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Effect of iron(II) and manganese(II) on oxidation and co-precipitation of cobalt(II) in ammonia/ammonium carbonate solutions during aeration - An update and insight to cobalt losses in the Caron process for laterite ores

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Abstract

The Caron process involves the roasting of nickel laterite ore at 750°C with fuel oil to produce a calcine containing Fe-Ni-Co alloy and other reacted or unreacted host minerals. The leaching of the calcine in the form of a quenched slurry in ammonia/ammonium carbonate solutions at pH ~10 and 45°C under anaerobic and aerobic conditions sequentially dissolves alloy to iron(II), nickel(II) and cobalt(II), oxidizes iron(II), precipitates iron(III) and allows the discard of iron rich tailings after counter current decantation and steam stripping of ammonia and carbon dioxide for recycling. Oxidation of aqueous cobalt(II) during aeration in the Caron Process is one of the critical steps to reduce the incorporation of cobalt into the tailings. Cobalt(II) species which are co-precipitated with the iron phase are not able to be leached back into solution and lost to the tailings, but cobalt(III) remains in solution. Fast oxidation of cobalt(II) to cobalt(III) is expected to minimise the co-precipitation of cobalt(II) during iron precipitation, resulting in smaller losses of cobalt to tailings. Results from this study show that the oxidation of cobalt(II) species (1 g L⁻¹) in a synthetic ammonium carbonate (SAC) solution containing 5.3 M NH₃/NH₄⁺ (total) and 1.5 M HCO₃⁻ is relatively slow at room temperature and follows first order kinetics with respect to cobalt(II) concentration. The rate of reaction is temperature dependent with an activation energy of 65.8 kJ mol⁻¹. The presence of manganese(II) and iron(II) increases the rate of oxidation of cobalt(II) when compared to that of cobalt(II) alone. The oxidation of cobalt(II) occurs only after most of iron(II) is oxidised to iron(III) solids which facilitates the co-precipitation of cobalt(II). The variation of the concentration of manganese(II) (0.025-1.25 g L⁻¹) in SAC solution demonstrates minimal effect on cobalt oxidation. Analysis of the solids, using XRD, show that the final solid formed in the laboratory test by the aeration of iron(II) in SAC solution consisted of goethite and ferrihydrite and that formed by the aeration of manganese(II) in SAC solution was rhodochrosite (MnCO₃). While the iron oxide precipitated during the oxidation of Fe(II)+Co(II) for 1 h in the laboratory test contains 0.38% Co, the solids formed in aerated tanks in the Caron processing plant increases from 0.15% in Tank 1 to 0.17% in Tank 4, but in all cases too low to be detected in XRD scans.

Keywords: Laterite; Caron process; ammoniacal carbonate leaching; oxidation & precipitation; Fe-Co-Co-Mn; Co-precipitation of Co(II)
1 Introduction

Laterite ores of low grade nickel and cobalt account for 70% of the world’s nickel reserves, but 60% of the world’s current nickel production originates from sulfide ores (Xavier and Ciminelli, 2008). Butt and Cluzel cite up to over 50% nickel and cobalt from laterite ores in 2010 and 60% by 2014 (Butt and Cluzel, 2013). Despite the total estimated value of cobalt consumed in 2016 worth $250 million in the United States alone, global cobalt mine production decreased in 2016, because of lower production from nickel operations. Growth in world refined cobalt supply is expected to be driven mainly by strong growth in the aerospace and rechargeable battery industries, for example, with the increased use of nickel-cobalt-manganese in lithium-ion batteries. In 2016 China was the world’s leading consumer of cobalt, with nearly 80% consumed by the rechargeable battery industry (US Geological Survey, 2017). These facts highlight the importance of improved recovery and efficiency of nickel and cobalt production from lateritic and other low-grade ores.

The use of ammonia/ammonium carbonate solutions for the extraction of nickel and cobalt from laterite ores using the roast-leach process is well documented (Caron, 1950) and practised in Nicaro and Punta-Gorda (Cuba), Yabulu (Australia) and Companhia Niquel Tatantins (Brazil) at present or in the past (Xavier and Ciminelli, 2008). The reduction roasting step at 750°C with fuel oil is necessary to transform serpentine to olivine and goethite to ferronickel alloy at very low oxygen partial pressures ($pO_2 \sim 10^{-15}$ Pa) as shown by reactions in Eqs. 1-3 (Rhamdhani et al., 2009a,b). Depending on the starting laterite ore, the calcine (~43 µm) is coarser than the feed (~21 µm); (particle sizes quoted are average $P_{80}$ values and are relevant to the Yabulu refinery) (Rhamdhani et al., 2009a,b); it consists of a mixture of α-Fe, Ni$_x$Fe$_{(1-x)}$, FeO, NiO, Fe$_3$O$_4$, NiFe$_2$O$_4$ or (Fe,Ni)$_3$O$_4$ with Fe-Ni alloy nanoparticles (taenite, 15-20 nm) interspersed in porous magnetite (Canterford, 1978; De Graaf, 1979, 1980; Richardson et al, 1981; Chander and Sharma, 1981). The majority of iron forms Fe$_3$O$_4$ during roasting with about 20% of iron reduced to the alloy (Fittoc, 2007).

