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Reagent Degradation In The Synergistic Solvent Extraction System LIX®63/Versatic™10/Nonyl-4PC

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Abstract

Direct solvent extraction of nickel and cobalt from nitrate-based leach liquors has become of interest due to the successful piloting of nitric acid processes for treating nickel laterite ores. The current study investigated the stability of both hydroxyoxime and nonyl-4PC (nonyl-4-pyridine carboxylate) in LIX 63/Versatic 10/nonyl-4PC under conditions relevant to the recovery of nickel and cobalt from a nitrate-based leach liquor with stripping into sulfuric acid. Nonyl-4PC increased both the rate of hydroxyoxime degradation under the pH 1.5 extract conditions required for a potential nickel–cobalt separation process and the rate of cobalt poisoning of LIX 63. Under strip conditions and the pH 4 extract conditions required for co-extraction of nickel and cobalt, nonyl-4PC did not otherwise affect the rate of hydroxyoxime loss. Additionally, the presence of nitrate anions did not increase the loss of either hydroxyoxime or nonyl-4PC. The combination LIX 63/Versatic 10/nonyl-4PC therefore appears prospective for the co-extraction of nickel and cobalt at pH 4 from nitrate-based leach liquors.

1. Introduction

1.1 Recovery of nickel and cobalt from nitrate-based liquors using direct solvent extraction

Direct solvent extraction (DSX) systems for the recovery of nickel and cobalt from concentrated nitrate-based liquors (~8 M nitrate) have recently been developed to support recent ongoing development of the Direct Nickel (DNi) nitric acid leaching process [1] and the nitric acid pressure leaching process [2] for nickel laterite ores. One of these is the synergistic combination of the hydroxyoxime LIX 63 (active component *anti*-5,8-diethyl-7-hydroxydodecan-6-oxime) and Versatic 10 (neodecanoic acid) with nonyl-4PC (nonyl-4-pyridine carboxylate) included as a nickel accelerator [3]. It has been discussed in other work [4] that this solvent system can be used to either co-extract nickel and cobalt at high pH (~4) or to selectively extract nickel from cobalt at low pH (~1.5) in a nitrate-based pregnant leach solution (PLS).

It has long been known that the combination of LIX 63 and organic acids is synergistic for nickel and cobalt extraction [5–10]. The combination of LIX 63 and Versatic 10 has more recently shown promise for commercial application to traditional sulfate-based laterite leach liquors [11]. Work by Cheng [12], however, revealed that nickel stripping and extraction kinetics were slow. TBP (tributyl phosphate) was used by Cheng [12] to accelerate nickel stripping rates, but this also increased the pH required for co-extraction of nickel and cobalt by 1.7 pH units. It was found in more recent research [13] that an alternate modifier, nonyl-4PC, acts as a phase-transfer

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catalyst, accelerating the extraction and stripping of nickel with LIX 63/Versatic 10 without increasing the extraction pH.

1.2 Stability of LIX 63 hydroxyoxime

One significant barrier to commercial acceptance of the synergistic combination of LIX 63/Versatic 10 is the relative instability of the hydroxyoxime reagent in LIX 63. This is of particular concern in the presence of organic acids, where more acidic organic acids accelerate the rate of hydroxyoxime degradation [14,15]. The impact of an organic base such as nonyl-4PC on LIX 63 stability has not previously been determined and therefore required investigation. In addition, apart from cursory studies in chloride media [16], the stability of hydroxyoxime has only been considered in contact with sulfate-based solutions [14,17,18] or under anhydrous conditions [17]. The effect of nitrate-based solutions on hydroxyoxime stability was therefore also unknown and required investigation.

Degradation of LIX 63 under aqueous-free conditions and under sulfate-based extract or strip conditions is first order or pseudo-first order with respect to hydroxyoxime [19]. As such, hydroxyoxime half-lives can be calculated for different operating environments, and comparisons can then be made between degradation rates from contact with different aqueous phases and temperatures. The various degradation products of LIX 63 have been well documented from sulfate-based solutions, and the primary degradation products, before formation of secondary products via carbon–carbon cleavage, are shown in Figure 1. These are diketone (5,8-diethyl-6,7-dodecanedione), keto-oxime (5,8-diethyldodecan-6-oxime-7-one), and acyloin (5,8-diethyl-7-hydroxy-6-dodecanone).

Under strip conditions in weak sulfuric acid (10 g/L) and a metal-free organic, the rate of hydroxyoxime degradation in the presence of Versatic 10 is comparable to that in the absence of an aqueous phase [17]. A linear relationship between acid strength in the aqueous strip solution and decreasing hydroxyoxime half-life was obtained at high temperatures (70 °C) [22]. In this high temperature work, the half-life almost doubled on decreasing the aqueous-phase acidity from 50 g/L sulfuric acid to 0 g/L. Acyloin and diketone are the favored primary degradation products under strip conditions [19,21]. Acyloin formation requires only hydrolysis of the oxime moiety to a ketone. Diketone formation would require both hydrolysis of the oxime and oxidation of the alcohol.

Under extract conditions, the rate of hydroxyoxime degradation in the presence of Versatic 10 increases depending on metal loading. In the presence of typical laterite PLS metal concentrations, hydroxyoxime loss is much faster under extract conditions when compared with strip conditions at the same temperature [19]. Metals in the organic phase act to decrease hydroxyoxime half-life in the order of copper > manganese > cobalt > zinc > nickel, where nickel loading up to 4.6 g/L had little effect on hydroxyoxime stability. Copper loading at pH 5.5 resulted in a decrease in hydroxyoxime half-life from 55 weeks in a copper-free system to 13 weeks with 2 g/L organic-phase copper [23]. Manganese loading at pH 6 decreased hydroxyoxime half-life from 66 weeks in a manganese-free system to only 24 weeks with 2.4 g/L manganese. In addition, increased manganese loading at high pH also resulted in increased cobalt poisoning of LIX 63 [18]. The favored primary degradation product under the extract conditions used in this earlier study at 30 °C was keto-oxime, which was particularly promoted by increased manganese loading. Diketone formation under extract conditions is only promoted

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at temperatures above 30 °C [19,21]. Keto-oxime formation requires oxidation of the hydroxyoxime alcohol group. This reaction can potentially be attributed to metal complexation making the hydroxyoxime alcohol group proton more labile, explaining why keto-oxime is only formed under extract conditions.

Temperature was shown to have a dramatic effect on hydroxyoxime degradation in the presence of Versatic 10 under both extract and strip conditions. Hydroxyoxime half-lives for LIX 63/Versatic 10/TBP under nickel laterite extract conditions roughly halved with every 10 °C increase in temperature, decreasing from 105 weeks at 30 °C to only 8 weeks at 60 °C [19]. Earlier work had suggested that TBP had little impact on the LIX 63 half-life [14]. Under strip conditions without TBP as a phase modifier this trend persisted, with hydroxyoxime half-life decreasing from 90 weeks at 40 °C to 49 weeks at 50 °C in the presence of 10 g/L sulfuric acid [17].

1.3 Stability of Versatic 10 and nonyl-4PC

Both Versatic 10 and nonyl-4PC are expected to be more stable under operational conditions than LIX 63. The Versatic 10 carboxylate group cannot be oxidized further, and it is therefore stable to oxidative degradation. Carboxylic acids are also not susceptible to hydrolysis. Although carboxylic acids can form esters by an acid-catalyzed reaction with an alcohol, this has not been reported under commercially relevant SX conditions. Previous work [23] revealed that only minimal loss of Versatic 10 (6% lost over 105 days) occurred from LIX 63/Versatic 10 under extract conditions. This was attributed to the aqueous solubility of Versatic 10 at higher pH, as has been documented by previous authors [24, 25].

In earlier work [26], only minimal degradation of the decyl analogue of nonyl-4PC in decyl-4PC/Versatic 10 was noted under sulfate-based strip conditions. A loss of 1% per annum was calculated at pH 1 and pH 3 at 40 °C compared with a loss of 5.9% per annum at pH 3 and 60 °C. Under sulfate-based extract conditions, there was no degradation of decyl-4PC measured under sulfate-based nickel laterite extract conditions after 16 days [26]. Similarly, the extraction pH$_{50}$ values for Nicksyn™ (believed to be a pyridine carboxylate based on the synergistic effects on nickel and cobalt when combined with Versatic 10)/Versatic 10 did not change over 90 days under otherwise similar conditions [27]. As hydrolysis (Figure 2) is the only pyridine carboxylate degradation mechanism noted in the literature, slow rates of degradation under high pH extract conditions are expected. The demonstrated stability of pyridine carboxylates under commercially relevant sulfate-based operating conditions is promising for operation of LIX 63/Versatic 10/nonyl-4PC at relatively low temperatures and low acidity for a nitrate-based process. The effect of nitrate anions that could potentially become entrained in the acidic strip liquor, however, was unknown and required investigation.

In summary, although there is a great deal of information available on the stability of hydroxyoxime in the presence of Versatic 10 in sulfate systems, both with and without TBP, no work has yet considered the effect of organic-phase additions of nonyl-4PC or concentrated nitrate aqueous matrices on hydroxyoxime stability. The effect of nitrate anions on nonyl-4PC stability was similarly unknown. The present work therefore aimed to assess hydroxyoxime and nonyl-4PC stability in LIX 63/Versatic 10/nonyl-4PC under conditions expected for a nitrate-based DSX process. The conditions used were based on those proposed previously [3], and are relevant to extraction from a concentrated magnesium nitrate PLS followed by a sulfuric acid

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strip. A subsequent nickel–cobalt separation using the conventional phosphinic acid-based reagent Cyanex®272 was previously proposed from the sulfate-based loaded strip liquor. The effect of nitrate-based extract conditions for a theoretical separation of nickel and cobalt using LIX 63/Versatic 10/nonyl-4PC at pH 1.5 was, however, additionally investigated in the current work to determine the potential for this novel process option.

