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The effect of heavy oxidation upon flotation and potential remedies for Merensky type sulfides

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Abstract

Surface oxidation of sulfide minerals, such as that found in the regions of a sulfide ore body near the water table, can have a significant impact upon flotation. This theme has been explored for Merensky ore type sulfides where an ore containing pyrrhotite, pentlandite and chalcopyrite was thermally oxidised and the role of potential remedies investigated. Back-scattered scanning electron microscope images are presented showing the oxidation layer which formed in the mineral surfaces. These oxidation layers were depleted in both sulfur and iron with incorporated oxygen. Flotation recovery rapidly decreased with increasing oxidation, particularly after 27 days and reached a plateau after 50 days. Up to 27 days, this effect could be partially overcome with higher collector additions. Oxidation had more impact upon the finer size fractions, particularly for pyrrhotite. For more heavily surface oxidised samples, ultrasonic treatment prior to collector conditioning was found to improve flotation recoveries. This treatment had the greatest effect upon chalcopyrite particles. Sulfidisation was successful in restoring the flotation recovery of the heavily oxidised sulfide minerals. Longer sulfidisation conditioning times were not conducive to good flotation recoveries of both oxidised pyrrhotite and pentlandite due to oxidation of the freshly formed sulfide surfaces. For maximum flotation recoveries of oxidised pyrrhotite, pentlandite and chalcopyrite, different sulfidisation conditions are indicated. It appears likely that in a mineral processing operation treating oxidised Merensky type ores, two stages of sulfidisation employing different conditions would be required.

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1. Introduction

The flotation process relies on exploiting differences in the surface chemistry between sulfide and non-sulfide minerals and this difference becomes increasingly marginal as the sulfide mineral surfaces become oxidised. In the case of heavily surface oxidised sulfides, such as those that may be found in oxidised Merensky type ores, no investigations of either the surface nature or the potential for improving the flotation recovery have been reported. Indeed, for base-metal sulfides, the literature is sparse on these topics, although for surface oxidised copper sulfides, often referred to as "tarnished" (De Waal, 1978), sulfidisation has been recommended (Malghan, 1986; Bulatovic and Wyslouzil, 1985).

The proposed benefits of this study are increased sulfide mineral, and by association platinum-group element (PGE), recoveries from oxidised Merensky type ores, which are present in substantial quantities in Southern Africa, particularly Zimbabwe (Oberthuer et al., 2003). Sulfidisation also has significant potential in the treatment of other Merensky type ore resources, including tailings dam material, smelter slags and "unoxidised" ores as well as oxidised sulfide minerals in general.

The oxidation of iron bearing sulfides, such as those found in Merensky type ores, in the presence of either air or air and water precede through a similar mechanism with the preferential loss of iron and subsequent sulfur enrichment of the underlying mineral lattice (Buckley and

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Woods, 1987; Smart et al., 2003). Oxidation products such as iron hydroxides, oxyhydroxides and oxides form a coating on the mineral surfaces for pyrite (Buckley and Woods, 1987) and pyrrhotite (Buckley and Woods, 1985a,b; Pratt et al., 1994; Jones et al., 1992). In addition to these iron oxidation products, nickel and copper oxides have been identified respectively on the surfaces of pentlandite (Richardson and Vaughan, 1989; Buckley and Woods, 1991) and chalcopyrite (Smart, 1991; Zachwieja et al., 1989; Buckley and Woods, 1984).

The enrichment in sulfur and base-metals of the underlying surface was found for pentlandite (Richardson and Vaughan, 1989; Buckley and Woods, 1991; Legrand et al., 1997) and chalcopyrite (Buckley and Woods, 1984; Luttrell and Yoon, 1984). This enrichment resulted in the formation of new, and sometimes, more stable sulfide minerals such as Fe_2S_3 in pyrrhotite (Jones et al., 1992), CuS (Luttrell and Yoon, 1984), CuS_2 (Buckley and Woods, 1984) in chalcopyrite and $FeNi_2S_4$ in pentlandite (Richardson and Vaughan, 1989).

