5–10 µm) aggregates (Fig. 5a) were observed in the dilute (< 1% w/w) sample of the pulp phase. However, in the non-dilutes samples the micro-aggregates were no longer identifiable and were observed to be integrated in form of a semitransparent cloudy planar network of size as large as 1–2 cm (Fig. 5a), an approximation based on optical microscopy). To obtain information on the size and morphology of individual particles constituting the aggregate, SEM images of the samples were taken. Fig. 5b shows that micro-aggregates comprise fibrous and fine particles (~ 500 nm). Based on XRD results the constituting particles were mostly fibrous (clinocrysotile) and fine (lizardite) particles. Thus, it was understood that certain type of minerals such as plate and fibrous types of minerals significantly influence the rheological behavior of pulp in flotation.

Pathways and mechanisms and their contributions to factors responsible for selective value mineral separation

One of the rheological properties that indicate pulp rheological behavior is yield stress. Fig. 4 shows correlation between yield stress values of ground pulp to the value mineral recoveries.

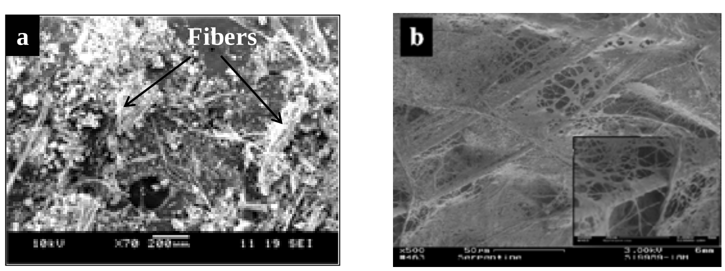
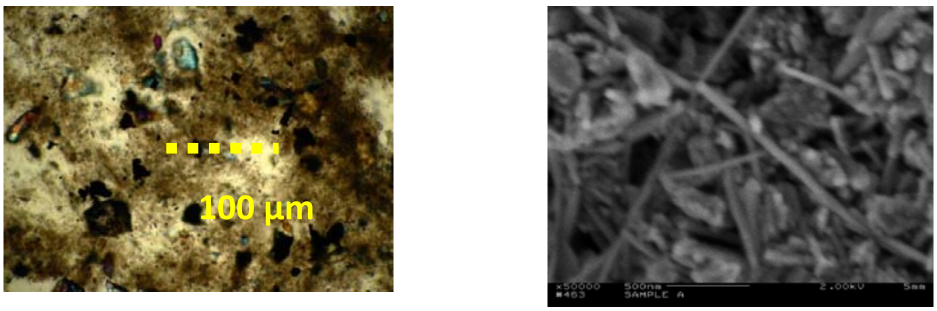


Fig. 4: SEM of serpentine ores containing fibers (a) dry conditions, (b) pulp containing fibrous serpentine (inset shows magnified image of the same network).

Fig. 3 shows that yield stress of the pulp increases with increase in the concentration of the fibrous mineral in the pulp. Furthermore, decrease in copper recovery (similar to Ni recovery) was observed with increase in yield stress values. However, a two step relationship was observed between copper recovery and yield stress values. For yield stress values 0–75 Pa the relationship showed a less steep slope than that for yield stress values above 75 Pa. This indicated that rheological behavior influences the fundamental pathways responsible for value mineral recovery in varying degrees. The impact of pulp rheology on the fundamental pathways is outlined below.



(a) (b)

Fig. 5: (a) Optical microscopic view of pulp phase, 10x, a semi-transparent macro-network phase. Insert shows particles of uniform sizes 5–10 microns, (b) SEM of pulp sample.

