

The flotation of millerite – A single mineral study

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ABSTRACT

While pentlandite is the dominant nickel sulphide mineral recovered from nickel ores, other nickel sulphide minerals can often be present. One such rare but important nickel sulphide mineral is millerite (NiS). There is very little information in the literature about the flotability of millerite, in particular its flotation behaviour relative to that of pentlandite under different flotation conditions. This paper details a single mineral investigation into the flotability of millerite, and compares its flotability with that of pentlandite and other nickel arsenides often present in nickel sulphide ores.

Millerite was found to be strongly floatable with xanthate collector at pH 9 but there was a noticeable decrease in recovery at pH 10 and a further decrease at pH 10.5. Size-recovery data suggests the recovery of millerite decreases at sizes above 75 µm and below 10 µm. In particular, fine millerite floats poorly in a similar fashion to fine pentlandite.

At pH 9 with xanthate collector millerite exhibits a lower limiting threshold potential at about – 100 mV SHE, about 300 mV below the lower limiting threshold potential for pentlandite.

Millerite is not readily depressed by cyanide at pH 9 and further, cyanide doses required to affect depression are much higher than those required to depress the nickel arsenide mineral gersdorffite. Cyanide should therefore be a suitable depressant for the separation of gersdorffite from other nickel sulphide minerals such as millerite and pentlandite.

1. Introduction

While there are over 45 different nickel minerals, only a few of them are of economic importance to the minerals industry (Dana and Ford, 1966). The principal nickel mineral in nickel sulphide ores is pentlandite ($(\text{Ni,Fe})_8\text{S}_9$) while the less common nickel sulphides include millerite (NiS), violarite (Ni_2FeS_4), polydymite (Ni_3S_4), siegenite ($(\text{Co,Ni})_3\text{S}_4$), and heazlewoodite (Ni_3S_2). As well, often present are nickel arsenides such as gersdorffite (NiAsS) and niccolite (NiAs).

Pentlandite is recovered primarily by froth flotation and the flotation behaviour of pentlandite is well known and defined. In the literature, however, there is very little data on the flotation behaviour of millerite (Bulatovic, 1979). Millerite is a relatively rare sulphide mineral and is mostly found in hydrothermal deposits as a replacement for pentlandite. Bulatovic (2007) claims millerite, gersdorffite and niccolite have similar flotation properties to pentlandite but tend to oxidise more readily in the presence of oxygen. As well, he claims nickel sulphide minerals in general can be depressed with lime at pH values greater than 9.5 whereas millerite is not depressed until pH 10.0. Evidence was presented to show a

combination of mercaptan and dithiophosphate collectors performed better than xanthate collector alone on a Canadian sulphide ore containing nickel present as violarite (70%) and millerite (30%).

Two micro-flotation test studies on closely sized fractions examined the collectorless flotation of millerite, one in acidic conditions (Nagaoka et al., 1999) and one in alkaline conditions (Lekki and Drzymala, 1990). In acidic conditions (pH 2) millerite was found to float strongly without collector but in alkaline conditions (pH 7.5–7.8) the recovery of millerite without collector was found to be not much higher than that expected from entrainment.

In terms of the relationship between the flotability of millerite and that of arsenides commonly found in sulphide nickel ores, such as niccolite and gersdorffite (Senior et al., 2009a,b, respectively) it is important to note that arsenic is a penalty element for many nickel smelters where it can cause environmental problems when volatile arsenic compounds are emitted during processing. Consequently, financial penalties are imposed by smelters to treat nickel concentrates with high arsenic content. In high-arsenic nickel ores, therefore, often a separation between nickel sulphide minerals, such as millerite, and nickel arsenides is desirable.

In light then of the limited reported studies on millerite flotability and the need for improved separation of millerite/pentlandite from nickel arsenides, single mineral flotation studies were undertaken on a relatively clean, naturally occurring millerite mineral sample. The aim of this work was to determine millerite flotability, as a function of

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several key flotation parameters, and to investigate the impact of some proposed methods for separating nickel arsenides from nickel sulphides on millerite recovery. The results of this single mineral study are presented in this paper.