2. Materials and Methods

2.1. Aqueous and organic solutions

Synthetic aqueous strip solutions were made up with analytical-grade reagents of nickel sulfate, nickel nitrate, sulfuric acid, and nitric acid in deionised water. A nitrate-based nickel laterite PLS was collected from the Direct Nickel (DNi, Australia) pilot plant mixed hydroxide precipitation feed tank [1] during operation. The solution was cooled to room temperature and filtered before use. Due to different goals of the pilot plant at the time this sample was collected, fluctuations in control parameters resulted in high aluminium concentrations in the MHP feed (438 mg/L). This high aluminium PLS (High Al) was used as a feed for extract conditions loaded at pH 1.5. Under normal operational conditions the aluminium concentration would be expected to be <10 mg/L after an additional aluminium removal stage [28]. A sample of the cooled liquor was therefore raised to pH 3.15 using sodium hydroxide at room temperature and filtered to produce a low aluminium feed (Low Al) for loading at pH 4. A sulfate-based laterite leach liquor sample used as a feed for comparative sulfate-based extract conditions was taken from a stock solution held by the Commonwealth Scientific Industrial Research Organisation (CSIRO, Australia), as used

in other work [11]. The metal concentrations in the three aqueous feed samples are shown in Table 1.

Organic solutions were prepared using technical-grade reagents diluted with ShellSol D70 (dearomatised diluent, Shell Chemicals). Reagents used were: Versatic 10 (neodecanoic acid, 97%, Shell Chemicals), LIX 63 (5,8-diethyl-7-hydroxy-6-dodecanone oxime, 55% determined by gas chromatography flame ionisation detection, as described previously [14], BASF), and nonyl-4PC (nonyl-4-pyridinecarboxylate, 95%, China Central South University). All solutions contained hexadecane (20 g/L) as an internal standard (>99%, Sigma Aldrich). All organic phases were initially washed with sulfuric acid (5 g/L) followed by sodium sulfate (50 g/L) before drying over anhydrous sodium sulfate (AR, Rowe Scientific).

2.2. Long-term shake tests

Stability tests were carried out by contacting organic and aqueous phases in 250 mL hexagonal glass jars in an orbital shaker incubator (Thermoline Scientific TU-454), at 200 rpm at an aqueous-to-organic (A:O) volumetric ratio of 1:1, and 40 °C. Some samples were originally loaded at A:O of 2:1 and the required raffinate volume was removed before starting the long-term study to maintain an A:O of 1:1. All jars were initially washed with soap and water, then DI water, and finally ethanol before drying in an oven at 100 °C before use. The top of each jar was covered with a chemically inert Teflon-coated glass fibre (Fiberflon 108.08, Fiberflon Asia Pacific) to avoid contamination from the jar lid. Experimental conditions and associated experimental codes are shown in Table 2. Higher loading A:O ratios for pH 1.5 extract conditions (Ex1.5-N) were applied to maximise nickel extraction at the lower operational pH.

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Samples of the organic phases were taken at regular intervals and the same volume of aqueous phase was removed with each organic sample to maintain the A:O at 1:1. Loaded organic phases were stripped (50 g/L sulfuric acid, A:O = 3:1, 40 °C for 20 minutes) and the stripped organic filtered through Whatman 1PS phase separation paper. All organic samples were then washed with sodium sulfate (50 g/L) at A:O of 3:1 for 20 seconds. The washed organic was removed from the aqueous wash liquor and dried over anhydrous sodium sulfate before storing in a fridge at 3 °C prior to analysis using gas chromatography with flame ionisation detection (GC-FID).

2.3. Cobalt poisoning tests

2.3.1 Poisoning as a function of standing time

The extent of cobalt poisoning over time was measured on four different organic phases: (1) 0.25 M LIX 63/0.25 M Versatic 10/0.36 M nonyl-4PC, (2) 0.25 M LIX 63/0.5 M Versatic 10/0.36 M nonyl-4PC, (3) 0.25 M LIX 63/0.25 M Versatic 10, and (4) 0.25 M LIX 63/0.5 M Versatic 10. Cobalt was loaded into the organic phases from a nitrate-based aqueous feed (1 M sodium nitrate, 0.01 M cobalt nitrate) by contacting the phases at A:O of 1:1 and pH 6 at 23 °C for 10 minutes. The loaded organic was filtered through Whatman 1PS paper before storing in a glass jar with a loose-fitting lid. Samples of the loaded organic were taken at: 1, 4, 8, 24, 48, 96, and 192 hours. Samples were then stripped twice (50 g/L sulfuric acid, A:O of 3:1, 40 °C, 20 minutes followed by 50 g/L sulfuric acid, A:O of 1:1, 40 °C, 20 minutes) before filtering through 1PS paper and drying over anhydrous sodium sulfate. The resulting stripped organic phase was then analysed for cobalt directly using atomic absorption spectroscopy (AAS, Section 2.5).

2.3.2 Poisoning as a function of cycling

Two organic phases (0.25 M LIX 63/0.25 M Versatic 10/0.36 M nonyl-4PC and 0.25 M LIX 63/0.25 M Versatic 10) were subjected to a sequential load–strip trial. The organic phases were loaded with cobalt (0.01 M cobalt nitrate in 1 M sodium nitrate) at A:O of 1:1 and pH 6 at 23 °C for 10 minutes. The phases were separated in a separating funnel, and the loaded organic was immediately stripped (50 g/L sulfuric acid) at A:O of 1:1 and 40 °C for 20 minutes and the phases separated in another separating funnel. A sample of the stripped organic was taken and washed (50 g/L sulfuric acid) at A:O of 2:1 for 20 seconds and dried over anhydrous sodium sulfate before direct analysis of organic phase cobalt using AAS. This load–strip procedure was repeated using fresh feed and fresh aqueous strip solutions a further nine times.

2.4. Gas Chromatography

All organic phases from stability studies were analysed using GC-FID (Varian, CP-3800 gas chromatograph). For hydroxyoxime, keto-oxime, and diketone analysis, samples were derivatised with BSTFA (N,O-bis(trimethylsilyl)trifluoroacetamide, Supelco) diluted in 50:50 toluene (AR, Rowe Scientific):DMF (N,N-dimethylformamide, AR, Rowe Scientific) at 80 °C for 20 minutes before analysis. A sub-sample (0.7 μL) was injected into an AT1-MS (Grace, 30 m column, 0.32 mm inside diameter, 0.25 μm film thickness) gas chromatography column with the injection port held at 220 °C at a split ratio of 80. The initial oven temperature (100 °C) was increased by 10 °C/min to 240 °C and held for 0.5 minutes. The detector port was held at 270 °C and FID sensitivity was set to 12.

For analysis of nonyl-4PC, nonanol, and acyloin, samples were diluted in 50:50 toluene:DMF and sub-samples (0.7 μL) were injected into an EC-1000 (Grace 30 m column, 0.32 mm inside diameter, 0.25 μm film thickness) GC column with an injection port held at 250 °C at a split ratio of 50. The initial oven temperature (85 °C) was increased by 10 °C/min to 170 °C, then by 2 °C/min to 178 °C, then by 15 °C/min to 220 °C and held for 2 minutes, and finally to 250 °C at 15 °C/min and held for 3 minutes. The detector port was held at 270 °C and FID sensitivity was set to 11.

Where quantified, hydroxyoxime [14], keto-oxime [29], and diketone [14] were calibrated against assumed pure reference samples. Acyloin was calibrated against a reference sample provided by Cognis (92.9%). A pure sample of nonyl-4PC could not be obtained and so the reported purity of 95% was assumed to be correct. The alcohol degradation product from nonyl-4PC was confirmed against a reference sample to be 2,4,4-trimethylhexanol. As a pure sample of this nonanol isomer could not be obtained, it was quantified against a pure sample of 1-nonanol (99%, Sigma Aldrich).

2.5. Atomic Absorption Spectroscopy

Organic-phase cobalt concentrations were determined via AAS (Agilent 240 FS) using standards made up by loading 0.25 M LIX 63/0.25 M Versatic 10/0.36 M nonyl-4PC with a cobalt nitrate analytical standard at pH 6 and A:O of exactly 1:1. The raffinate from this process was analysed by AAS to ensure complete loading had occurred. The organic standard was then diluted accordingly with fresh organic to the required standard concentrations. Metal concentrations in

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the aqueous feed, raffinate, and loaded strip liquor samples from stability studies were also analysed using AAS to determine the loaded organic metal concentrations by difference.

3. Results and Discussion

3.1. Stability of hydroxyoxime in LIX 63/Versatic 10/nonyl-4PC under strip conditions

3.1.1 Rates of hydroxyoxime loss

The effects of strip conditions on reagent stability were studied with both sulfuric acid and nitric acid. Varying levels of nitrate (0, 5, 10 g/L) in sulfuric acid were also assessed to determine the effect of nitrate anions in a potential strip circuit. Results for the hydroxyoxime concentration over time as a percentage of the initial day 0 concentration are shown in Table 3. Hydroxyoxime half-lives were calculated using the first-order reaction plots of $-\ln([\text{LIX } 63]/[\text{LIX } 63]_0)$ over time (Figure 3). Straight-line trends with low standard error (SE) values were obtained in each case, consistent with first-order kinetics. Half-lives were thus obtained from each plot using the relationship $t_{1/2} = \ln(2)/k$, where the rate constant (k) is equal to the plot slope. Errors values were calculated for all half-lives as the change in half-life assuming a 2% decrease in the final day LIX 63 analysis. This method for error analysis was chosen as per previous work [18, 30]. These values provide an indication of the experimental error and accuracy of the calculated half-lives during this research.