$$2(Mg,Fe,Ni)_3Si_2O_5(OH)_4 \rightarrow 3(Mg,Fe,Ni)_2SiO_4 + SiO_2 + 4H_2O(g)$$ (1)

$$6(Fe,Ni)O.OH \rightarrow 2(Fe,Ni)_3O_4 + 3H_2O(g) + 0.5O_2(g)$$ (2)

$$(Fe,Ni)_3O_4 \rightarrow 3(Ni,Fe)_{alloy} + 2O_2(g)$$ (3)
The Fe-Ni-Co alloy in the calcine is leached using NH$_3$/NH$_4^+$/$\text{HCO}_3^-$ solutions at pH ~10 and 45°C, first in an anaerobic environment to avoid oxidation of the alloy formed in the roasting step during quenching, which may lead to the passivation of the alloy and retard leaching. In the absence of oxygen in the quench tank, iron dissolves as Fe(NH$_3$)$_4^{2+}$. The subsequent aerobic treatment in the integrated leaching train (Fig. 1a) oxidises iron(II) to iron(III) and leaches nickel and cobalt which initially dissolve as ammine complexes of Ni(II) and Co(II). The solids containing unleached material and precipitated Fe(III) oxide(s) are separated by counter current decantation (CCD) and the tailings from the final thickener underflow are discarded (Fig. 1a) after steam stripping to recover NH$_3$ and CO$_2$ (Richardson et al., 1981; Reid and Fittock, 2004; Fittock, 2007).

Depending upon the composition of laterite feed, typical composition of the recycled Caron leach liquors at 45°C has been reported as: 5.3 M NH$_3$/NH$_4^+$ (total), 1.0 M HCO$_3^-$, 150 mM Ni (8.8 g L$^{-1}$), 12 mM Co (0.7 g L$^{-1}$), 22 mM S$_2$O$_3^{2-}$, 0.8-1.6 mM Cu (0.05-0.10 g L$^{-1}$) as well as SO$_4^{2-}$ and ions of other metals: Fe, Mn and Mg (Nicol et al., 2004). Whilst the leaching of nickel and cobalt in the quench circuit is 40-60% with an increase in dissolved iron concentration in solution by 10-20%, further leaching occurs in aerobic leach and CCD circuits shown in Fig. 1a (Nicol et al., 2004). Relevant reactions for leaching, supported by electrochemical studies, have been reported previously (Senaputra et al., 2008; Senanayake et al., 2010).

The actual composition of laterite ores is complex and variable. This variation influences the process used and final recovery of product. The Caron plant in Australia at Yabulu, Queensland treated a mixture of limonitic (~70%) and saprolitic (~30%) ores. Average analysis of an ore imported into Australia for the Yabulu plant is given in Table 1. Because of the different optimum conditions required for roasting saprolite and limonite, the nickel recoveries from the calcine of limonitic components are higher than that from saprolitic components.

The recovery and recycling of ammonia and carbon dioxide, which are the two main reagents in the process, is an economic benefit against the cost of reductive roasting (Table 2). However, the recovery of nickel and cobalt has been relatively low. In particular, the recovery of cobalt has historically been 35-40% and nickel 75–85% at the Yabulu refinery (Reid and Fittock, 2004). Low recovery of nickel and cobalt has not only resulted in a significant loss in revenue but possible future environmental problems due to the disposal of tailings containing heavy metals (Tables 1, 2). It is
important to understand and minimise losses to improve recovery and be competitive to meet market demand for these metals. The main objective of this study is to present an update and insight into nickel and cobalt losses in the Caron process and present the results of a study on the effect of Fe(II) and Mn(II) on the oxidation of Co(II) in SAC solutions and the characterisation of solids to examine the co-precipitation of Co(II) during aeration.

2. Nickel and cobalt losses: Status of understanding

Previous studies have related the low metal recovery in the Caron process to the unreduced Ni-Co oxides entrapped in magnetite and forsterite (Fe$_3$O$_4$ and Mg$_2$SiO$_4$), depending on the mineralogy and roasting temperature (De Graff, 1979, 1980; Richardson et al., 1981; Rhamdhani et al., 2009a,b) as well as the formation of nickel sulfides during roasting due to the sulfur content in fuel oil (Bhuntumkomol et al., 1980, 1982; Senaputra et al., 2008). Further bench scale studies with different feed material (pure nickel, ferronickel and roasted calcines) in a typical Caron lixiviant system showed similar behaviour with 70-90% Ni extracted depending on the mole fraction of nickel in the feed. The rate of nickel dissolution from particles are of the same order as that from flat surfaces based on electrochemical data: $\sim 10^{-4}$ mol m$^{-2}$ s$^{-1}$ (Senanayake et al., 2010). The rate of iron dissolution is slow even at the beginning, with about 10% leached as Fe(II) after 30 min but less than 2% leached at 2 h due to oxidation and precipitation of Fe(III) oxides/hydroxides. Incomplete dissolution of nickel is a result of surface blockage by M(OH)$_3$, MOOH or MFe$_2$O$_4$ causing passivation, a view supported by: (i) the solid species identified at the measured current-potential peak positions, (ii) shrinking core kinetic model and (iii) thermodynamic predictions.