Effects of pulp rheology on the fundamental pathways in value mineral separation

Dispersion of air bubble and particle in flotation pulp

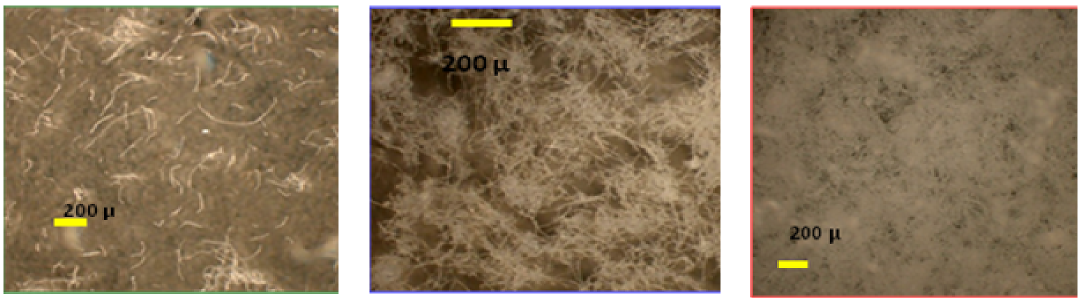
Pulp rheological conditions significantly influence the dispersion of particles and air bubbles in pulp. Transport of air bubbles in pulp phase is also dependent on rheological properties. Thus, it indicates that extent of dispersion of particles and air bubbles are contingent upon the rheological properties of the pulp. This impedes the bubble-particle collision which is dependent on the dispersion characteristics of both air bubbles and particles. Thus, pulp rheological properties dictate the bubble-particle collision which is critical to value mineral separation.

Effect of pulp rheological behavior on bubble size distribution in flotation

Mean bubble size distribution is one of the critical and fundamental parameter for selective separation of value minerals in flotation.[11] In has been reported that as the viscosity of the pulp increases it lead to increase in mean bubble sizes.[12]

Impact of rheology on froth phase

As the concentration of the fibers in the suspension increases it lead to formation of dense network with variable pore sizes. Our first thought was whether the bubbles can penetrate through the macro-network. In this regard, it has been reported that the sizes of the “pores” in a network (similar to that in this research work) is in submicron range.[13] If pores are of submicron in sizes then they are relatively small compared to the bubble size (1–2 mm) used in flotation.[15] SEM of serpentine ore pulp was studied. Fig. 6 b and c shows that the pore size is smaller than 500 microns in the nylon fiber network. Fig. 5b shows that the pore sizes in serpentine ore pulp are less than 100 microns. Furthermore, the SEM micrographs (Fig. 4b) depicted that the network are in form of layers thus minimizing the overall pore size. Thus, due to relatively lower mean pore diameter of the network than the air-bubbles it is likely that bubbles will not be able to penetrate the network and froth phase formation will be impeded. Stable and adequate froth phase formation is essential for recovery of value minerals. Thus, this can be one of the important reasons as to how pulp rheological behavior affects the very fundamental pathways of value mineral recovery, *e.g*. formation of froth phase.



(a) (b) (c)

Fig. 6: Optical Microscopic pictures of nylon fibers in suspension.
(a) <1% v/v, (b) >2.5% v/v (c) > 5% v/v

Entrapment of valuable particles in the network

As the concentration of the fibers increases the particles that can be entrapped in the network also increases. Fig. 4b shows that the pore size is around 20 microns in size. This indicates that particles smaller than 20 microns can easily be entrapped inside the network. Additionally, Fig. 8 shows that finer particles are trapped in the network. A similar phenomenon can be envisaged where fine valuable minerals are trapped in the network.

Impact of pulp hydrodynamics on particle-particle interactions

Particle-particle interaction forces such as vandewaals forces play an important role in aggregation between particles. Under pulp hydrodynamics typically observed in flotation these forces are broken and this lead to dispersion of particles.[14] For heavy and coarse particles pulp hydrodynamic forces are significantly higher than the vanderwaals forces and thus coarse particles are easily dispersed. Whereas for finer and plate/fibrous like particles the particle-particle interaction forces are higher than the hydrodynamic forces and thus are aggregates.[15]

Reagents entrapment in nanopores

It can be seen from Figs. 5b and 6 that the pores formed in the aggregates are very small (a few nanometer thick). Thus, these nanometer thick pores can act as capillaries and will entrap water. The entrapped water can contain reagents intended for value mineral separation.