2. Experimental details

2.1. Mineral preparation

The millerite sample used in this study was concentrated from a high grade specimen supplied by WMC Resources Limited (now part of BHP Billiton). Non-sulphides were first rejected by careful hand sorting and the upgraded portion was then stage-crushed in a laboratory jaw crusher to pass 10 mesh (1.65 mm) and screened at 212 μm to remove low grade fines. A bulk – 1650 + 212 μm millerite composite was thus prepared. Using a sample of this size range in single mineral tests ensured that after grinding only a minimum quantity of the original surface remained. Charges of 50 g were riffled from the composite for flotation testing together with sub-samples for chemical and mineralogical analyses.

High quality quartz, obtained and prepared locally, was used as the gangue mineral in all the single mineral flotation tests. The amount used in each test was 450 g of – 1650 + 212 μm quartz. The combined weight of the individual flotation charges (millerite composite plus quartz diluents) was 500 g.

2.2. Grinding

For all flotation tests 50 g of millerite and 450 g of quartz were mixed with distilled water and ground for 20 min in an iron mill with 25 mm mild steel balls at the natural pH and at 67% solids by weight. Before each test the mill and ball charge were cleaned by grinding a sample of quartz for 10 min. For flotation tests conducted below the air-set potential, the grinding mill was purged with nitrogen prior to the addition of the minerals and the distilled water used was deoxygenated by bubbling gaseous nitrogen through the water for 20 min prior to use.

2.3. Flotation

2.3.1. Flotation reagents

was fitted with a rubber diaphragm, sight tube, and electronic sensor for automatic detection and control of the pulp level.

For both conditioning and flotation the impeller speed was 1200 rev/min. Air was delivered to the cell at 8 dm³/min. Frother was added continually during flotation via a motorised variable speed dispenser, commencing 1 min before flotation. The frother addition rate was set so as to maintain a high active froth column that would not limit flotation rates and which was similar to rougher flotation practice.

The pulp potential was measured continuously during testing using a high-impedance, differential voltmeter with a polished platinum flag electrode and a Ag/AgCl reference electrode. The performance of the electrode system was checked using standard ferric–ferrous ion solution (Light, 1972). Measured potential values were converted to the standard hydrogen electrode (SHE) scale by the addition of 200 mV and these values are referred to in this paper as Eh values, in units of mV SHE.

A Radiometer glass electrode was used to measure pH continuously during testing. Before each test the pH of the system was calibrated using standard pH 7 and pH 10 buffer solutions. Radiometer TTT80 titrators and ABUS0 burettes were used to add oxidant/reductant and acid/base to set and maintain the Eh and the pH respectively.

2.3.3. Flotation procedures

The flotation procedures used for the mineral–quartz mixtures followed a standard procedure developed by CSIRO. The ground pulp was transferred to the flotation cell and the water level was raised. The pH was adjusted to the test value and the pulp aerated for 5 min. Collector was then added and the pulp conditioned for 5 min. When cyanide was used it was added after the pH was adjusted and before the pulp was aerated. In this case the pulp was conditioned for an extra 2 min. Flotation concentrates were collected at 0.5, 1, 2, 4, and 8 min by hand scraping at a constant depth and rate.