Low concentrations of nitrate from 0 to 10 g/L (St0.5-S_0 to St0.5-S_10) had no clear trending effect on the rate of hydroxyoxime loss, suggesting that low nitrate entrainment in a sulfuric acid strip would not affect the rate of hydroxyoxime degradation in a commercial operation. This is encouraging for the proposed DSX process implementing an acid-exchange strip circuit from nitrate to sulfate where some entrainment of nitrate would be expected. There was, however, a clear increase in hydroxyoxime loss on moving from a pH 1 sulfuric acid strip (St1.0-S_0), to a pH 0.5 sulfuric acid strip (St0.5-S_0), to a pH 0.5 nitric acid strip (St0.5-N), suggesting faster degradation rates both at lower pH and when stripping with nitric acid.

The sulfate-based strip solution of 60 g/L nickel at pH 1 (St1.0-S_0) was used to determine hydroxyoxime loss from a strip solution in a potential commercial operation, as proposed by previous research [3], and as a comparison with earlier stability work. The pH 1 sulfate-based strip resulted in slow hydroxyoxime degradation with a calculated half-life of 110 weeks at 40 °C (Table 3). This can be compared with previous observations [17] for LIX 63/Versatic 10 in contact with 10 g/L sulfuric acid in deionised water (approximately pH 1), resulting in a similar half-life of 90 weeks at 40 °C. The comparable half-life obtained between these two experiments, with and without nonyl-4PC but under otherwise similar conditions, suggested that the presence of nonyl-4PC under sulfuric acid strip conditions did not accelerate hydroxyoxime loss.

3.1.2 Analysis of hydroxyoxime degradation products

As expected from earlier work, the primary degradation product obtained under the tested strip conditions was acyloin (Table 4); keto-oxime concentration did not materially change under strip conditions. Diketone only increased materially in the nitric acid strip (St0.5-N). The reagent

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sums, or mass balances, for hydroxyoxime and degradation products were all between 85 and 94%. Although these fell below that obtained by Barnard and Turner [19] at 60 °C (95%), they are still above 80% and suggest reliable analysis results that capture the majority of the degradation products generated.

As the nitrate concentration increased, the oxidizing nature of the aqueous phase also increased from 496 mV (vs. Ag/AgCl) in the sulfate-only strip at pH 0.5 to 615 mV in the nitrate-only strip at pH 0.5. From the data in Table 4, the net amount of the oxidation-hydrolysis product (diketone) formed in the nitrate-only strip solution as a percentage of total hydroxyoxime loss was 7.0%, higher than the average of 1.3% for the other, primarily sulfate-based, strip solutions. In contrast, the formation of the hydrolysis-only product (acyloin) was only 38% of total hydroxyoxime loss, compared with 45% for the mostly sulfate-based strips. It is therefore suspected that the more oxidizing nature of nitric acid promoted formation of diketone via oxidation of the hydroxyoxime alcohol group.

In all cases, both with and without nitrate, the aqueous phase pH increased over the course of the long-term study (Table 3). In order for the pH to increase, acid must be consumed. Two possible mechanisms exist to consume acid: acid consumption by hydroxyoxime degradation and acid consumption via nitrate reduction to NO_x and water. Because the pH rose both in the presence and absence of nitrate over the course of the investigation, nitrate reduction cannot be the sole reaction consuming acid. Hydrolysis of the oxime functional group will result in a carbonyl and hydroxylamine. Once in the aqueous phase, hydroxylamine can react with the mineral acid

present to generate a hydroxylammonium salt, consuming available acid and preventing the reverse reaction back to the oxime [31].

At higher nitrate concentrations, the final aqueous phase pH increased to higher values than at lower nitrate concentrations (0.63 compared with 0.53). This discrepancy is likely due to the sulfate-bisulfate equilibrium:

$$SO_4^{-2} + H^+ \rightleftharpoons HSO_4^-$$
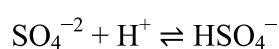
As a result of this equilibrium, more acid addition would be required to decrease the aqueous phase pH to 0.5 in the presence of more sulfate anions. Due to the lower buffering capacity, the pH increased faster in the aqueous phases containing more nitrate over the long-term stability study. Because of the minimal buffering capacity of the nitrate-only strip, a pH change of 0.5 to 0.63 can be used to approximate consumption of 82 mM of acid. This approximation corresponds well with the loss of 81 mM of hydroxyoxime over the same time frame, suggesting that a hydroxyoxime degradation reaction was consuming acid in the aqueous phase at a molar ratio of 1:1, for example hydroxylamine generation via oxime hydrolysis. Although this is of interest, total acidity would not be neutralised over time in a continuous operation where the aqueous phase is continuously replaced.

3.2. Stability of hydroxyoxime in LIX 63/Versatic 10/nonyl-4PC under extract conditions

3.2.1 Rates of hydroxyoxime loss

Fresh organic phases were loaded from a nitrate-based PLS at pH 4 (Ex4.0-N) or sulfate-based PLS at pH 6.0 (Ex6.0-S_0) for co-extraction of nickel and cobalt. These pH values produced similar levels of loaded metals that are known to accelerate hydroxyoxime degradation: manganese (5–8 mg/L), cobalt (155–178 mg/L), and copper (9–18 mg/L). A fresh organic phase was also loaded at A:O of 2:1 and a lower pH of 1.5 (Ex1.5-N) to investigate the stability of LIX 63/Versatic 10/nonyl-4PC under the potential operating conditions for separation of nickel from cobalt. The lower loading pH and higher A:O ratio for Ex1.5-N resulted in very low levels of organic-phase cobalt (9 mg/L) and manganese (2 mg/L), but slightly higher levels of copper (21 mg/L).

Hydroxyoxime concentrations over time and the corresponding half-lives for these three samples are shown in Table 5 along with the estimated half-life error. Results for an aqueous-free system are included for comparison with an earlier anhydrous study [17] discussed later. First-order reaction plots presented in Figure 4 with low SE values confirmed first-order reaction kinetics and allowed generation of the rate constant (k). Hydroxyoxime half-lives under conditions required for co-extraction of nickel and cobalt at high loading pH were very similar between a sulfate (34 weeks) and nitrate (35 weeks) PLS, irrespective of the loading pH and slight differences in organic phase metal concentrations (Table 5 and Figure 4). Co-extraction of nickel

and cobalt from a nitrate-based PLS using LIX63/Versatic 10/nonyl-4PC therefore appears prospective.

A correlation of a doubling in the rate of degradation with a 10 °C increase in temperature [19] can be used to compare the current half-life results to degradation rates reported previously. This comparison is presented in Table 6 for loaded organic phases with similar concentrations of cobalt, copper, and manganese. From this comparison, the rate of hydroxyoxime loss was unaffected by the presence of nonyl-4PC under aqueous-free conditions. Very similar half-lives were also obtained between sulfate-based extract conditions in general and the DNi nitrate-based extract conditions tested here. This comparison supported a conclusion that neither nonyl-4PC nor the high nitrate concentration in the DNi PLS will have an impact on hydroxyoxime stability under high pH extract conditions for co-extraction of nickel and cobalt.

In comparison with co-extraction of nickel and cobalt at pH 4, separation of nickel from cobalt at pH 1.5 resulted in rapid degradation of hydroxyoxime, with total loss occurring after only 4 weeks (Table 5). Such rapid degradation of hydroxyoxime from LIX 63/Versatic 10 has not previously been reported. Although LIX 63/Versatic 10/nonyl-4PC does appear to be suitable for co-extraction of nickel and cobalt at pH 4, it does not, therefore, appear suitable for separation of nickel from cobalt at pH 1.5.

3.2.2 Analysis of hydroxyoxime degradation products

The degradation products formed under extract conditions and the resulting reagent sum accountabilities are shown in Table 7. As expected from previous work, only diketone and keto-

oxime were formed under extract conditions. The reagent sum for the quantified primary degradation products were all above 80%, except for at pH 1.5 (Ex1.5-N). These accountabilities were slightly lower than the 87–93% obtained by Barnard, Turner [18] under various extract conditions at 30 °C, but comparable to those obtained by Turner and Barnard [23] under nickel laterite extract conditions at 45 °C (68–83%). The very low reagent sum for extract conditions at pH 1.5 (50%) can potentially be attributed to the formation of additional secondary degradation products after carbon–carbon cleavage.

For the studies at pH values of pH 4 and pH 6 for co-extraction of nickel and cobalt, as well as under aqueous-free conditions, diketone fluctuated within 20% of the initial concentration (17 mM) over the course of the study and acyloin was also mostly unchanged. Only keto-oxime was found to increase consistently over time under these conditions (Table 7), agreeing with observations near 40 °C of previous authors [18, 19].

In contrast with extract conditions at higher pH values, the only primary degradation product generated in the final day sample of the pH 1.5 extract experiment was diketone. Initially, there was a spike of keto-oxime (21 mM), before it decreased in concentration with a concurrent increase in diketone concentration (Figure 5). Extensive formation of diketone under extract conditions has not previously been reported below 50 °C. Similarly, loss of keto-oxime under extract conditions has not been reported.

Comparison tests were set up using synthetic nitrate PLS with and without cobalt to further investigate the particularly rapid hydroxyoxime degradation under nitrate-based extract conditions at low pH (Ex1.5-N). This was done to ascertain whether cobalt was playing a major

role in accelerating hydroxyoxime loss at the lower pH. After 7 days, 53% of the initial hydroxyoxime concentration remained in the cobalt-free system and 37% remained in the cobalt-bearing synthetic system. Although a substantial decrease in the rate of hydroxyoxime degradation in the absence of cobalt agreed with earlier observations [18], a hydroxyoxime half-life of just over a week under these conditions was still very low compared with the other conditions tested here.