In other studies, focussing more on the cobalt losses, modifications made to the original Caron process established at the Yabulu refinery have achieved a recovery of cobalt around 55% and sometimes better (Reid and Fittock, 2004; King, 2005). The loss of cobalt from solution occurs during both the aeration stage of leaching and the anaerobic phase of the counter-current decantation process. Factors that contribute to the low cobalt recovery include:

i. co-precipitation of cobalt(II) with iron species during the aerated leach, as in the case of nickel(II) described earlier (Senanayake et al., 2010),
ii. adsorption of cobalt on solids, largely precipitated iron compounds (Caron, 1950; Roach, 1977; Osseo-Asare and Fuerstenau, 1978; Osseo-Asare and Fuerstenau, 1979; De Graaf, 1979; Osseo-Asare and Fuerstenau, 1980; Han and Fuerstenau, 2003; Narita and Lawson, 1982; Fuerstenau and Osseo-Asare, 1987), and

iii. passivation during the leaching stage (Kim et al., 1991; Kho et al., 1992; Nikoloski and Nicol, 2006; D’Aloya and Nikoloski, 2013).

Thermodynamic and electrochemical studies on Fe-Ni-Co-NH$_3$ system at 25-60°C show that high temperatures closer to 60°C reduces the stability fields of ammine complexes, but maintaining reducing conditions during the initial leaching stages may help minimise the effect of alloy passivation and cobalt losses by enabling iron dissolution, as in the quenching stage (Asselin, 2008).--Based on significant differences in adsorption capacity between various iron oxide phases, ferrihydrite being the primary phase, the material present in the residue will make a significant difference in cobalt losses due to adsorption of cobalt solution species on the precipitated iron oxide phase (Dyer et al., 2012). Tests, based on the analytical procedure described in Section 3, that have been carried out at the Yabulu Refinery have shown that 70-80% of the cobalt present in the solution entering the first aerator in the train is in the form of cobalt(II) (Benjamin and Fittock, 2003; Anderson and Fittock, 2004). If cobalt(II) is co-precipitated with iron it is not recoverable under the leaching conditions used in the Caron Process (McCulloch and Fittock, 2006). This view is supported by the calculated values of equilibrium constants for the reactions in Eqs. 4 and 5 (Senanayake et al., 2010) which show that the dissolution of M(II) from MFe$_2$O$_4$ for M=Co is possible only in the presence of a reducing agent such as SO$_3^{2-}$ ions. For example, the small value of log K = -7.5 for Eq. 4 without sulfite ions changes to a large value of log K = 24.4 for Eq. 5 with sulfite ions, where the role of sulfite is to reduce Fe(III) of MFe$_2$O$_4$ (MO.Fe$_2$O$_3$) to Fe(II) in Fe$_3$O$_4$. The potential-pH diagrams of Fe-Co-Mn-H$_2$O system at 25°C also show CoFe$_2$O$_4$ as the predominant species at pH 10 and Eh ~ -0.2 and over a wide Eh range, whilst Fe$_3$O$_4$ is stable only at low Eh < -0.4 V in Ni-Fe-Mn-H$_2$O system (Senanayake, 2011). It has been shown, with varying degrees of success, that the presence of sulfite improves the recovery of cobalt during the processing in the Yabulu refinery, but increased recovery that has been demonstrated due to the addition of sulfite is not economical (Bare and Horst, 1960; Clark, 2005; Clark et al., 2007). This led to a suggested modification of the flow of slurry from the quench tank into the aerator train in the plant as a possible means to decrease the amount of cobalt(II) in the early stages of aeration. The proposal was to change the first two sequential aeration
tanks into a parallel configuration which both receive slurry from the anaerobic leach tank directly as shown in Fig 1b (Benjamin and Fittock, 2003). This would enable an increase in the rate of oxidation of cobalt(II) to cobalt(III), thus decreasing the loss of cobalt due to co-precipitation, but the outcome has not been reported.

\[
\begin{align*}
MFe_2O_4 + Fe(NH_3)_4^{2+} + 2NH_3 & \rightarrow M(NH_3)_6^{2+} + Fe_2O_4 \\
(\text{at } 45^\circ C \log K \text{ for Eq. (4)} & = -7.5 \text{ (M=Co), 3.4 (M=Ni)})
\end{align*}
\]

\[
3MFe_2O_4 + 6NH_3^+ + 12NH_3 + SO_3^{2-} \rightarrow 3M(NH_3)_4^{2+} + 2Fe_2O_4 + SO_4^{2-} + 3H_2O
\]

(at 45°C log K for Eq. (5) = 24.4 (M=Co), 2.8 (M=Ni))