For tests where the pulp potential (Eh) was controlled during flotation there were some minor differences in test procedures for tests conducted below and above the air-set potential. These modifications were necessary to ensure the reducing or oxidising conditions required during flotation were not compromised during any prior steps, such as slurry transfer from mill to cell, when setting the pulp Eh or pH, or when conditioning the pulp. The pH and Eh were set to their test values using the automatic titrators, with the potential being set upscale, that is, at a more oxidising condition than that

A high purity potassium ethyl xanthate (KEX), synthesised from re-distilled high grade chemicals and recrystallised from ethanol, was used as a flotation collector. A dilute solution of xanthate was prepared fresh each day as 0.1% w/v solution. The frother used was a commercial quality polypropylene glycol (Cytec Aerofroth 65) prepared as a 0.25% w/v solution. Analar grade sodium cyanide was prepared as a 0.5% solution. The initial pH was set using lime in the form of a 2.5% suspension by weight of Analar grade calcium hydroxide. Dilute solutions of Analar grade sodium hydroxide or nitric acid were added to maintain the pulp pH after it had been set to the test value with lime.

The flotation gas was either high purity bottled synthetic air (a synthetic mixture of O_2 and N_2) or high purity bottled nitrogen. Either distilled water or deoxygenated distilled water was used to maintain the pulp level in the cell at a preset level. For the tests at different pulp potential values, dilute solutions of laboratory grade sodium hypochlorite ($NaClO$) and sodium dithionite ($Na_2S_2O_4$) were used as oxidants and reductants, respectively, to set and control the pulp potential during flotation.

2.3.2. Flotation equipment

Samples were floated in a 3 dm³ modified stainless steel Denver cell (Guy, 1992) in which the impeller was fitted with a variable speed drive and was driven from below to allow the whole surface of the froth to be scraped with a paddle at a constant depth and rate. The cell

reached after grinding in an iron mill. There was no aeration stage but a standard addition of 120 g/t KEX was made as soon as the selected pulp potential was reached and the pulp conditioned for 5 min. Flotation concentrates were then collected as noted above.

For tests below the air-set potential, the mill was flushed with nitrogen before grinding, the ground slurry was transferred from the mill to the cell under nitrogen and a blanket of nitrogen was maintained above the pulp until flotation concentrates were taken. This helped minimise exposure to air before flotation commenced and ensured that the potential remained reducing until the potential was adjusted to a more oxidising value. In these tests nitrogen was the flotation gas and the makeup water used during grinding and flotation was deoxygenated distilled water.

For tests above the air-set potential, the flotation feed was prepared in the same way as for tests below the air-set potential except that none of the above precautions to avoid exposure of the pulp to oxygen was taken, and the flotation gas was synthetic air rather than nitrogen. The potential was still adjusted to a more oxidising condition than that reached after grinding. The order of addition of reagents and the conditioning times were unchanged.

2.4. Analysis of products

Flotation products were weighed both wet (to allow calculation of water recoveries) and dry and were prepared for analysis in a

standard manner. The millerite composite head sample and all the flotation products were assayed for a suite of elements, including nickel, iron, arsenic, and sulphur, by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Where sizing was required sub-samples were sized using the modified cyclosizing procedure of Kelsall et al. (1974).

An X-ray diffraction pattern of the millerite composite was recorded on a Philips PW 1050 goniometer with a PW 1710 diffraction controller using CuK α radiation. Phases present were identified by comparison of the peak positions and intensities with data published by the International Centre for Diffraction Data (ICDD).

A sub-sample of the millerite composite was processed using QEMSCAN. The QEMSCAN analysis involves preparing a polished section of the sample and scanning the mount systematically with an electron beam such that an image of each particle is created. The minerals present at each point in these images are identified by rapidly collecting an energy dispersive X-ray spectrum (EDS) that is analysed to give the chemical composition. By reference to an extensive mineralogical database the chemical composition information is converted to quantitative mineralogical data.

3. Results and discussion

3.1. Analysis of millerite sample

The chemical and mineralogical analysis data for the millerite sample are presented in Table 1. The chemical data show the composite sample contained 49.9% Ni and so assuming all the nickel is present as millerite (NiS, 64.7% Ni), the millerite composition of the composite based on the nickel assay is 77%. This is consistent with the QEMSCAN data which gives a value of 74% millerite. The QEMSCAN results also show that the major contaminant was dolomite.