3.3. Effect of nonyl-4PC on hydroxyoxime degradation under pH 1.5 extract conditions

3.3.1 Rates of hydroxyoxime loss

The rate of hydroxyoxime degradation in LIX 63/Versatic 10/nonyl-4PC under extract conditions at pH 1.5 for separation of nickel from cobalt was rapid, resulting in complete hydroxyoxime loss within 4 weeks. Under strip conditions in nitric acid at pH 0.5, hydroxyoxime stability was still comparatively high, with a half-life of 28 weeks (Section 3.1). Under nitrate-based extract conditions at pH 4.0, the rate of hydroxyoxime degradation was the same as under sulfate-based extract conditions at pH 6.0 and as in earlier work using LIX 63/Versatic 10 without nonyl-4PC (Section 3.2). Additionally, the presence of nonyl-4PC did not appear to affect the rate of hydroxyoxime loss under strip or aqueous-free conditions.

As nonyl-4PC in contact with low pH nitric acid in the absence of metals had only a small effect on the rate of hydroxyoxime degradation, rapid hydroxyoxime loss under extract conditions at pH 1.5 could either be due to metal loading of LIX 63/Versatic 10 at low pH or to the presence

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of nonyl-4PC in an organic phase loaded from a nitrate-based matrix at low pH. LIX 63/Versatic 10 was therefore loaded at pH 1.5 from a nitrate matrix in the absence of nonyl-4PC to compare the rate of degradation with that obtained in the presence of nonyl-4PC from Table 5. LIX 63/Versatic 10 loaded at pH 1.5 resulted in comparable concentrations of metals in the organic phase as LIX 63/Versatic 10/nonyl-4PC loaded at pH 1.5. These were: copper 11 mg/L, cobalt 16 mg/L, and manganese 8 mg/L.

The rate of hydroxyoxime loss under extract conditions at pH 1.5 in the presence of nonyl-4PC was much faster than in the absence of nonyl-4PC (Ex1.5-N-woPC). In the presence of nonyl-4PC, complete hydroxyoxime loss occurred after 4 weeks. In the absence of nonyl-4PC, a first-order reaction plot similar to hydroxyoxime loss from LIX 63/Versatic 10/nonyl-4PC under higher pH extract conditions was obtained (Figure 6). The small standard error calculated from the straight line regression was similar to that generated under nitrate-based extract conditions at pH 4. A half-life of 36 weeks was calculated for hydroxyoxime loss in Ex1.5-N-woPC from the slope in Figure 6, very similar to the 35 weeks obtained under pH 4 nitrate-based extract conditions. It is clear from this data that nonyl-4PC greatly increased hydroxyoxime degradation when the organic phase was loaded at a pH of 1.5 for separation of nickel from cobalt. If a DSX system for the separation of nickel from cobalt in a nitrate matrix is desired, a nickel kinetics accelerator other than nonyl-4PC must be found.

3.3.2 Analysis of hydroxyoxime degradation products

The results for hydroxyoxime, diketone, keto-oxime, and acyloin concentrations in the final day pH 1.5 extract sample without nonyl-4PC are shown in Table 8, with a comparison with the

organic phases containing nonyl-4PC at both pH 1.5 and 4. The final day reagent sum accountability was 76%, which was much higher than 50% obtained with the addition of nonyl-4PC, but lower than 84% at pH 4. Despite slightly acidic conditions, there was minimal acyloin formation at pH 1.5, either with or without nonyl-4PC. Unlike LIX 63/Versatic 10/nonyl-4PC loaded from a nitrate-based PLS at pH 1.5, diketone was not generated in the absence of nonyl-4PC; the only degradation product found to increase was keto-oxime. This can be compared with high pH sulfate-based extract conditions tested in earlier work where diketone was not generated in significant concentrations from LIX 63/Versatic 10 at 37 °C [21].

As for LIX 63/Versatic 10/nonyl-4PC loaded with a nitrate-based PLS at pH 4, only keto-oxime was formed in the absence of nonyl-4PC at pH 1.5 (Ex1.5-N-woPC). The increase in keto-oxime detected in Ex1.5-N-woPC, however, was much lower than in Ex4.0-N. When considered next to the lower reagent sum of 76% and lack of change in the diketone concentration, this suggests that loss of keto-oxime via carbon–carbon cleavage was slightly accelerated under pH 1.5 extract conditions. This presumably can be attributed to the acid-catalyzed Beckmann rearrangement of keto-oxime, and formation of 2-ethylhexyl amide and 2-ethylhexanoic acid [21], being favored at higher acidity.

Three conditions (presence of nonyl-4PC, metal loading, and low pH) appear to be required to cause both rapid hydroxyoxime loss as well as extensive diketone formation under nitrate-based extract conditions. It is currently unclear why these conditions should combine to result in these two observations, or if there is a connection between them. Nonyl-4PC is an organic base, and extraction of mineral acids into the organic phase at low pH is known to occur for other pyridine

carboxylates [32]. Perhaps generation of keto-oxime is promoted under metal-loaded extract conditions by formation of organic-phase pyridinium carboxylate nitrate. This would increase the concentration of nitric acid in the organic phase, which may then act as an oxidizing agent. Under strip conditions, keto-oxime generation is not favoured, and so formation of pyridinium carboxylate nitrate under these conditions may not be able to promote hydroxyoxime oxidation. Accelerated hydrolysis of keto-oxime to diketone, as well as a Beckmann rearrangement to secondary products, is then perhaps also accelerated by the presence of the organic base nonyl-4PC increasing the proton activity in the organic phase. That acyloin was not formed or consumed either with or without the presence of nonyl-4PC suggests that keto-oxime is more prone to hydrolysis than hydroxyoxime.

3.4. Effect of nonyl-4PC on cobalt poisoning of LIX 63

3.4.1 Poisoning as a function of standing time

Incomplete cobalt mass balances (about 30% of feed concentration) from the aqueous analyses during the course of all the stability studies under extract conditions suggested that cobalt poisoning was occurring over time. This occurred despite previous work suggesting that Versatic 10 would prevent this phenomenon [12]. Although cobalt poisoning has been reported for LIX 63/Versatic 10 previously [18], mass balances were still relatively high (80% of feed concentration) after 12 weeks when loaded below pH 6 and with organic-phase manganese below 1000 mg/L. In the current investigation, low cobalt recovery was calculated from organic phases in contact with either nitrate or sulfate aqueous phases, and even with low pH values and

minimal manganese loading. Hence, the cause of increased cobalt poisoning was suspected to be a result of organic-phase composition. The effect of both Versatic 10 concentration and the presence of nonyl-4PC on cobalt poisoning were therefore assessed by oxidation studies over time (as an indication of rate), as well as by sequential load–strip studies.

The presence of Versatic 10 at concentrations greater than a theoretical stoichiometric requirement of cobalt:Versatic 10 of 1:2 [7,33,34] had no effect on the rate of cobalt poisoning. The rate of cobalt poisoning of LIX 63 was considerably faster in the presence of nonyl-4PC than when nonyl-4PC was not present (Figure 7). The residual organic-phase cobalt concentration after 1 hour was approximately the same in all cases, averaging 0.05 mM cobalt. After 192 hours, however, there was 20 times the concentration of residual cobalt remaining in the organic phase containing nonyl-4PC (1.05 mM) than in the organic phase without nonyl-4PC (0.06 mM). Given the initial loading of 10 mM cobalt, this equated to a cobalt mass recovery from LIX 63/Versatic 10/nonyl-4PC of only 90% after 192 hours.

3.4.2 Poisoning as a function of load–strip cycles

Very low levels of residual irreversibly loaded cobalt were measured after only one hour in all cases during the timed studies. Given that an organic phase would not be left loaded for over an hour under commercially relevant conditions, a sequential load–strip experiment was carried out to determine the accumulation of cobalt over more relevant timeframes.

Cobalt progressively accumulated in the stripped organic phase after each load–strip cycle, both with and without nonyl-4PC present (Figure 8). After 10 cycles, 0.13 mM cobalt poisoned the

organic phase containing nonyl-4PC, compared with only 0.04 mM for the organic phase without nonyl-4PC. The plotted trend lines further suggested that in the presence of nonyl-4PC 0.008 mM of cobalt (0.08% of feed) poisoned the organic phase per load–strip cycle, whereas in the absence of nonyl-4PC, only 0.002 mg/L (0.02% of feed) of cobalt poisoned the organic per cycle. It is clear from this result that cobalt poisoning will be an important concern for the LIX 63/Versatic 10/nonyl-4PC system, and that any potential process should consider implementing a reductive strip bleed to allow full cobalt recovery and regeneration of hydroxyoxime. A reductive strip bleed stream will, however, increase the cost of a potential operation by adding an extra process unit. In addition, there is potential for increased reagent degradation, based on results from earlier work where some keto-oxime was formed during the reductive stripping of cobalt from LIX 63/Versatic 10 [18].

3.4.3 Possible cobalt poisoning mechanism

Cobalt poisoning of commercial solvent-extraction reagents occurs via oxidation of cobalt(II) to cobalt(III) in the organic phase [35–37]. It is widely believed that an initial tetragonal distortion of square planar cobalt(II) complexes is required, via binding of an organic base, to allow axial oxygen binding and subsequent oxidation of cobalt(II) to cobalt(III). In previous work, this mechanism was supported by using organic bases such as pyridine [38] or imidazole [39]. Nonyl-4PC (PC) potentially acts in a similar manner to these organic bases by allowing formation of a PC-Co(II)-O_2 complex, thereby facilitating cobalt poisoning.