The complexity and varying nature of the problem experienced in the Yabulu refinery can be illustrated by the change in amount of cobalt present in solids at different points in the circuit. One such set of results is shown in Fig. 2 (Benjamin, 2002), which shows the cobalt grade of solids washed with fresh Leach Liquor (FLL) and dried before analysis. Numerous similar surveys have been completed (Fittock, private communication) and it has been shown that there are differences in the amounts of cobalt present at different stages. The variation would be most commonly attributed to differences of sources and types of ore (Benjamin, 2002). For example, the cobalt grade in the plant solids shown in Table 1 and Fig. 2 vary from 0.15% (ore) to 0.26% (roasted ore), 0.15-0.17% (aerators) and 0.06% (tailings). The Quench Liquor (QL) which is added to the hot calcine in the quench tank, is taken from the overflow of Thickeners 1 and 2 and has variable composition with the following typical averages: ~10 g L\(^{-1}\) Ni, ~0.8 g L\(^{-1}\) Co, 95 g L\(^{-1}\) NH\(_3\), 60 g L\(^{-1}\) CO\(_2\) along with other metal ion species. The consensus from Fig. 2 is that cobalt leached in the quenched slurry can precipitate in the aerators as shown by the increase in cobalt grade of solids from 0.15 (A1) to 0.17% (A4), but subsequently leached in the thickeners in the CCD circuit as shown by the decrease in cobalt grade from 0.17 (A4) to 0.06% (T7), as noted earlier (Nicol et al., 2004).

The relative rate of oxidation of iron(II) and cobalt(II) species in SAC solution is an important factor to be considered in the minimisation of the loss of cobalt due to co-precipitation in the aerators. The presence of other ions such as Mn(II) may influence this oxidation. The Potential-pH (Eh-pH) diagrams which also represent the ORP (oxidation reduction potential) at different temperatures closer to the Caron conditions and standard reduction potentials in Eqs. 6-7 presented in previous studies have shown a range of ammine complexes such as Co(NH\(_3\))\(_5\)^{2+}, Mn(NH\(_3\))\(_4\)^{2+} and Fe(NH\(_3\))\(_4\)^{3+}, as well as solids
such as Co(OH)$_2$, Co(OH)$_3$, Fe(OH)$_3$, CoOOH, and MnOOH (Queneau, 1986; Benjamin, 2003; Nikoloski et al., 2005; Senaputra et al. 2008; Asselin, 2008; Senanayake et al., 2010; Senanayake, 2011, Senanayake et al., 2017). The oxidation of cobalt(II) pentammine complex to cobalt(III) hexammine complex occurs in the potential range 0.15-0.22 V, which can be achieved by aeration, as $E^\circ$ for Eq. 8 is higher than those for Eqs. 6 and 7.

$$\text{Co(NH}_3\text{)}^3_6+ e^- \rightarrow \text{Co(NH}_3\text{)}^2_6+ (E^\circ = 0.17 \text{ V at 25}^\circ\text{C})$$

$$\text{Co(NH}_3\text{)}^3_6+ e^- \rightarrow \text{Co(NH}_3\text{)}^2_5 + \text{NH}_3 (E^\circ = 0.16 \text{ V at 25}^\circ\text{C})$$

$$\text{O}_2 + 4\text{NH}_4^+ + 4e^- \rightarrow 2\text{H}_2\text{O} + 4\text{NH}_3 (E^\circ = 0.73 \text{ V at 25}^\circ\text{C})$$

The above discussion highlights the need for a systematic study on the oxidation of cobalt(II) in SAC solution under different conditions and in the presence of Fe(II) and Mn(II) species (with and without the presence of sulfite and thiosulfate) and the characterisation of the precipitated solids. The main objective of this study is to examine the relative rates of oxidation of Co(II), Fe(II) and Mn(II) during the aeration step in the Caron refining process. As cobalt is often closely associated with iron and manganese in the laterite ore (Table 1) and in the liquor during leaching (Nicol et al., 2004), this study focusses on SAC solutions containing single metal ions Fe(II), Co(II) or Mn(II) and their binary or ternary mixtures in the absence of sulfite and thiosulfate, in the first instance, to shed light on cobalt losses in the Caron process and next phase of the experimental program.

3. Experimental

The synthetic ammonium carbonate (SAC) solution used in this series of experiments was prepared by dissolving 580 g of ammonium carbonate in 1.1 L of concentrated (28%) ammonia solution and making up to 5 L using de-ionised water. This gave a solution of ~5.3 M NH$_3$ and ~1.5 M CO$_2$. The experiments were carried out in a 1 L reactor vessel with overhead stirrer and thermostat control. The air was sparged through a dreschel bottle containing 150 mL SAC solution before bubbling through the experimental solution at the desired volumetric rate using sintered glass spargers. Unless otherwise stated the conditions used were as stated in Table 3.

The SAC solution was placed in the reactor vessel, heated to the designated temperature and selected masses of CoSO$_4$.7H$_2$O, and none, one or both of MnSO$_4$.H$_2$O or FeSO$_4$.7H$_2$O, were added as
aqueous solutions. The solids were individually dissolved in minimal DI water, with a small amount (~2 mL) of sulfuric acid added to the FeSO₄ to prevent oxidation by air before adding. At set times during the experiments, samples of the aerated slurry were withdrawn from the reactor vessel using a micropipette and analysed, where appropriate, for iron, manganese, cobalt(总), cobalt(II), cobalt(III) concentrations using the procedure described below.

