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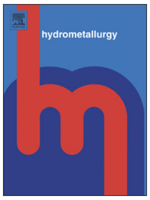

Effect of long term exposure of aliphatic ELIXORE 205 diluent to acidic and oxidising conditions on copper extraction

K.R. Barnard *, N.J. Kelly

CSIRO Mineral Resources, PO Box 7229, Karawara, WA 6152, Australia

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ABSTRACT

The impact of six months continuous mixing of aliphatic diluent ELIXORE 205 at 50 °C and 180 g/L H_2SO_4 both with and without ongoing addition of potassium permanganate oxidant was assessed in both the absence and presence of 15% v/v Acorga M5640 extractant. Compositional changes were assessed using FT-IR, GC, GC–MS and HPLC analysis of the organic solutions. No diluent degradation was observed in the acid-only diluent or diluent plus Acorga M5640 systems, or in the oxidised system where Acorga M5640 was present. In the latter system, preferential degradation of the extractant occurred. Small quantities of ELIXORE 205 degradation products suspected to be ketone and alcohol species were evident in the oxidised diluent-only system.

The impact of the organic 'ageing' process on copper loading, metal selectivity, extraction and stripping kinetics, phase disengagement times, and aqueous in organic entrainment was also assessed. This was achieved by adding fresh Acorga M5640 (and supplemental diluent as needed) to each degraded organic system to achieve a 10% v/v solution. The properties of these 'aged' solutions were compared to reference solutions containing only fresh extractant and diluent. Relative to the fresh reference solutions, extended exposure to acid conditions had no clear effect for either the diluent-only or the diluent plus extractant degraded systems. A small adverse effect in copper loading was evident in the oxidised diluent-only degraded system. A clear deterioration in performance was evident in the oxidised Acorga M5640-containing degraded system, expected under the very harsh conditions used.

1. Introduction

Solvent extraction (SX) is an important unit operation in hydrometallurgical processing of various base and precious metals, facilitated by exploiting the immiscible nature of aqueous and organic phases. The organic phase typically comprises a hydrogenated and desulfonated kerosene-based solvent (routinely termed as a 'diluent') along with an active 'extractant' which, under suitable operating conditions, is capable of reversibly complexing/solvating selected metal ions. In some instances and for a variety of reasons, an additional component, termed a 'modifier', can be added to the organic phase.

There are various extractants used commercially in SX operations for recovery of various metals, including copper. The SX extractants of choice for copper operations are phenolic hydroxyoxime-based, such as Acorga M5640, which contains 5-nonylsalicylaldoxime (aldoxime, Fig. 1) as its active component. In addition to this extractant, Acorga M5640 also contains the diester TXIB (2,2,4-trimethyl-1,3-pentanediol diisobutyrate) which acts as a strip modifier, allowing copper to be more readily stripped from the copper-aldoxime complex than would otherwise be the case.

Economic and other factors dictate that organic SX solutions are continually recycled, allowing organic degradation products and impurities entering the circuit to accrue to an equilibrium level in the organic phase. Phenolic oxime reagents have been used commercially for over 40 years to extract copper from acidic sulfate solutions and, due to their cost, much work regarding phenolic oxime degradation has focussed on these conditions. Known phenolic oxime degradation mechanisms and their effect on SX operation have been summarised previously (e.g. Hurtado-Guzman and Menacho, 2003). Hydrolysis of the oxime group is the most common degradation reaction and occurs under normal operating conditions, resulting in the formation of the corresponding aldehyde or ketone species (Fig. 2). In the case of Acorga M5640 aldoxime, this is 5-nonylsalicylaldehyde ('aldehyde'). Increasing either acid concentration and/or temperature increases the rate of hydrolysis (Tumilty et al., 1979; Whewell et al., 1981). This hydrolysis product typically has no material adverse effect on the organic phase, although its presence does slightly increase the viscosity and density of the organic solution, and it may act as a weak phase modifier (Hurtado-Guzman and Menacho, 2003).