Nonyl-4PC may alternatively promote cobalt poisoning by assisting in deprotonation of the hydroxyoxime (HL) and facilitating formation of the expected Co(III)L_3 complex that has been

suggested by previous authors [35,40]. This agrees with the supposition made by the present authors in a previous publication [13] that nonyl-4PC may enhance nickel extraction rates by acting as an organic base, helping to deprotonate the hydroxyoxime so it can preferentially orientate at the interface. This hypothesis is further supported by the observation that higher pH values, where oxime deprotonation will be favored, result in higher cobalt poisoning of LIX 63/Versatic 10 over time [18].

3.5. Stability of nonyl-4PC in LIX 63/Versatic 10/nonyl-4PC under strip conditions

3.5.1 Rates of nonyl-4PC loss

Based on previous work and work by other authors, loss of nonyl-4PC from low acidity sulfate-based strip solutions and under extract conditions was expected to be minimal. The effect of higher acidity and the effect of nitrate anions under strip conditions on nonyl-4PC stability, however, required investigation. The results for nonyl-4PC loss under strip conditions at pH 0.5 with varying levels of nitrate concentration are given in Table 9. The corresponding first-order reaction plots, along with the calculated SE values are shown in Figure 9. The straight lines and low SE values obtained supported a conclusion that nonyl-4PC was lost from LIX 63/Versatic 10/nonyl-4PC via a first-order reaction under strip conditions. Hence, half-lives calculated from the resulting slopes, along with their associated error values, were used to compare nonyl-4PC loss in each system.

No nonyl-4PC loss was detected from the pH 1 sulfate-based strip (St1.0-S_0) over 112 days (Table 9). Similarly, only minimal loss of nonyl-4PC was found under extract conditions. Nonyl-4PC loss under pH 0.5 sulfate-based strip conditions, however, was relatively rapid, resulting in half-lives between 21 and 27 weeks. Low nitrate concentrations in the sulfate-based aqueous strip solutions had no clear trending effect on nonyl-4PC stability at pH 0.5. The nonyl-4PC half-life doubled to 50 weeks on moving from a sulfate-only (St0.5-S_0) to nitrate-only strip (St0.5-N) at pH 0.5, despite the same starting pH value. In the case of nonyl-4PC, the only degradation product detected was nonanol (identified using GC analysis as 2,4,4-trimethyl hexanol by comparison with a reference sample under various operating conditions), suggesting that hydrolysis was the only mechanism for nonyl-4PC loss. As a result, the lower buffering capacity in the nitrate-only strip likely resulted in a more rapid pH increase over the course of the stability study, decreasing the rate of acid-catalyzed hydrolysis of nonyl-4PC.

3.5.2 Analysis of nonyl-4PC degradation product

The reagent sum accountability between nonyl-4PC and nonanol for the final day sample in each investigation is given in Table 10. In all cases, the reagent sum was greater than 90%, supporting hydrolysis to isonicotinic acid and nonanol (Figure 2) as the primary or only mechanism for degradation of nonyl-4PC under strip conditions, regardless of the presence of nitrate anions.

As with hydroxyoxime loss, degradation at pH 0.5 was generally rapid, and the obtained half-lives (23 to 27 weeks) would not be acceptable for a commercial operation. In contrast, there was no nonyl-4PC loss or nonanol generation noted at pH 1. Nonyl-4PC concentrations at pH 1.0 in sulfuric acid fluctuated in the range 98–102% of the original concentration and nonanol

fluctuated in the range 41–44 mM. In order to avoid hydrolysis of nonyl-4PC, it is recommended to maintain a stripping circuit with a pH at 1.0 or above for LIX 63/Versatic 10/nonyl-4PC.

4. Conclusions

The stability of LIX 63 and nonyl-4PC in an organic system comprising of LIX 63/Versatic 10/nonyl-4PC has been assessed under nitrate-based operating conditions. The presence of low concentrations of nitrate (0, 5, 10 g/L) in a sulfate-based strip at pH 0.5 and 40 °C had no clear adverse effect on the rate of hydroxyoxime degradation ($t_{1/2}$ of 38, 53, and 44 weeks, respectively), suggesting that low nitrate concentrations becoming entrained in the loaded strip liquor would not be a concern for a potential commercial application. In addition, the rate of hydroxyoxime loss from LIX 63/Versatic 10/nonyl-4PC under sulfate-based strip conditions at pH 1.0 with no nitrate anions and 40 °C ($t_{1/2}$ of 110 weeks) aligned with the outcome from previous work under similar conditions using just LIX 63/Versatic 10. Hence, it is concluded that neither the presence of nitrate nor nonyl-4PC had an effect on the rate of hydroxyoxime loss under sulfate-based strip conditions.

The rates of hydroxyoxime degradation for co-extraction of nickel and cobalt were the same for nitrate-based extract conditions at pH 4.0 ($t_{1/2}$ of 35 weeks) and sulfate-based extract conditions at pH 6.0 ($t_{1/2}$ of 34 weeks). When compared with previously published work, there was also no difference in the rate of degradation between systems with and without nonyl-4PC under either aqueous-free conditions or for sulfate-based extract conditions. Commercial application of LIX

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63/Versatic 10/nonyl-4PC to a nitrate-based PLS for co-extraction of nickel and cobalt at pH 4, therefore, appears prospective.

Under the nitrate-based extract conditions at pH 1.5 required for nickel–cobalt separation there was rapid degradation of hydroxyoxime (complete loss in 4 weeks) and concurrent formation of diketone. Hydroxyoxime stability was similar between LIX 63/Versatic 10 loaded from a nitrate-based aqueous at pH 1.5 ($t_{1/2}$ of 36 weeks) and LIX 63/Versatic 10/nonyl-4PC loaded from a nitrate-based aqueous at pH 4.0 ($t_{1/2}$ of 35 weeks). It therefore appeared that the following three conditions combined to cause both rapid hydroxyoxime degradation and extensive diketone formation: the presence of nonyl-4PC, metal loading, and low operating pH (1.5 pH units). A process for selective extraction of nickel from cobalt in a nitrate matrix using LIX 63/Versatic 10/nonyl-4PC does not, therefore, appear viable. If LIX 63/Versatic 10 is to be considered further for the separation of nickel from cobalt in concentrated nitrate matrices, then nickel accelerators other than nonyl-4PC must be investigated.

An investigation into the effect of Versatic 10 concentrations and the presence of nonyl-4PC on cobalt poisoning of LIX 63 found that Versatic 10 concentrations above stoichiometric requirements did not affect the extent of cobalt poisoning. The presence of nonyl-4PC, however, was found to dramatically accelerate the rate of cobalt poisoning, to a point where a reductive strip bleed stream would have to be considered if LIX 63/Versatic 10/nonyl-4PC were to be used for the extraction of cobalt.

Nonyl-4PC in LIX 63/Versatic 10/nonyl-4PC was stable in a sulfuric acid strip solution at pH 1.0. In contrast, at pH 0.5, nonyl-4PC loss via hydrolysis to nonanol was rapid, with half-lives of

21–27 weeks. Low concentrations of nitrate had no clear adverse effect on the rate of nonyl-4PC loss. If a strip pH of 1 or above were maintained, low nonyl-4PC degradation could be expected from a sulfate-based strip circuit with low concentrations of entrained nitrate.