X-ray diffraction analysis (not shown here) confirmed that the predominant mineral in the composite was millerite with lesser amounts of dolomite, pyrite and magnesite and trace amounts of quartz and nickel hexahydrate (NiSO $_4$ ·6H $_2$ O), again consistent with the QEMSCAN data. It has been observed previously (Legrand et al., 1998) that discrete crystallites of hydrated NiSO $_4$ can form on the surface of millerite upon exposure to air.

3.2. Flotation with xanthate

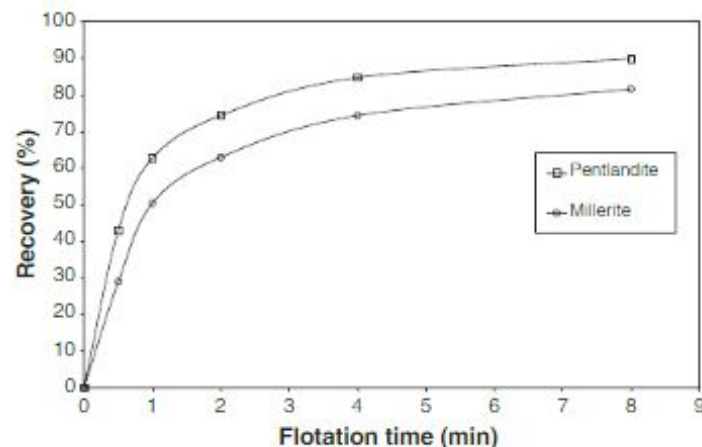


Fig. 1. Comparison of the flotability of millerite at pH 9 with that of pentlandite at the same pH (120 g/t KEX).

floatable, its response is indicative of the contribution of entrainment to the recovery of fine particles. When the entrainment contribution is taken into account, it can be seen that very little of the fine millerite was recovered by true flotation. The poor response of millerite at fine sizes is also characteristic of pentlandite (Senior et al., 1994) although, by contrast, pentlandite usually floats strongly at sizes coarser than 100 μ m.

Part of the slight difference in overall recovery between millerite and pentlandite observed in Fig. 1 can be attributed to differences in the feed size distribution of the minerals. As can be seen from Table 2 the feed distribution for millerite was finer than that for pentlandite. Using millerite with the same size distribution as that of pentlandite in Table 2, and maintaining the size-recovery curve shown in Fig. 2, would lead to an overall millerite recovery of 87% after 8 min flotation, comparable to that of pentlandite.

3.3. Effect of pH

Flotation tests were conducted using millerite and quartz at pH values of 9.0, 10.0 and 10.5, using lime as the pH modifier. The results, shown in Fig. 3, indicate that there is a noticeable decrease in millerite recovery in going from pH 9 to pH 10, and a further decrease at pH 10.5. Pentlandite exhibits a similar decrease in recovery with increasing pH (Senior et al., 1994; Smith et al., 2009).

The flotation response of millerite at pH 9 using a xanthate collector is shown in Fig. 1. Also included for comparison is the flotability of pentlandite prepared under similar conditions. Both minerals float strongly with recoveries in excess of 80%.

Fig. 2 shows the particle size behaviour of millerite during flotation in the presence of xanthate. Millerite floats strongly at intermediate sizes but at sizes above 75 μm and below 10 μm the recovery of millerite decreases sharply. In particular, fine millerite floats very poorly. Included in Fig. 2 is the size-by-size flotation response of quartz, as calculated by difference. As quartz in this system is not

Table 1
Chemical and mineralogical data for millerite composite sample.

