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The use of canola oil as an environmentally friendly flotation collector in sulphide mineral processing

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ABSTRACT

The efficiency of mineral flotation relies on the ability to selectively recover different value minerals into their respective concentrates at optimum grades and recoveries based on the differing hydrophobicities. Many of the common hydrophobizing reagents (collectors) currently used in flotation have significant occupational and environmental implications, and hence there is a quest for environmentally benign chemical additives that give similar or better performance than the more toxic conventional reagents. In this paper, we provide substantial experimental evidence that the use of edible, fatty acid-based oils (canola and palm) can foster the flotation recovery of chalcopyrite and molybdenite minerals more selectively against pyrite than the conventional collectors, sodium isopropyl, potassium amyl xanthates and diesel oil.

Single and mixed chalcopyrite/pyrite minerals and plant sulphide ores' flotation studies using canola and palm oils, in contrast with conventional collectors, are reported herein. The results indicate greater efficacy of the canola and palm oils in comparison with the conventional collectors for chalcopyrite and molybdenite recoveries and product upgrades. This is believed to be due to the edible oils' specific interactions with iron oxides sites preferentially formed *in situ* on the surfaces of the chalcopyrite or molybdenite in the pulp rather than on the pyrite surfaces, causing limited recovery of the pyrite. Complementary contact angle results confirmed that more canola oil is adsorbed onto chalcopyrite surfaces than onto pyrite surfaces. For the mineral mixtures tested, the edible oil's degree of unsaturation had a noticeable effect on its performance as a collector. A higher pyrite recovery and slightly lower chalcopyrite grade was obtained with palm oil than with canola oil. These findings suggest that the use of canola oil has a potential to add to the existing array of flotation collectors and would represent a combined opportunity for both the mining and agricultural sectors, with concomitant health, environmental and economic benefits.

1. Introduction

The prescient use of natural and processed oils (e.g. canola or rapeseed oil) in the mining sector dates from the beginnings of the application of froth flotation as a means of selectively concentrating minerals. Peterson and Clayton (1916) tested 162 oils, including rapeseed (or canola) oil, as possible collectors for separating galena and dolomite by laboratory batch flotation. A total of 155 flotation tests were conducted. The relevant, key conclusions showed that oleic acids floated dolomite whilst pine oil and essential oils selectively floated galena. The floatability of galena with the essential oils was correlated with their solubility in water.

Canola oil is a typical edible oil comprising mainly unsaturated triglycerides like oleic acid, linoleic acid and linolenic acid with one, two and three double bonds/molecule, respectively. Ozcan et al. (2012) analysed the fatty acid compositions of six different Turkish canola oil samples extracted from oil bearing plant seeds. The reported compositional data are given in Table 1, which displays the number of carbon atoms followed by the number of double bonds/molecule (e.g. C18.1 is oleic acid) and the %saturation/unsaturation.

From Table 1 it can be seen that the fatty acids in canola oils are predominantly unsaturated, C18 compounds comprising either oleic or linoleic acids. According to Johansson and Svensson (2001) and Young et al. (2004), canola oil may contain high levels of erucic acid (C22.1), however this acid was not reported for the Turkish canola oils listed in Table 1. Furthermore, Ghazani and Marangoni

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Table 1
Fatty acid compositions (in %) of six Turkish canola oils (Ozcan et al., 2012).

Sample	C16.0	C18.0	C18.1	C18.2	C18.3	Saturated	Unsaturated
Forte	5.00	1.61	19.22	69.56	4.58	5.00	94.97
Forza	4.27	1.66	21.77	63.15	9.12	4.27	95.70
Heros	5.08	1.59	67.76	18.80	6.66	5.08	94.81
Juna	11.46	1.30	61.40	18.67	7.15	11.46	88.52
Plente	5.05	1.43	67.79	20.51	5.20	5.05	94.93
Ras 6	4.92	1.45	66.16	20.98	6.46	4.92	95.05

(2013) reported that, in general, canola oils contain 6–14% α-linolenic acid, 50–66% oleic acid, and <7% of saturated fatty acids.

It is pertinent to note that both oleic and linoleic acids are commonly used as flotation collectors for oxide minerals like hematite (Cooke et al., 1959), but in this paper we examine their use as selective collectors in sulphide mineral flotation. The alternative use of local edible oils and intermediate products in their manufacture has the potential to add value to or broaden the application of these product streams. One such industry where these products may be utilised is the mining industry. Waste edible oils, after significant reprocessing, may be converted into fuel products like biodiesel. In this study we investigate the efficacy of using edible oils as processed at the farm gate as alternative, environmentally-benign and cost effective reagents in metal sulphide mineral flotation.

Flotation, patented at Broken Hill (Australia) in the early 1900s, is one of the prominent techniques employed in mineral processing for recovering and concentrating valuable minerals from ores. It has permitted the mining of low-grade and complex ores which initially were considered uneconomical. The process can be highly selective and is employed to separate specific complex ores (Wills and Napier-Munn, 2006). The principle of flotation is centred on the ability to use chemical reagents (i.e. promoters or collectors) to selectively increase the surface hydrophobicity of the mineral of interest to be beneficiated to form a concentrate. Other chemical reagents (i.e. depressants) can also be added to decrease the hydrophobicity of the unwanted gangue minerals to cause them to report to tails.