Acknowledgements

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Figure 1: Active *anti*-hydroxyoxime and primary degradation products. R1 = 1-ethylpentyl.
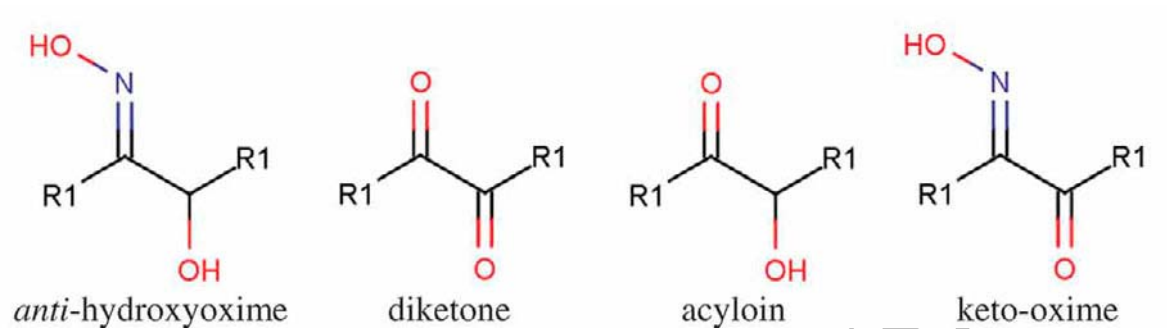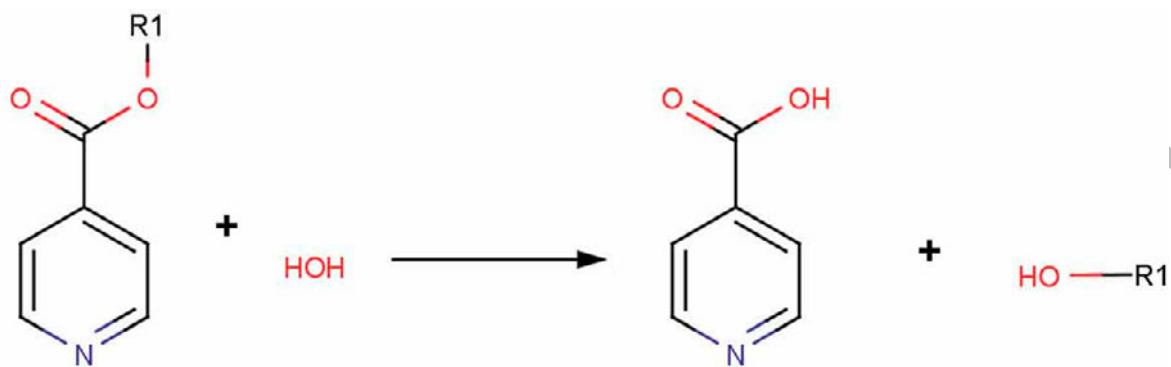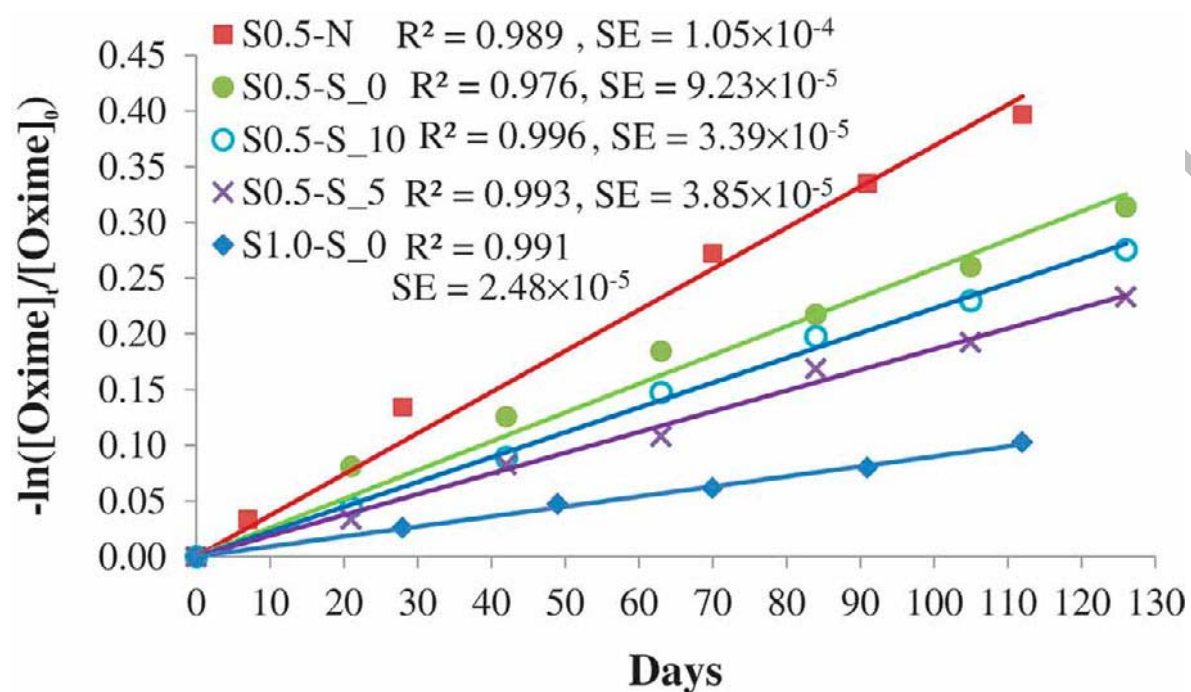
Adapted from previous work.[14,20,21]

Figure 2: Degradation of alkyl-4-pyridine carboxylate to isonicotinic acid and the corresponding alcohol.
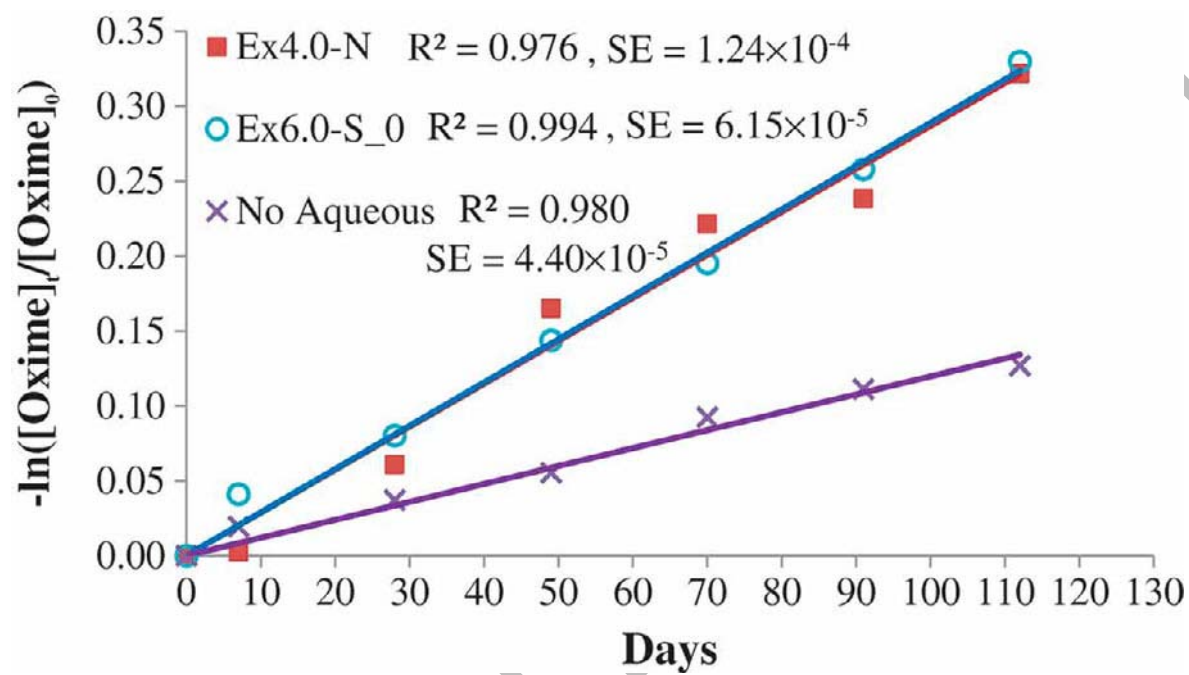
Figure 3: First-order reaction plots for hydroxyoxime loss over time under strip conditions at 40 °C with varying nitrate concentrations. R^2 and standard error (SE) included on plot.

Figure 4: First-order reaction plots for hydroxyoxime loss at 40 °C under both nitrate (pH 4.0) and sulphate (pH 6.0) conditions with an aqueous free sample for comparison with earlier work. Trend-lines for Ex4.0-N and Ex6.0-S_0 obscure each other. R^2 and standard error (SE) included on plot.