During the initial stages of oxidation in either air or water, the sulfur from the mineral lattice appeared on the surface as sulfide ions that formed as polysulfide chains of greater length with increased oxidation (Buckley and Woods, 1987; Mycroft et al., 1995; Schauffuß et al., 1998). Under more intense oxidation, sulfates started to form with air (Pratt et al., 1994). Thus it appears that oxidation by either air or air and water produced similar outcomes, particularly in terms of the mineral surface layer.

Most oxidation studies, whether of thermal or otherwise nature, did not extend beyond a few days, except for Buckley and Woods (1984) who studied the air oxidation of chalcopyrite over 50 days. With increasing oxidation the primary sulfide minerals oxidise through a series of secondary sulfide minerals and eventually to "oxide" minerals, the nature of which is dependent upon the weathering environment and oxidising conditions (Garrels, 1953; Sato, 1961; Blain, 1977; De Waal, 1978; Thornber, 1983). In extensive oxidation studies, the intent was to form "oxide" minerals rather than heavily oxidised sulfide surfaces as was the case in this study (Sato, 1961).

Little has been reported on the effect of sulfidisation upon the flotation of gangue minerals. Goethite was found to float with sulfhydryl collectors after sulfidisation (Mitrofanov et al., 1957) while hematite did not (Hu et al., 1986). Merensky type ores consist of mainly silicate minerals, the most predominate being pyroxene and feldspar, as well as smaller quantities of oxides such as iron and chrome. Based on solubility considerations of these gangue mineral surfaces and of any sulfide entity that may form, sulfidisation is not expected to have any effect on the floatability of gangue minerals typically associated with Merensky type ores.

This paper reports the flotation response of surface oxidised sulfide minerals such as pyrrhotite, pentlandite and chalcopyrite and the subsequent effect of three potential remedies. These remedies included treatment in an ultrasonic bath, collector concentration and sulfidisation as well as selected combinations of these techniques. Scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDS) were used to indicate both the extent and nature of the surface oxidation of the sulfide particles.

2. Experimental methods

2.1. Mineral sample

N'komati massive sulfide ores contain the same base-metal sulfide minerals as Merensky ores and was thus selected as the study material. Although this mineral sample does not contain exactly the same sulfide mineral proportions, the investigation of the behaviour and subsequent trends of the sulfide minerals are nonetheless possible. The head grade of the mineral sample was determined by AAS analysis to be 55.3% iron, 31.4% sulfur, 2.93% nickel and 1.85% copper. Based on chemical and mineralogical reconciliations of all the samples used in the test work, the sulfide mineral proportions were calculated as 78.3% pyrrhotite, 10.5% pentlandite, 7.2% chalcopyrite and 4.1% pyrite (refer to Table 1). Iron oxide minerals were identified (13.6%) as well as other non-sulfide minerals (1.3%). X-ray diffraction (XRD) analyses indicated that the pyrrhotite was present as both the hexagonal and monoclinic varieties. The most commonly identified chemical formula was $Fe_{0.97}S$ followed by $Fe_{0.95}S$, based on SEM-EDS analyses of the pyrrhotite particles.

Lump samples were hand picked from N'komati massive sulfide ore and carefully crushed and dry ground with chrome steel media to obtain three size fractions namely, −106/+74 μm, −74/+53 μm and −53/+38 μm using dry screening. The upper and lower limit of the size ranges were based on the requirements of the micro-flotation unit and the relative density of the sample. Sample exposure to air during preparation was less than 2 h. The three size ranges were individually wet screened on a 38 μm screen before oxidation to remove any adhering fines. This procedure was also used for unoxidised samples prior to flotation. Unoxidised samples were sealed in plastic bags, stored under refrigeration and floated within two weeks of preparation.

Table 2 shows that in the resultant size ranges, the sulfide minerals were reasonably well liberated based on

Table 1
Sample mineral composition

Mineral	Percent mass	
	EDS[a]	Chemical[b]
Pyrrhotite	66.3	66.7
Pentlandite	8.4	9.0
Chalcopyrite	5.4	6.1
Pyrite	3.2	3.5
Iron oxides	15.2	13.6
Silicates	1.5	1.3

[a] Average of three QEM * SEM samples.
[b] Reconciliation based on all test work samples.

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