The maximum values of iron in solution, in various leach circuit analyses conducted in the Yabulu Refinery, ranged from 1.2 g L⁻¹ to 2 g L⁻¹ and that of cobalt ranged from 0.5 g L⁻¹ to 1 g L⁻¹. The maximum values in these ranges was used in this study (Table 3). The concentrations of Fe(II), Mn(II) and Co(II) used in this study are well within their solubility limits in ~5.3 M NH₃ and ~1.5 M CO₂ corresponding to ~80 g L⁻¹ NH₃ and NH₃/CO₂ ratio of ~1.4 reported by Benjamin (2003), as shown in Table 3.

To maintain a pH of around 9.5 in the reactor vessel, small amounts of concentrated ammonia were added periodically, and pH monitored. This also maintained concentration of ammonia in the solution at a relatively constant value. The amounts added were <10 mL, so no adjustment was made for an increase in volume.

During the experiment the amounts of cobalt(总), manganese and iron remaining in solution were determined by removing ~4 mL of the reactor solution and filtered, using a syringe with 0.45 μm filters attached. A 2.0 mL aliquot of the filtrate was placed in a 50 mL volumetric flask containing ~2 mL of 2 M sulfuric acid to prevent any further precipitation. This was made up to the mark using DI water and the solution was further diluted, as needed, and analysed for cobalt, manganese and iron, where appropriate, using Atomic Absorption Spectrophotometry (AAS).

The concentration of cobalt(II) was determined by quantitatively extracting cobalt(II) from the aqueous solution by shaking 4 mL of reactor solution diluted using 15 mL of DI water, with 20 mL of a 20% (v/v) solution of LIX 84IC (from BASF- Mining Solutions) in Shellsol 2046. The residual aqueous phase was separated, filtered (as above) and analysed for cobalt using AAS. The pH and ORP were measured using commercial probes. The precipitated solids were filtered, washed with SAC and water and subjected to XRD scans for characterisation. The reported values of equilibrium constants are based on HSC6.1 database.
4. Results and Discussion

4.1 Single Metal Ions

4.1.1 Cobalt(II)

When cobalt(II) alone is present in the SAC solution being aerated, the rate of oxidation is relatively slow, with some cobalt(II) present after 5 h of oxidation (Fig. 3a). During the oxidation of cobalt(II) alone, there is no observable signs of any precipitation of Co(III) occurring, as Co(OH)$_3$ dissolves in ammoniacal solutions as Co(NH$_3$)$_6^{3+}$ as shown by the large equilibrium constant of Log $K = 4.60$ for Eq. (9). The overall reaction for oxidation is expressed by Eq (10) (Queneau and Weir, 1986).

\[
\text{Co(OH)}_3 + 3\text{NH}_4^+ \rightarrow \text{Co(NH}_3)_6^{3+} + 3\text{NH}_3 + 3\text{H}_2\text{O} \quad (9)
\]

\[
[4\text{Co(NH}_3)_5\text{H}_2\text{O}]^{2+} + 4\text{NH}_4^+ + \text{O}_2 \rightarrow [4\text{Co(NH}_3)_6]^{3+} + 3\text{H}_2\text{O} \quad (10)
\]

This slow rate is in stark contrast to what is found in plant conditions, whereby the majority of cobalt(II) has become cobalt(III) in less than an hour (Fittock, 2007). The oxidation of Co(II) follows a complex path with intermediates of peroxo or superoxo bridging complexes (Cotton and Wilkinson, 1980). Never-the-less, the initial concentration of Co(II) ($C_o$) and the concentration at time $t$ ($C_t$) can be related to first order kinetics: $\log \left( \frac{C_t}{C_o} \right) = (-k/2.303)t$ with respect to Co(II) concentration as demonstrated by the linear relationship in Fig. 3b, with a rate constant $k = 0.41 \text{ h}^{-1}$ calculated from the slope.

As can be seen from Fig. 4 the reaction rate is temperature dependent. From the data obtained, it was established that the activation energy ($E_a$) for the oxidation of cobalt(II) in SAC is 65.8 kJ mol$^{-1}$, based on the Arrhenius equation; this supports a chemically controlled reaction mechanism. A comparison of the change of rate constant and oxygen solubility (in water) with a change in temperature is shown in Fig. 5. It should be noted that the solubility of oxygen is less in solutions containing ammonium carbonate and decreases with the increase in temperature (Narita et al., 1983). The increase in measured rate constant, as expected from the Arrhenius equation suggests that the change in dissolved oxygen concentration has no significant effect on the rate of cobalt(II) oxidation. Dyer et al. (2012) also concluded that based on the adsorption studies of cobalt on iron oxide before and after
precipitation of iron oxide at different temperatures did not display a significant impact on cobalt loss or the nature of the precipitated phase of iron.