Figure 5: Diketone and keto-oxime concentrations under low pH extract conditions for nickel–cobalt separation (Ex1.5-N) over time at 40 °C.
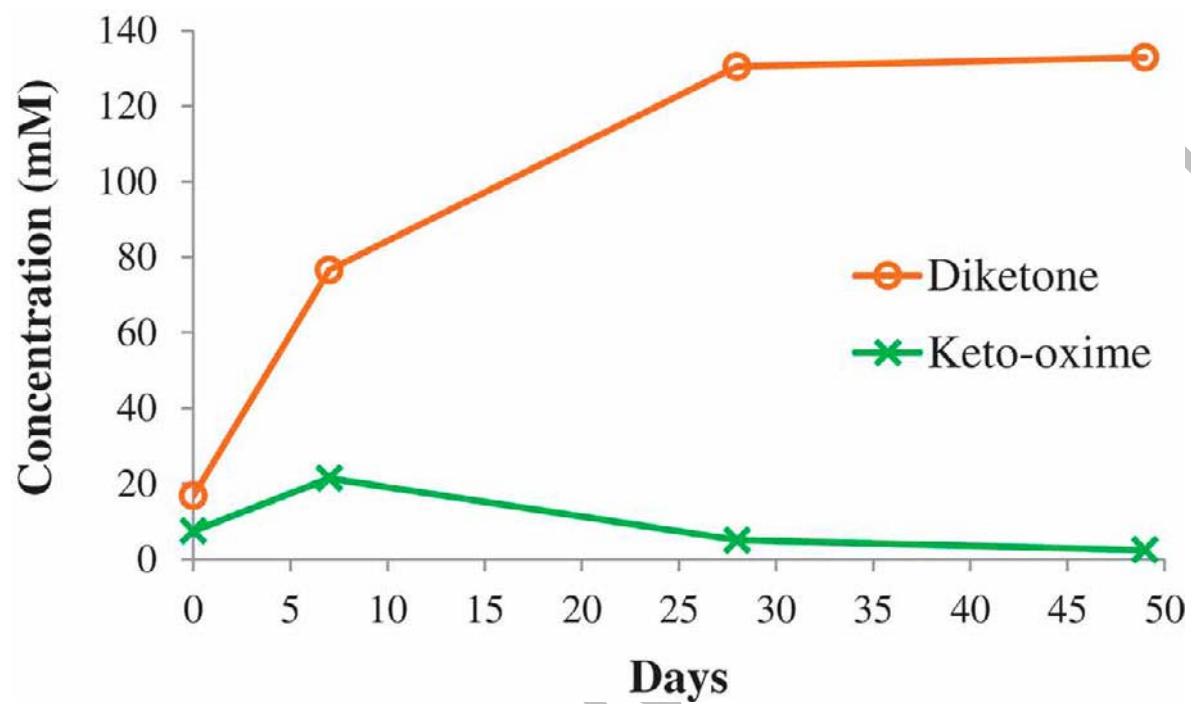
Figure 6: First-order reaction plots comparing hydroxyoxime loss at 40 °C under nitrate-based extract conditions (pH 1.5 without nonyl-4PC and 4.0 with nonyl-4PC) and sulphate-based extract conditions (pH 6.0 with nonyl-4PC). Trend-lines for Ex4.0-N and Ex6.0-S_0 obscure each other. R^2 and standard error (SE) included on plot.
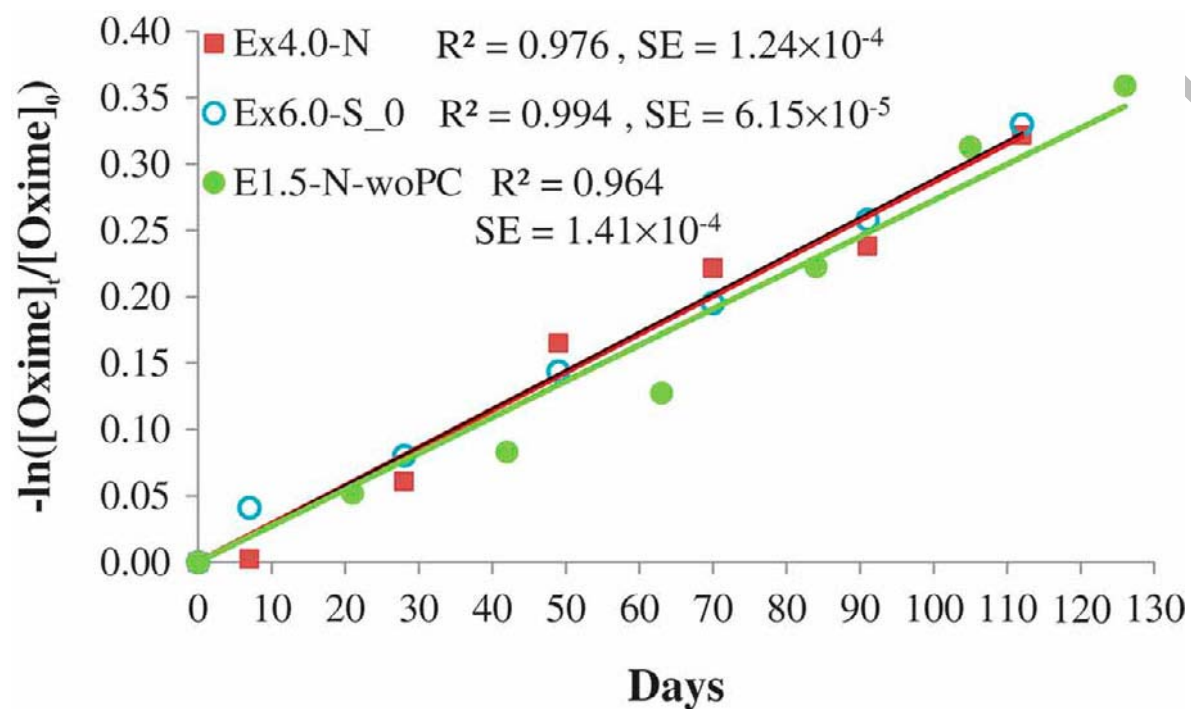
Figure 7: Effect of Versatic 10 concentration and presence of nonyl-4PC on irreversibly loaded cobalt concentration for LIX 63/Versatic 10 with or without nonyl-4PC loaded at pH 5.5 and 23 °C at A:O of 1:1.
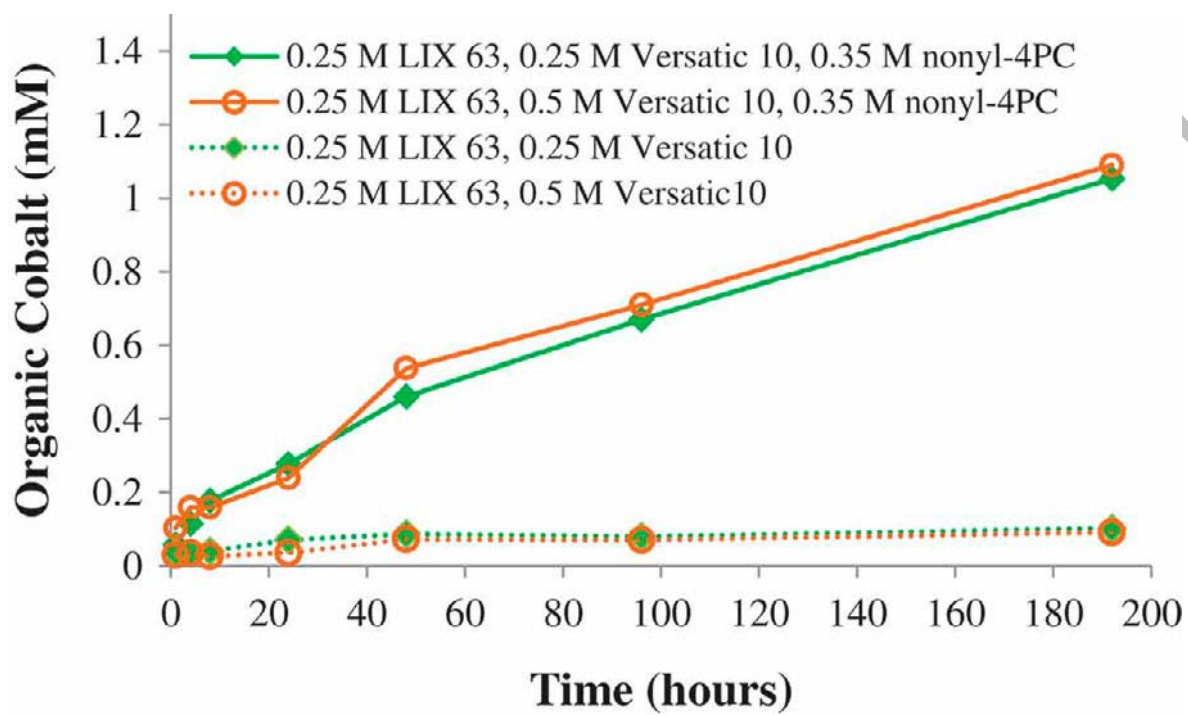
Figure 8: Organic-phase cobalt concentrations in the stripped organic (SO) after sequential load-strip cycles for LIX 63/Versatic 10 with and without nonyl-4PC loaded at pH 5.5 and 23 °C and stripped using 50 g/L sulphuric acid at 50 °C.
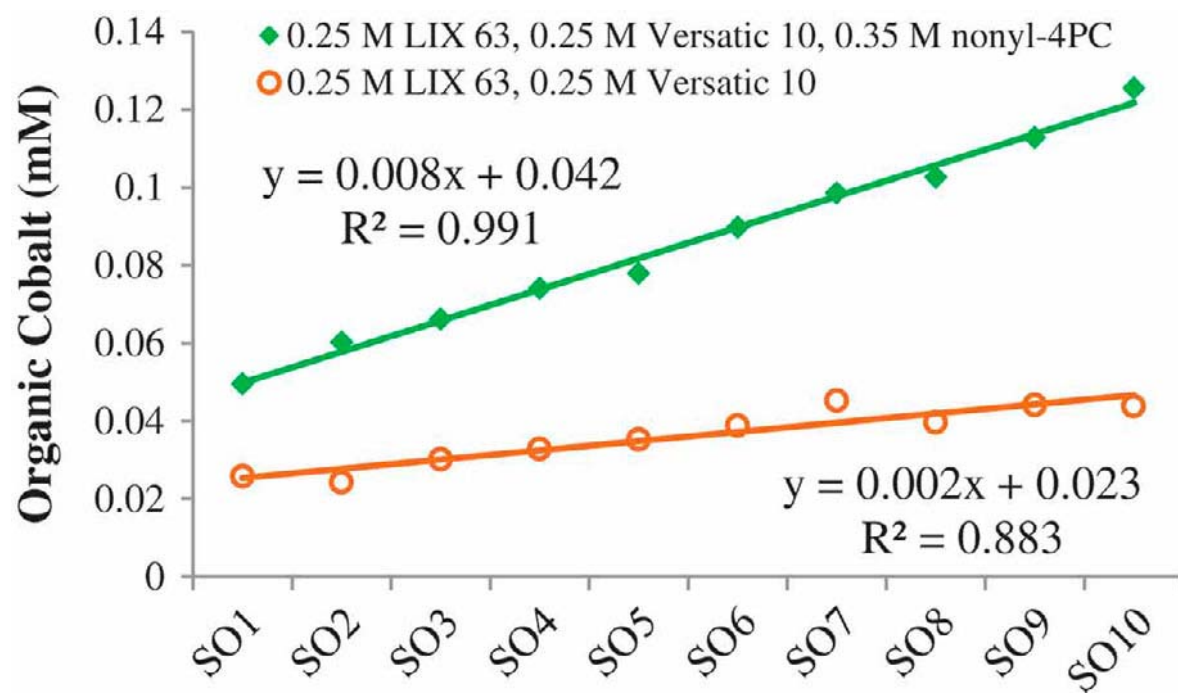
Figure 9: First-order reaction plots for nonyl-4PC loss over time at 40 °C under strip conditions with varying nitrate concentrations at pH 0.5. R^2 and standard error (SE) included on plot.
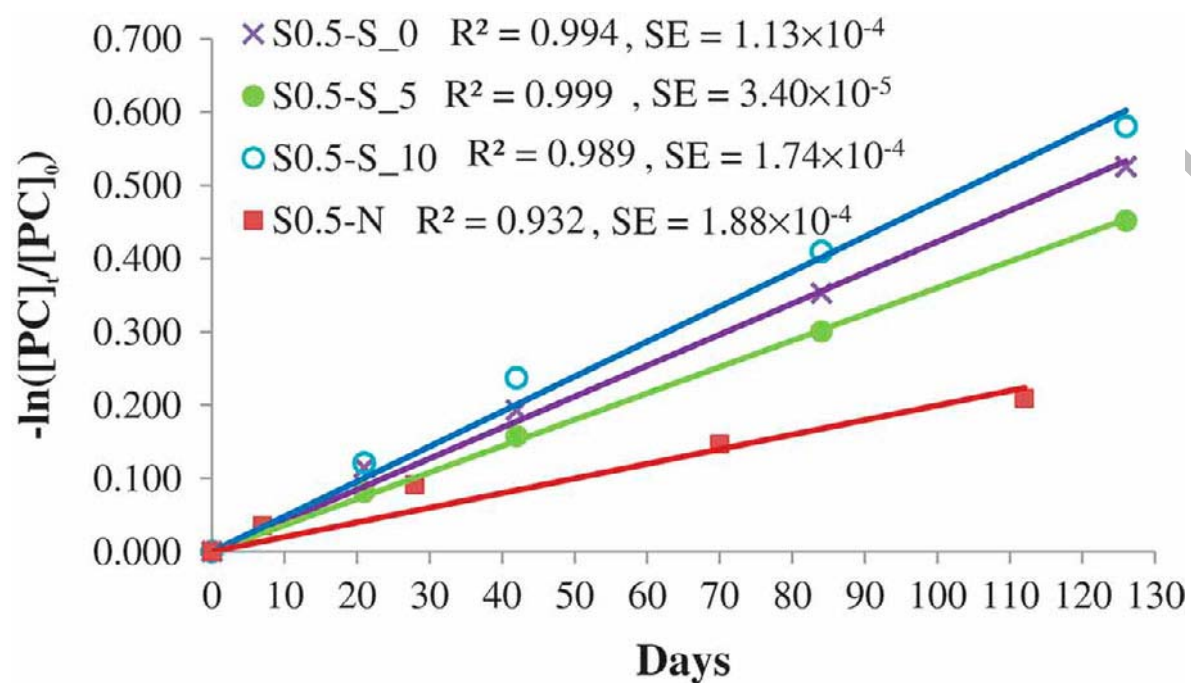
Table 1: Metal concentrations (mg/L) of the three feed samples used for stability studies under extract conditions.