Mineral	Assay (%)		Composition (%)		
			Principal component	Principal contaminants	Minor contaminants
Millerite	Ni	49.9	74 millerite	17 dolomite	<6 pyrite
	Mg	3.69			<5 magnesite
	S	29.8			<3 quartz
	Fe	2.68			<2 nickel hexahydrate
	As	<0.01			
	Cu	0.01			
	Si	1.11			

3.4. Effect of pulp potential

The effect of pulp potential on millerite flotability at pH 9 with ethyl xanthate as collector is shown in Fig. 4 as a plot of mineral recovery at 8 min against pulp potential. The air set potential for this

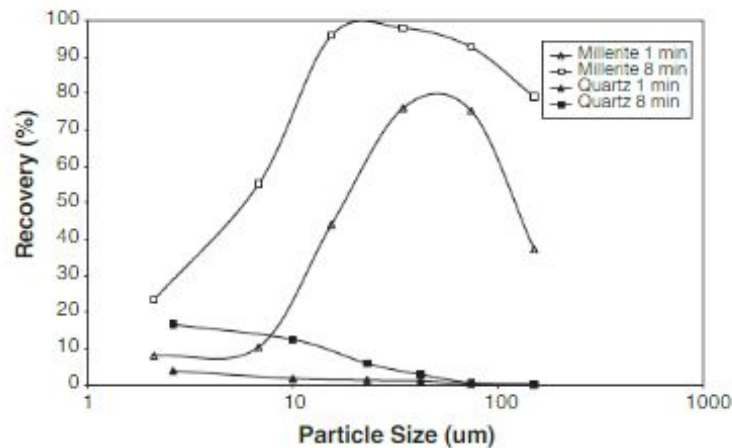


Fig. 2. Recovery-size curves for millerite-quartz mixtures at pH 9 (120 g/t KEX) showing the millerite and quartz responses at 1 and 8 min flotation.

Table 2
Flotation feed size distributions of millerite and pentlandite in mixtures with quartz.

Size range (µm)	Size distribution (%)	
	Pentlandite	Millerite
+ 212	–	0.15
– 212 + 106	9.88	6.81
– 106 + 53	26.2	15.6
– 53 + 21 ^a	36.5	33.7
– 21 ^a + 10 ^a	15.5	21.9
– 10 ^a + 4.1 ^a	7.54	12.1
– 4.1 ^a	4.38	9.72
Total	100.0	100.0

^a Nominal Cyclosizer cut points for a mineral of SG 5.2 (millerite SG 5.3 and pentlandite SG 5.0).

system was about +200 mV SHE. Under reducing conditions, there is a flotation edge below –100 mV SHE as the mineral goes from being non-flotable to being strongly flotable. The threshold potential for the transition, which we define here as the potential at which recovery after 8 min is 50%, is about –100 mV SHE. As far as it was tested (up to +400 mV SHE), no upper limiting potential was found.

It is normal for sulphide minerals to exhibit a limiting threshold potential with xanthate collectors. What is unusual about the data here for millerite is that this potential is relatively low in comparison with that for pentlandite (Senior et al., 1994) which is also shown in Fig. 4. It is also important to note that these results relate to single mineral flotation tests using only millerite and quartz diluent or pentlandite and quartz diluents. Using potential control as a means of separating one mineral from another will depend largely upon the extent to which the sulphide minerals present interact – this is normally determined in mixed mineral flotation tests.

It has not been possible to relate the potential of the flotation edge to the thermodynamic conditions for the formation of nickel xanthate or dixanthogen. If it is assumed that a possible reaction between millerite and xanthate can be described by the equation:



then a standard redox potential of about –0.11 V can be calculated. To calculate this value we have used the data given by Warner et al. (1996) and the solubility product of nickel ethyl xanthate given by Kakovsky (1957). For pH 9 and a xanthate concentration of 1.4×10^{-4} M the formation potential for nickel ethyl xanthate is 0.12 V which is well above the experimental edge in Fig. 4. Alternatively, if it is assumed that the hydrophobic entity responsible for flotation is dixanthogen, the formation potential for dixanthogen can be calculated from the relationship:

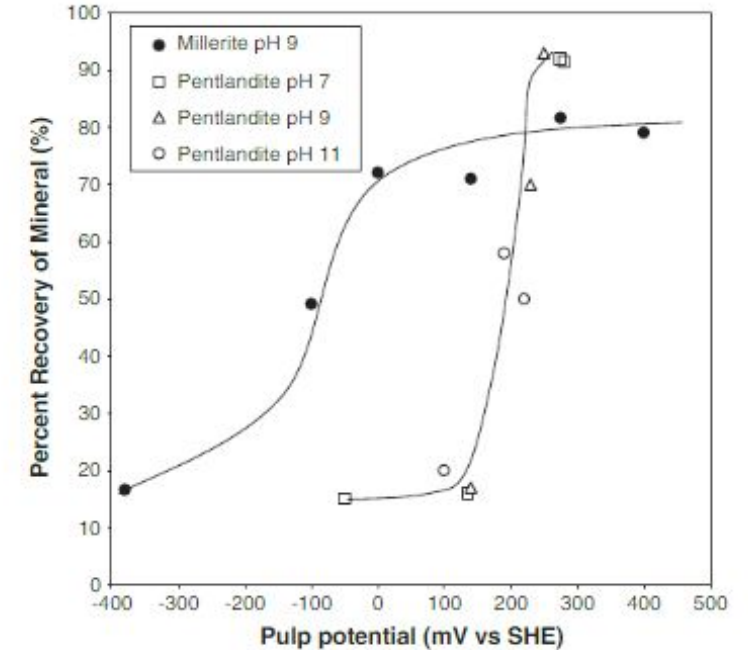


Fig. 4. Mineral recovery at 8 min as a function of pulp potential for millerite and pentlandite (120 g/t KEX).

given by Hepel and Pomianowski (1977). For a xanthate concentration of 1.4×10^{-4} M the potential is 0.16 V which again is much higher than the observed flotation edge. Some more detailed surface characterization studies are needed to determine the entity responsible for millerite flotation, particularly at the region of the flotation edge identified in this study.

Finally, it is noted that the data shown in Fig. 4 are for millerite flotation at pH 9. The flotation response as a function of Eh at different pH values has not been determined in this study.

3.5. Effect of cyanide addition

Cyanide has been shown to be a depressant for nickel arsenide minerals such as gersdorffite and niccolite (Senior et al., 2009a,b). However, in order to use cyanide to make a separation between the nickel sulphide minerals (such as millerite or pentlandite) and nickel arsenides, it is necessary that cyanide has no or limited effect on the flotability of the nickel sulphide minerals (Smith et al., 2009). Given the effect of cyanide on millerite flotation was not evident in the literature it was deemed important to conduct testwork to determine such.

$$E_{th} = -0.070 - 0.0591 \log [X^-]$$

(2)

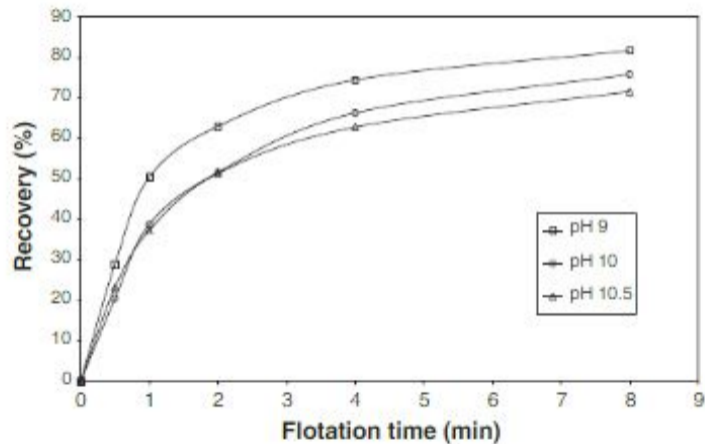


Fig. 3. Effect of pulp pH on millerite flotability with 120 g/t KEX.