4.1.2 Manganese(II)

With experiments involving just 1 g L\(^{-1}\) Mn(II), there was a gradual decrease in the concentration of manganese in solution over time, as illustrated in Fig. 6, which plots the fraction of residual manganese ions in solution. The actual precipitation process was very slow, compared to the oxidation of Co(II) to Co(III), with 40% of the Mn(II) remaining in solution after 4 h as shown in Fig. 6a, compared to less than 20% Co(II) in Fig. 3a. The Eh-pH diagram in Appendix 1 shows that dissolved oxygen can oxidise Mn(NH\(_3\))\(_4^{2+}\) and precipitate MnOOH or Mn\(_3\)O\(_4\) depending upon pH. When a larger concentration of manganese(II) was used (>1 g L\(^{-1}\)), there was enough precipitate formed to enable analysis using XRD. From the XRD, shown in Fig. 6b, the solid formed was established to be MnCO\(_3\) (Eq. 11). This was not surprising as 1 g L\(^{-1}\) exceeded the maximum solubility of Mn(II) in the SAC solution (0.04 g L\(^{-1}\) in Table 3), warranting further studies.

\[
\text{Mn(NH}_3\text{)}_4^{2+} + \text{CO}_3^{2-} \rightarrow \text{MnCO}_3 + 4\text{NH}_3 \\
(11)
\]

4.1.3 Iron(II)

With the aeration of a SAC solution containing only Fe(II), the bulk of the iron tends to precipitate within 0.5 h (Fig. 7a). The XRD scans of the solid that is produced is shown in (Fig. 7b) which indicates that the bulk of it to be goethite, although there is some possible evidence of some ferrhydrite being present. A possible reaction that is occurring in this instance forming goethite is given by Eq. (12). Thus, further characterization was conducted using the solids from the Caron Processing Plant at Yabulu (CPPY). The XRD scans of CPPY solids shown in Fig. 8a indicate that the solid consist of trevorite (NiFe\(_2\)O\(_4\)), maghemite (Fe\(_2\)O\(_3\)), forsterite (Mg\(_2\)SiO\(_4\)), quartz (SiO\(_2\)), magnetite (Fe\(_3\)O\(_4\)) and possibly magnesioferrite (MgFe\(_2\)O\(_4\)). This would most likely be due to the complexity of the laterite ore used in the Caron process, and species present, both solution and solid, when compared to the test solutions/solids used in the laboratory experiments. There is some evidence that magnetite (Fe\(_3\)O\(_4\)) may be formed initially as shown by the XRD scan of solids precipitated in the laboratory experiments after 30 min (Eq. (13)), albeit briefly (Fig. 8b).
Fe(NH$_3$)$_4^{2+}$ + 2.5H$_2$O + 0.25O$_2$ → FeOOH + H$_2$O + 2NH$_3$ + 2NH$_4^+$  \hspace{1cm} (12) \\
6Fe(NH$_3$)$_4^{2+}$ (aq) + 6H$_2$O + O$_2$(aq) → 2Fe$_2$O$_4$(s) + 12NH$_4^+$ (aq) + 12NH$_3$(aq)  \hspace{1cm} (13) 

However, the magnetite formed in test solution of Fe(II) used in this study has disappeared from
the scan after 3 h as shown in Fig. 8b. While the precipitate in Figure 7b is predominantly goethite, the
same cannot be said for those in 8b. Dyer et al. (2012) reported 6-line ferrihydrite 5Fe$_2$O$_3$.9H$_2$O (or
Fe$_5$HO$_8$.4H$_2$O, Cornell and Schwertmann, 1996) as the primary product of iron precipitation and not the
2-line product (Fe$_2$O$_3$.0.5H$_2$O; Su, 2011). The difference between generating only ferrihydrite, goethite and
ferrihydrite (Fig. 8b), and many other products including magnetite in CPPY (Fig. 8a) can be a result of different
factors such as the actual pH, concentration, rate of oxidation of Fe(II), temperature, other ions present in solution,
aeration, seeding effect of undissolved calcine (largely magnetite) and supersaturation of dissolved iron (Cornell
and Schwertmann, 1996; Dyer et al., 2012) warranting. In the case of individual metal ions, the percentages
of Co(II), Mn(II) and Fe(II) oxidized or precipitated from the initial concentration after 0.5 h are 80%
(Fig. 3a), 5% (Fig. 6a) and 100% (Fig. 7a), respectively, indicating the importance of investigation of
the behaviour of mixtures of metal ions during oxidation/precipitation to examine the mutual effects
described below.

4.2 Cobalt and manganese

When a SAC solution containing both manganese(II) and cobalt(II) is aerated, it is found that
both cobalt(II) and manganese(II) species are oxidised/precipitated at a faster rate than when they were
alone. In fact, most of cobalt(II) is oxidised within 0.4 h (Fig. 9a). This is more in line with the
observations made under plant conditions for the oxidation of cobalt(II), noted previously. Thus, it can
be concluded that the manganese species (or manganese product formed during oxidation) acts as a
catalyst for the oxidation of Co(II). As can be seen in Fig. 9b, it is of interest to note that there is
minimal difference in the effect when the original concentration of manganese is increased from 0.025 g
L$^{-1}$ to 1.25 g L$^{-1}$. However, the remnant Co(II) in solution after 2 h at different concentrations of Mn(II):
0, 0.025, 0.05, 0.1 and 1.25 g L$^{-1}$ vary as 85, 28, 11, 12 and 2% respectively (Fig. 9b), indicating that a
higher concentration of Mn(II) facilitate the oxidation of Co(II) to Co(III). According to the Eh-pH
diagrams, the oxidation of cobalt(II) manganese(II) can occur at potential range close to 0.1 V and -0.1
V, respectively, which are both lower than that of oxygen (Appendix 1). The oxidised Mn(II) in the form of MnOOH can act as an oxidant for Co(NH₃)₆²⁺ precipitating MnCO₃ according to Eq. 14, as evident from high equilibrium constant of log K = 1.5 based on the standard free energy data in the HSC 6.1 data base. The cobalt content of the manganese solids after 1 h leaching was 2.25% (w/w). Further studies are in progress to rationalise the beneficial effect of high Mn(II) concentration within the solubility limit of Mn(II) (0.04 g L⁻¹, Table 3) on oxidation of Co(II) and the role of the reaction in Eq.14 to rationalise the mutual beneficial effect of Mn(II) and Co(II) to enhance the decrease in remnant concentrations of these ions in Fig. 9a.