Effect of spatial pulp dynamics

The rheological behavior of pulp is different in different region of the flotation cell and can have a significant impact on recovery.

CONCLUSION

Morphology of particles (minerals or composite of minerals) in pulp, particularly if there is a significant difference in length, width and depth, significantly alters the pulp rheological behavior. The mechanisms, by which this occurs are different, *e.g*. increase in effective volume fraction by plate like particles, house of card structure formation by clay type minerals and network formation by fibrous minerals due to their entanglement. But there is not a single mechanism by which the rheological behavior alters the value mineral separation. These include impact on bubble –particle interaction, froth phase development and stability, entrapment of reagents and value particles in nano-pores as well in aggregates. All these factors are either directly or indirectly influenced by pulp rheological behavior. However, the contributions of rheological properties on each of the factors are a challenging area of research. Furthermore, by developing methods to correlate rheological properties to the fundamental pathways responsible for value mineral recovery will lead to efficient beneficiation of the serpentine rich ore types.

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REFERENCES

[1] Conference: Rheology in the mineral industry, February 16–21, 1997, Bahia Resort Hotel and Conference Center 998 West Mission Bay Drive San Diego, CA 92109.

[2] Rinaudo, C. and Gastaldi, D and Belluso, E., 2003, Characterization of chrysotile, antigorite and lizardite by ft-raman spectroscopy, *The Canadian Mineralogist*, 41, p. 883

[3] Mueller, S., Llewellin, E. W. and Mader, H. M., 2009, The rheology of suspensions of solid particles, *Proceeding of, the Royal Society* A, December 16, 2009, 466

[4] Hess, P.C., Origins of Igneous Rocks, Harvard University Press, Cambridge (1989) p. 336.

[5] Edwards, C. R., Kipkie, W. B. and Agar, G. E., 1980. The effect of slime coatings of the serpentine minerals, chrysotile and lizardite, on pentlandite flotation. *Int. J. Miner. Process.* 7, p. 33.

[6] Nguyen, Q.D. and Boger, D.V., 1983, “Yield Stress Measurement for Concentrated Suspension.” *J. Rheol,* 27, No. 4, p. 321.

[7] Cerpa, A., Garcia-Gonzalez, M.T., Tartaj, P., Requena, J. Garcell, L.R., and Serna, C. J., 1996, “Rheological properties of concentrated lateritic suspensions.” *Progr. Colloid Polym. Sci.,* 266.

[9] Fullston, D., Fornasiero, D. and Ralston, J., 1999, Zeta potential study of the oxidation of copper sulfide minerals, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 146, Issues 1-3, 15 January 1999, p. 113.

[10] Kereke, R. I. and Schell, C.J., “Characterization of fiber flocculation regimes by a crowding factor”, *Journal of Pulp and Paper Science*, 18, 1992, p. 32.

[11] Cho, Y. S., Effect of flotation frother on bubble size and foam stability. Masters Thesis, 2001, Department of Mining and Mineral Processing Engineering, University of British Columbia.

[12] Grau R. A.; and Heiskanen, K., 2005, Bubble size distribution in laboratory scale flotation cells, *Minerals Engineering*, 18, Issue 12, October, p. 1164

[13] Johnston, P.R., Revisiting the most probable pore size distribution in filtermedia, *J. Testing Evaluation*, 1983, 11(2), p. 117.

[13] Kondrat'ev, S.A. and Bochkarev, G.R., 1998, Stabilization of bubble size in a flotation cell, *Journal of Mining Science*, 34, Number 3/May, p. 272.

[14] Prestidge, C.A., 1999, Rheological Investigations of DLVO and Non-DLVO Particle Interactions in Concentrated Mineral Suspensions, M*ineral Processing and Extractive Metallurgy Review*, 20, Issue 1, p. 57.

[15] Vesaratchanon, J.S., Nikolov, A. and Wasan, D.T., 2008, Sedimentation of concentrated monodisperse colloidal suspensions: Role of collective particle interaction forces, *Journal of Colloid and Interface Science*, 322, Issue 1, 1 June, p. 180.