Fig. 5 shows the effect of adding cyanide to the flotation cell (5 min before flotation) on the flotability of millerite at pH 9. As can be seen, a

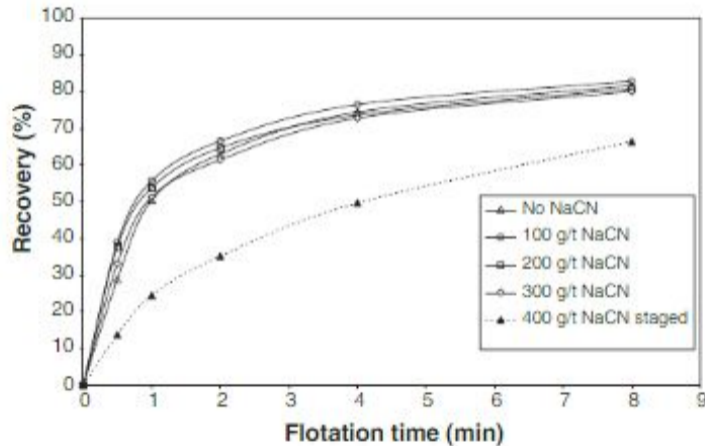


Fig. 5. The effect of cyanide addition on the flotation of millerite at pH 9 (120 g/t KEX).

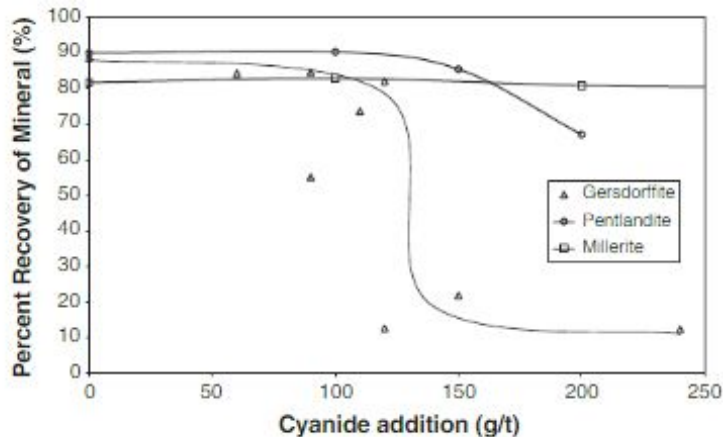


Fig. 6. Comparison of the effect of cyanide on the flotation of pentlandite, millerite and gersdorffite at pH 9 (120 g/t KEX).

single addition of cyanide up to an addition of 300 g/t had no discernable effect on millerite flotability. One additional test was completed in which the cyanide was added in two staged additions of 200 g/t (400 g/t total addition). In this test the second cyanide addition was made 2 min prior to flotation. In this test there was a significant deleterious effect upon the rate of nickel (millerite) recovery.

The results of these tests indicate that cyanide can have a depressant effect on millerite flotation but the levels of cyanide required for this are very high. Previous studies have shown that much lower cyanide additions can have a much greater depressant effect on nickel arsenides such as gersdorffite, as can be seen from Fig. 6, which also includes the effect of cyanide on pentlandite for comparison. Overall this data show that there is a threshold cyanide addition above which gersdorffite does not float but both pentlandite and millerite do. Cyanide could, therefore, be suitable as a depressant for gersdorffite in the presence of nickel sulphides such as millerite or pentlandite.

this potential the mineral is strongly floatable and below it the mineral is not floatable. As far as it was tested (up to +400 mV SHE), no upper limiting potential was found for millerite.

Cyanide has a depressant effect on millerite flotation at pH 9 but the level of cyanide needed to influence millerite flotability is very high (up to 400 g/t NaCN), much higher than that required to depress the nickel arsenide mineral, gersdorffite. Cyanide could, therefore, be a suitable depressant for the separation gersdorffite in the presence of nickel sulphide minerals such as millerite and pentlandite.