\[
\text{MnOOH}(s) + \text{Co(NH}_{3}\text{)}_{6}^{2+} + 2\text{NH}_4^{+} + \text{HCO}_3^{-} = \text{Co(NH}_{3}\text{)}_{6}^{3+} + \text{MnCO}_3(s) + 2\text{NH}_3 + 2\text{H}_2\text{O} \quad (14)
\]

4.3 Cobalt and iron

As shown in Fig. 10 when the mixture of both iron(II) and cobalt(II) in SAC is aerated, there are two regions of interest for the residual cobalt(II): (i) during the first 0.2 h, the decrease in residual cobalt(II) follow the same trend as in cobalt(II) alone, but the oxidation of iron(II) is nearly complete during this period, (ii) during 0.2-0.35 h the decrease is due to rapid decrease of cobalt(II) than when on its own. Once again, most of cobalt(II) is oxidised within the hour (Fig. 10), indicating that the iron precipitate (goethite) is acting as a catalyst in the oxidation of cobalt(II). An important difference occurs with iron(II)/cobalt(II) when compared with manganese(II)/cobalt(II). There is no oxidation of cobalt(II) until the iron has completely precipitated. The reason for this is that any cobalt(III) species formed would immediately act as an oxidising agent for iron(II), as the Co(III)/Co(II) redox couple has a higher electrode potential than that of FeOOH/Fe(II). As can be seen in Figure 10, the ORP is less than -0.15 V during the precipitation of iron which correspond to the Fe(OH)₃/Fe(NH₃)₄²⁺ in the Eh-pH diagrams reported by Asselin (2008). Despite the continuous aeration, cobalt oxidation occurring predominantly after iron is removed from solution is the result of the lower ORP (measured) associated with the Fe(III)/Fe(II) redox couple, but needs further investigation based on detailed kinetic analysis on relative rates. The increase in ORP after the precipitation of iron reflects an increase in the concentration ratio of [Co(III)]/[Co(II)] according to the Nernst equation \( E_{\text{Co(III)/Co(II)}} = E^o_{\text{Co(III)/Co(II)}} + \frac{RT}{F} \ln\left(\frac{[\text{Co(III)}]}{[\text{Co(II)}]}\right) \), due to the decrease in concentration of Co(II). This view is supported by the final ORP of ~0.2 V in Fig. 10 which is close to the Co(III)/Co(II) couple in Eq. 6-7 and Appendix 1.
One suggested reaction in literature (Queneau and Weir, 1986) for the co-precipitation that is occurring is given by Eq. (15). Considering the evidence for the presence of FeOOH in the XRD scans of solids obtained in this work, the reaction may be better written as Eq. 16. This is followed by a dehydration to goethite and cobalt oxide (Queneau and Weir, 1986). As the dehydration occurs, the cobalt gets locked into the solid (Eq. 17) which becomes unrecoverable by washing. Considering the evidence of the existence of Fe$_3$O$_4$ in the precipitate found early in experiments, an intermediate reaction for the formation of the spinel would be given by Eq. (18), followed possibly by Eq. (19). Due to the very low amount of cobalt(II) co-precipitating, or being adsorbed, the average value over 3 trials was that the precipitated solids formed contained only 0.38% cobalt after 60 minutes of reaction time. Thus, the cobalt content in goethite precipitated in the laboratory test (0.38%) is higher than that of the four aerator tanks of the Yabulu refinery (0.15-0.17%, Fig. 2). Moreover, there is no indication of any significant variation in the XRD of goethite precipitate obtained in the absence or presence of cobalt(II) during iron precipitation.

\[
\text{xFe(OH)}_3 + \text{Co(NH}_3)_2^{2+} + 2\text{H}_2\text{O} \rightarrow [\text{Fe(OH)}_3]_x[\text{Co(OH)}_2] + 2\text{NH}_4^+ + 3\text{NH}_3 \quad (15)
\]

\[
\text{xFeOOH} + \text{Co(NH}_3)_2^{2+} + 2\text{H}_2\text{O} \rightarrow [\text{FeOOH}]_x[\text{Co(OH)}_2] + 2\text{NH}_4^+ + 3\text{NH}_3 \quad (16)
\]

\[
[\text{Fe(OH)}_3]_x[\text{Co(OH)}_2] \rightarrow [\text{FeOOH}]_x[\text{CoO}] + (x+1)\text{H}_2\text{O} \quad (17)
\]

\[
4\text{Fe(NH}_3)_2^{2+} + 2\text{Co(NH}_3)_2^{2+} + 6\text{H}_2\text{O} + \text{O}_2\rightarrow 2\text{CoFe}_2\text{O}_4 + 12\text{NH}_4^+ + 14\text{NH}_3\quad (18)
\]

\[
\text{CoFe}_2\text{O}_4 + \text{H}_2\text{O} \rightarrow [\text{FeOOH}]_2[\text{CoO}] \quad (19)
\]