Oxidation of phenolic oximes is a less common but very important degradation mechanism. Oxidation, e.g. by high oxidation state manganese species in acidic conditions, has been linked to poor circuit performance (Cheng et al., 2000; Miller, 1995; Miller et al., 1997; Ritcey, 2006;

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* Corresponding author.
E-mail address: Keith.Barnard@csiro.au (K.R. Barnard).

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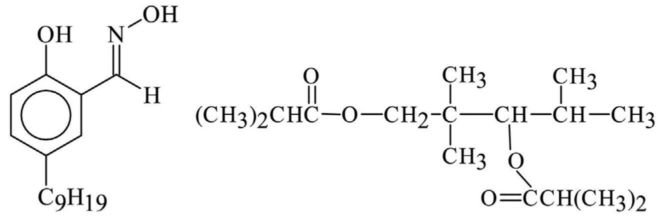

Fig. 1. Structures of the active component in Acorga M5640, 5-nonylsalicylaldoxime (aldoxime, left), and TXIB modifier (right).

West and Connor, 1996). Effects include a reduction in reaction kinetics and extractant capacity, a decrease in interfacial tension and Cu/Fe selectivity, increased phase disengagement times, entrainment, and crud production. The type of modifier present can also influence the degradation process (Kordosky and Virnig, 2003).

In contrast to the phenolic oxime extractant, the reactivity of the cheaper organic component, the diluent, and its potential impact on the system, has received little attention in copper-based SX systems, although diluent degradation in general has been suggested as an area worthy of further investigation (Ritcey, 2006). This may be attributable to the paraffinic and naphthenic components of diluents being relatively inert, requiring generally severe conditions to undergo reaction, predominantly via free radical addition (Morrison and Boyd, 1983). If present, aromatic components of diluents are less chemically stable (Haig and Duthie, 2011).

Diluent degradation has been explored in other sulfate-based SX systems where a different extractant has been used. For example, Flett and West (1986) were the first to report diluent oxidation in cobalt-based SX operations, at the Rustenberg plant. This led them to assess the oxidisability of three different diluents-aliphatic Escaid 110, aromatic Solvesso 150 and Escaid 100 containing both aliphatic and aromatic components-when used in the presence of phosphoric, phosphonic and phosphinic-based extractants, being D2EHPA, PC88A and Cyanex 272, respectively. Tests were performed at high temperature (50 °C) and pressures (150 psig) to accelerate the degradation process. Significant degradation only occurred in the presence of cobalt. It was found that the higher the aromatic content of the diluent, the faster the rate of oxidation. Although oxidation products were monitored using infrared (IR) and gas chromatography–mass spectrometry (GC–MS) analysis, no oxidation products were identified in this study. Only species seen in the Rustenberg plant were tentatively identified as phenyl ethanones and methyl esters of benzoic acid.

Following on from the earlier work of Flett and West (1986), cobalt-catalysed oxidation of tetradecane, used as a reference aliphatic diluent, was undertaken in an organic system containing the phosphinic acid extractant Cyanex 272 (Rickelton et al., 1991). This work was performed in the presence of 10 g/L each of Ni and Co at pH 5.0 over eight days at high temperature (100 °C) and pressure (600 psig) to greatly accelerate the degradation process. It resulted in the detection of carboxylic acids of varying carbon chain length, from C2 to C14, with most in the C5–C10 range. These had an adverse impact on cobalt over nickel selectivity, a key issue for that system. Although no supporting evidence was provided, small concentrations of ketones, alcohols and aldehydes were also reported to form. No adverse effect on phase disengagement with degradation was noted.