	High Al	Low Al	Sulphate
Aluminium	438	58	9.1
Calcium	1875	1905	413
Cobalt	179	177	244
Chromium	5.6	5.5	8.7
Iron	2.9	0.3	2.7
Magnesium	86066	86286	37886
Manganese	604	599	1857
Nickel	4675	4518	5695
Zinc	46	39	144

| Copper | 8.8 | 1.6 | 16 |

Table 2: Experimental conditions for stability experiments on 0.25 M LIX 63/0.25 M Versatic 10/0.36 M nonyl-4PC.

Experiment Code[*]	Start pH	Aqueous Phase	Organic Phase
Ex1.5-N	1.93	High Al (raffinate)	Load at pH 1.5 A:O = 2:1
Ex1.5-N-woPC	1.50	High Al (raffinate)	Load at pH 1.5 A:O = 2:1 (no nonyl-4PC)
Ex4.0-N	4.87	Low Al (raffinate)	Load at pH 4 A:O = 1
Ex6.0-S_0	5.79	Sulphate (raffinate)	Load at pH 6 A:O = 1
St1.0-S_0	0.87	60 g/L Ni as SO_4^{2-}, H_2SO_4	Fresh Organic
St0.5-S_0	0.50	30 g/L Ni, 0 g/L NO_3^-, H_2SO_4	Fresh Organic
St0.5-S_5	0.50	30 g/L Ni, 5 g/L NO_3^-, H_2SO_4	Fresh Organic

St0.5-S_10	0.50	30 g/L Ni, 10 g/L NO_3^-, H_2SO_4	Fresh Organic
St0.5-N	0.50	30 g/L Ni as NO_3^-, HNO_3	Fresh Organic

* ExX = Extract at pH X, StX = Strip at pH X, N = nitrate-based, S_Y = sulphate based with Y

g/L nitrate, woPC = without nonyl-4PC

Table 3: Aqueous-phase pH, hydroxyoxime concentration as a percentage of the day 0 values, and hydroxyoxime half-lives under strip conditions at 40 °C.

Experimental Code	Start pH	Final pH	Day						$t_{\frac{1}{2}}$ weeks	Error* weeks
			21	42	63	84	105	126		
St0.5-S_0	0.50	0.53	92	88	83	80	77	73	38	0.9
St0.5-S_5	0.50	0.57	97	92	90	84	83	79	53	1.8
St0.5-S_10	0.50	0.63	96	91	86	82	79	76	44	1.2
			7	28	49	70	91	112		
St1.0-S_0	0.87	0.98	98	96	95	93	91	89	110	8.8
St0.5-N	0.50	0.63	93	87	80	74	67	61	27	0.6

* Error – the change in half-life assuming a decrease in the measured final day LIX 63 concentration of 2%

Table 4: Reagent sum and accountability for hydroxyoxime and primary degradation products between fresh (day 0) organic and final-day samples for stability studies under strip conditions.

Experiment Code	Hydroxyoxime	Diketone	Keto-oxime	Acyloin	Reagent Sum	
	mM	mM	mM	mM	mM	%
Fresh Organic	246	17	9	6	278	100
St0.5-S_0	180	20	9	44	253	91
St0.5-S_5	195	19	9	28	251	90
St0.5-S_10	187	17	10	25	239	86
St0.5_N	165	23	10	37	235	85
St1.0-S_0	222	13	11	14	260	94

Table 5: Aqueous-phase pH, hydroxyoxime concentration as a percentage of the day 0 values, and hydroxyoxime half-lives under extract conditions at 40 °C.

Experiment Code	Start pH	Final pH	Day						t½	Error*
			7	28	49	70	91	112	weeks	weeks
Ex4.0-N	4.87	3.89	100	94	85	80	79	72	35	0.9
Ex6.0-S_0	5.79	5.69	96	92	87	82	77	72	34	0.9
Ex1.5-N	1.93	2.00	23	Not detected					N/A	N/A
No Aqueous	N/A	N/A	98	96	95	91	89	88	83	5.1

* Error − the change in half-life assuming a decrease in the measured final day LIX 63 concentration of 2%

N/A – Not applicable, no aqueous phase used or not enough data to calculate

Table 6: Comparison of hydroxyoxime half-lives in LIX 63/Versatic 10 under comparable extract conditions.

Aqueous Matrix	Organic Metal mg/L			Tested Temp °C	$t_{\frac{1}{2}}$ weeks	$t_{\frac{1}{2}}$ at 40 °C weeks	Reference
	Co	Cu	Mn				
No Aqueous	N/A	N/A	N/A	40	76	76	[17]
No Aqueous †	N/A	N/A	N/A	40	88	83	This work
Sulphate pH 4.5	570	3	190	30	67	34	[18]
Sulphate * pH 5.5	270	190	140	37	47	36	[19]
Sulphate † pH 6.0	178	18	8	40	34	34	This work

| Nitrate† pH 4.0 | 155 | 9 | 5 | 40 | 35 | 35 | This work |

N/A = not applicable – no aqueous phase, † Organic phase contains nonyl-4PC, * Organic phase contains TBP

Table 7: Reagent sum and accountability for hydroxyoxime and primary degradation products between fresh (day 0) organic and final day samples for stability studies under extract condtions.

Experiment Code	Hydroxyoxime	Diketone	Keto-oxime	Acyloin	Reagent Sum	
	mM	mM	mM	mM	mM	%
Fresh Organic	246	17	9	6	278	100
Ex4.0-N	178	18	34	4	234	84
Ex6.0-S_0	177	19	29	4	229	82
Ex1.5-N	Not detected	133	2	4	139	50
No Aqueous	217	14	13	7	251	90

Table 8: Concentrations (mM) for hydroxyoxime and its primary degradation products from LIX 63/Versatic 10 loaded at pH 1.5 from a nitrate-based PLS (Ex1.5-N-woPC) with comparisons to LIX 63/Versatic 10/nonyl-4PC loaded at pH 1.5 and pH 4.

Experiment Code	Hydroxyoxime	Diketone	Keto-oxime	Acyloin	Reagent Sum	
	mM	mM	mM	mM	mM	%
Fresh Organic	246	17	9	6	278	100
Ex4.0-N	178	18	34	4	234	84
Ex1.5-N	0	133	2	4	139	50
Ex1.5-N-woPC	172	17	17	6	212	76

Table 9: Aqueous-phase pH, nonyl-4PC concentration as a percentage of the day 0 values, and calculated nonyl-4PC half-lives under strip conditions at 40 °C.

Experiment Code	Start pH	Final pH	Day				$t^{1/2}$ weeks	Error* weeks
			21	**42**	**84**	**126**		
St0.5-S_0	0.50	0.53	89	82	70	59	23	1.0
St0.5-S_5	0.50	0.57	92	85	74	64	27	1.0
St0.5-S_10	0.50	0.63	89	79	66	56	21	0.4
			7	**28**	**70**	**112**		
St0.5-N	0.50	0.63	97	91	86	81	50	3
St1.0-S_0	0.87	0.97	102	100	100	98	N/A	N/A

* Error – the change in half-life assuming a decrease in the measured final day nonyl-4PC concentration of 2%

N/A – not applicable, no degradation measured

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Table 10: Reagent sum and accountability for nonyl-4PC and nonanol between fresh (day 0) organic and final-day samples for stability studies under strip conditions.

Experiment Code	Nonyl-4PC	Nonanol	Reagent Sum	
	mM	mM	mM	%
Fresh Organic	360	46	406	100
St0.5-S_0	213	181	394	97
St0.5-S_5	229	161	390	96
St0.5-S_10	201	175	377	93
St0.5-N	292	82	374	92
St1.0-S_0	352	43	395	97