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References

- Bulatovic, S.M., 1979. Process development for treatment of nickel ore containing violarite and millerite. Report of Investigation LR2010, May.
- Bulatovic, S.M., 2007. Flotation of sulfide ores. *Handbook of Flotation Reagents: Chemistry, Theory and Practice*. Elsevier, Amsterdam.
- Dana, E.S., Ford, W.E., 1966. *A Textbook of Mineralogy* 4th ed. John Wiley & Sons, New York.
- Guy, P.J., 1992. The development of laboratory batch flotation equipment and practice at CSIRO, Australia. The AusIMM Annual Conference, Broken Hill. The Australasian Institute of Mining and Metallurgy, Melbourne, pp. 75–79.
- Hepel, T., Pomianowski, A., 1977. Diagrams of electrochemical equilibria of the system copper–potassium ethylxanthate–water at 25 °C. *Int. J. Miner. Process.* 4, 345–361.
- Kakovsky, I.A., 1957. Physicochemical properties of some flotation reagents and their salts with ions of heavy non-ferrous metals. *Proceedings, 2nd International Congress of Surface Activity, Vol.4*. Butterworths, London, pp. 225–237.
- Kelsall, D.F., Restarick, C.J., Stewart, P.S.B., 1974. Technical note on an improved cyclosizing technique. *Proc. Australas. Inst. Min. Metall.*, No 251, pp. 9–10.
- Legrand, D.L., Nesbitt, H.W., Bancroft, G.M., 1998. X-ray photoelectron spectroscopic study of a pristine millerite (NiS) surface and the effect of air and water oxidation. *Am. Mineralog.* 83, 1256–1265.
- Lekki, J., Drzymala, J., 1990. Flotometric analysis of the collectorless flotation of sulphide minerals. *Colloids Surf.* 44, 179–190.

4. Conclusions

A single mineral batch flotation study was undertaken on a sample of millerite using a quartz diluent to determine the flotation response of this mineral in a clean system as function of a number of key flotation parameters. At pH 9, millerite floats strongly with xanthate but there was a noticeable decrease in recovery at pH 10 and a further decrease at pH 10.5. Analysis of millerite recovery at pH 9 on a size-by-size basis revealed that the recovery of millerite decreases at sizes above 75 μm and below 10 μm . In particular, fine millerite floats poorly which is also characteristic of fine pentlandite.

Millerite flotation at pH 9 with xanthate exhibits a lower limiting threshold potential at about -100 mV SHE (which is about 300 mV below the lower limiting threshold potential for pentlandite). Above

- Light, T.S., 1972. Standard solution for redox potential measurement. *Anal. Chem.* 48, 1038–1039.
- Nagaoka, T., Ohmura, N., Saiki, H., 1999. A novel mineral flotation process using *Thiobacillus ferrooxidans*. *App. Environ. Microbiol.* Vol. 65 (No. 8), 3588–3593.
- Senior, G.D., Shannon, L.K., Trahar, W.J., 1994. The flotation of pentlandite from pyrrhotite with particular reference to the effects of particle size. *Int. J. Miner. Process.* 42, 169–190.
- Senior, G.D., Smith, L.K., Bruckard, W.J., 2009a. The flotation of niccolite – a single mineral study. *Int. J. Miner. Process.* 94, 92–96.
- Senior, G.D., Smith, L.K., Silvester, E., Bruckard, W.J., 2009b. The flotation of gersdorffite in sulphide nickel systems – a single mineral study. *Int. J. Miner. Process.* 93, 165–171.
- Smith, L.K., Bruckard, W.J., Davey, K.J., 2009. The flotation behaviour of arsenic-bearing minerals in nickel sulphide flotation systems. *Enviromine 2009, Proceedings of the First International Seminar on Environmental Issues in the Mining Industry*, 30 September–2 October, Santiago, Chile.
- Warner, T.E., Rice, N.M., Taylor, N., 1996. Thermodynamic stability of pentlandite and violarite and new E_{H} -pH diagrams for the iron-nickel sulphur aqueous system. *Hydrometallurgy* 41, 107–118.