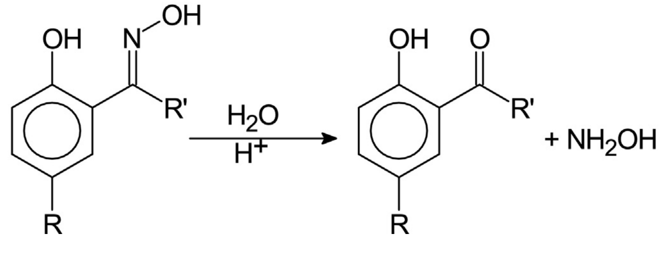

Fig. 2. Generalised reaction for oxime acid hydrolysis ($R = C_9H_{19}, C_{12}H_{25}$; $R' = H, CH_3$).

In another study, this time at atmospheric pressure, both aliphatic ShellSol D70 and aromatic containing ShellSol 2046 diluents containing the phosphinic acid-based cobalt extractant Cyanex 272 were subjected to mixing with mildly acidic (pH 5.3) solution for 20 weeks under atmospheric pressure and 75 °C with regular oxygen sparging (Maxwell et al., 1999). In the absence of an antioxidant, aliphatic carboxylic acids were found to be generated in both diluent systems, along with increased crud formation. Due to the focus of that work, no other degradation products were sought, although the generation of alcohols, aldehydes and other oxygenated species was ‘expected’. A beneficial effect on phase disengagement behaviour was observed.

Short term permanganate oxidation of partially aromatic ShellSol 2046 diluent (no extractant present) in the presence of 150 g/L H_2SO_4 has been shown to result in the generation of insoluble crud and the formation of organic-soluble species identified by gas chromatography–mass spectrometry as naphthoquinones, naphthalenecarboxaldehydes, binaphthalenes, indenones and hydroxybiphenyl species (Barnard and Hughes, 2000). Detection of aliphatic degradation products such as carboxylic acids was not attempted in that work. The resulting dark yellow organic solution exhibited good phase separation properties.

Exposure of partially aromatic-containing Escaid 100 to ultra-violet light was undertaken over a year (Whewell et al., 1981). This was found to result in a yellowing of the diluent, a decrease in interfacial tension and, when combined with oxime extractant, a decrease in copper extraction kinetics. Attempted identification of the diluent degradation products was not pursued.

Although not sulfate-based, radiolytic and chemical degradation of paraffinic diluent in the PUREX process has been found to result in the generation of alcohols, aldehydes, ketones, esters and carboxylic acids in addition to nitrated species (Ishihara and Ohwada, 1966; Neace, 1983; Smith et al., 1997 and references therein). Outside of SX systems, permanganate oxidation of alkanes to ketones, aldehydes, alcohols and carboxylic acids is known (Lau et al., 1995; Strassner and Houk, 2000 and refs therein).

The entry of the low (<300 ppm) aromatic content diluent ELIXORE 205 to the SX diluent market provided an opportunity to specifically assess the stability of this diluent under very harsh operating conditions (6 months continuous mixing at 50 °C and 180 g/L H_2SO_4 with/without permanganate addition) in both the presence and absence of Acorga M5640 reagent. The resulting aged/degraded organic samples were spectroscopically assessed before being reconstituted to contain 10% v/v Acorga M5640 and their SX performance assessed against corresponding fresh (undegraded) organic solutions. These reference solutions were prepared using ELIXORE 205 as well as two alternate, commercially proven diluents. Behaviour was assessed via metal extraction kinetics, metal selectivity, phase disengagement behaviour and aqueous in organic entrainment.

2. Experimental

2.1. Organic and aqueous reagents

Aliphatic diluent ELIXORE 205 was supplied by TOTAL Special Fluides. A CSIRO stock sample of Acorga M5640 (ICI Australia Operations, Sample No. 5064, packed 10/11/1997) was also used, along with two commercially-proven aliphatic diluents, ‘Aliph1’ and ‘Aliph2’. All organic reagents were used as supplied. Organic solutions prepared using fresh reagents were washed three times using 0.3 M sodium sulfate at an aqueous to organic ratio (A:O) of ~1:3 to remove aqueous-soluble impurities. Aqueous solutions were prepared using AR grade copper, cobalt, iron and sodium sulfates and sulfuric acid.