Generally, sulphur-based chemicals (e.g., xanthates, thionocarbonates and dithiophosphates) are used as collectors for the flotation of sulphide minerals. Typical examples of collectors mostly used for the flotation of chalcopyrite (Cp), the major sulphide mineral for copper production in the world, from associated iron sulphide gangue minerals (e.g., pyrite, Py) are sodium isopropyl xanthate (SIPX) and potassium amyl xanthate (PAX). Recent studies have shown that the use of these types of collectors for the selective flotation of Cp from Py is usually compromised due to several interactions that occur at the minerals' surfaces during the processes of grinding and conditioning (Owusu et al., 2013, 2014). Galvanic interactions occurring between Py and Cp surfaces during grinding and conditioning, prior to flotation, lead to Cp oxidation and copper activation of the former. This also results in the formation of hydrophilic surface coatings of iron oxide/hydroxide which decreases the Cp surface affinity for collector adsorption and hence inhibits its flotation. Activation of Py by copper ions from Cp increases collector adsorption on Py surface, promoting its flotation which subsequently lowers the overall Cp recovery and grade. Moreover, it must be noted that the effects initiated by galvanic interactions are also greatly influenced by the proportion of Py in the ore and the type of mill and grinding media used.

Additionally, the conventional S-based collectors, aside from being expensive, have problems with toxicity and/or repugnant odour. The use of xanthates introduces many occupational health and environmental risks that are often overlooked. Xanthates are highly flammable and can decompose to toxic carbon disulphide gas (CS_2) in manufacture, transport and use (Ellis, 2011; Singh et al., 2011). Recently, regulatory bodies in Ontario, Canada, reduced the carbon disulphide Time Weighted Average (TWA) to 1 ppm, one tenth of the previous limit (Williams et al., 2013). Xanthates are known to be toxic to aquatic life (Boening, 1998). Tightening regulations may eventually lead to further restrictions on the use of xanthates in the mining industry, hence the impetus for the search for "green" sulphide mineral collectors that reduce or eliminate the generation of hazardous substances in the mineral processing industry. Thus, a need exists for an improved copper sulphide minerals' (e.g. chalcopyrite, Cp) processing operation using alternative flotation reagents which have high specificity against iron sulphide gangue minerals (e.g. pyrite, Py) at competitive cost and markedly reduced toxicity.

Benn et al. (1996) patented the use of rapeseed oil as a selective collector for galena (PbS) recovery against pyrite. The composition of the rapeseed oil used was 50% erucic acid, 32% oleic acid, 15% linoleic acid, 1% linolenic acid and 1% palmitic acid. A laboratory flotation test using a complex sulphide ore containing lead, zinc, copper and iron sulphides using 240 g/t of rapeseed oil as collector gave a higher recovery of lead, copper and zinc minerals than when typical, conventional sulphydryl collectors (xanthate, dithiophosphate, mercaptan, etc.) were used. Pyrite recovery was similar to that obtained using the conventional collectors.

Bauer et al. (2000) and Greene et al. (2012) patented the use of various oils as collectors for the recovery of chalcopyrite and molybdenite from an ore containing 0.579% Cu and 0.010% Mo. One of the triglycerides used was canola oil containing 8% saturated oil, 59% mono-unsaturated oil, 22% unsaturated oil containing two double bonds and 11% oil containing three double bonds. Standard flotation conditions included 5.5 g/t thiophosphate collector, 7.7 g/t of diesel oil and 10 g/t of Nalco 9743 frother at pH 10.4 using lime to raise the pH. Under standard conditions, the grades of the concentrate were 4.94% Cu and 0.071% Mo for recoveries of 88.3% Cu and 79.2% Mo. When lime, 24 g/t of canola oil and 10 g/t of frother were added to the grind, and flotation conducted on the ground pulp, concentrate grades for Cu and Mo were 8.43% and 0.130% respectively. Corresponding recoveries were 82.0% Cu and 80.6% Mo showing that the use of canola oil gave a higher Cu grade at a lower Cu recovery, and the Mo grade was increased at a slightly increased Mo recovery. There was no mention of the pyrite content of the test ore.

The current work examines the use of commercial edible oils (canola, derived from rapeseed, and palm oil) as potential flotation reagents to add to the existing array of conventional collectors (SIPX and PAX) normally deployed for the selective flotation of copper sulphide minerals (e.g., Cp) from associated gangue iron sulphide minerals (e.g. Py). Specifically, we investigated the selective flotation recovery of chalcopyrite and molybdenite against pyrite in single mineral (chalcopyrite, pyrite) and their mixed mineral systems, as well as plant ores ((i) copper and (ii) porphyry copper-molybdenum) using canola or palm oil versus SIPX or PAX and diesel oil and their mixtures as collectors in Adelaide tap water and synthetic saline/sea water pulp conditions. Palm oil was selected as a typical saturated oil for comparison with the predominantly unsaturated canola oil. This was aimed at a testable hypothesis that the edible oil's degree of unsaturation has no noticeable or significant effect on its performance as a selective collector.

2. Experimental

2.1. Materials and reagents

2.1.1. Single and mixed minerals studies

Chalcopyrite (from Mannum Minerals) and pyrite (from a Peruvian Mine) crushed to <2 mm in size were used for the single