However, Dyer et al. (2012) reports variation of the XRD patterns obtained in the presence and absence of cobalt, where in the absence of cobalt, the pattern has sharper peaks and less appearance of broad peaks relating to X-ray amorphous phases. Contrastingly, in the presence of cobalt, the peaks are broader and less intense with greater evidence of ferrihydrite. According to Dyer et al. (2012) this could be due to rapid oxidation of iron(II) in the presence of cobalt, which is consistent with the observations in Fig. 7a (Fe(II) alone) and Fig.10a (Fe(II)+Co(II)). It may also be due to the incorporation of species as impurities in ferrihydrite which is known to favour less crystalline phases and retard the transformation of ferrihydrite.
The fact mentioned above that the cobalt losses in aerator tanks in Yabulu plant are lower, than the laboratory results, may be caused by the greater adsorption onto ferrihydrite due to its vastly larger surface area reported by Dyer et al. (2012). Moderately crystalline goethite generated in laboratory precipitation tests are likely to have somewhat elevated surface area in comparison to the solid samples from Yabulu plant, due to the high crystallinity of the latter (Fig. 7-8). Thus, further studies and discussion would be of including the uptake of Co(III) in the place of Fe(III) in either goethite and ferrihydrite, relevant to cobalt losses during iron precipitation in the Caron process.

4.4 Cobalt, iron and manganese

When all three metal ion species are present in the mixture, the result is similar to that as when just cobalt(II) and iron(II) were present. The sharp decrease in ORP and residual Fe(II) in Fig. 11 (similar to Fig. 10) represents the initial precipitation of iron. Again, the oxidation of the cobalt(II) does not begin until basically all the iron has precipitated and is nearly all oxidised within the hour (Fig 11). This is more complete than with iron(II) alone (Fig. 10). Moreover, there is only a small decrease of cobalt(II) occurring during the precipitation of iron. Although the fraction of residual iron reaches zero after about 0.25 h in both Fig. 10 and 11, the decrease in Co(II) concentration in Fig. 11 is much faster than that in Fig. 10, supporting the role of Mn(II) described in Section 4.2. For example, the residual Co(II) after 0.50 h in the three different systems Co(II), Co(II)+Fe(II) and Co(II)+Fe(II)+Mn(II) are 85%, 35% and 25%, respectively. The comparison of the experimentally measured ORP values at the completion of the oxidation of cobalt(II) in Figs. 10 and 11 (~0.2 V) agree well with those determined from the Eh-pH diagrams (Appendix 1) and other calculations (0.16-0.22 V) noted in Section 2.

5. Conclusions

The oxidation of cobalt(II) to cobalt(III) in SAC solution is a first order reaction with respect to the concentration of Co(II), which is slow at 25°C, but there is no precipitation of Co(III). The chemically controlled oxidation of Co(II) is evident from the high activation energy of the reaction (65.8 kJ mol⁻¹). Manganese(II) alone precipitate as MnCO₃ at higher Mn(II) concentrations but iron(II) precipitates as goethite/hemihydrite during aeration of the SAC
solutions containing these ions. At 40°C the percentages of Co(II), Mn(II) and Fe(II) oxidized or precipitated from the initial concentration after 0.5 h from individual solutions are 80, 5 and 100, respectively. Both manganese and iron in the solid phase catalyse the oxidation reaction of Co(II) to Co(III) by oxygen. However, when iron(II) is present in the mixture, cobalt(II) does not begin to oxidise until the majority of the iron(II) has precipitated indicating that Co(III) if formed by aeration is capable of oxidizing Fe(II). Although there is evidence that magnetite is formed as an intermediate in the oxidations of iron, it is converted to goethite later in the reaction. Results from this study and previous studies (Dyer et al., 2012) show the importance of controlling the characteristics of the iron/manganese/cobalt oxide precipitated under Caron conditions, depending upon Eh-pH and many other factors, in order to minimise the cobalt losses. For example, the higher loss of cobalt during the precipitation of iron(III) in the absence or presence of Mn(II) evident from the assays of precipitated solids in the laboratory experiments highlight that further work is essential with the Caron process liquors/solids and tailings to determine the effectiveness of what changes may assist in the Caron Process.

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Appendix 1

(a)

Eh-pH diagram for Mn-Co-NH$_3$-H$_2$O system. (a) $10^{-6}$ Mn and 1 M NH$_3$ at 25°C (b) $10^{-6}$ Co and 1 M NH$_3$ at 25°C. (a. Senanayake, et al. 2017; b. Senaputra and Senanayake, unpublished)
Table 1
Typical composition of nickel laterite ore and Yabulu plant tailings

<table>
<thead>
<tr>
<th>Element</th>
<th>Ni</th>
<th>Co</th>
<th>Fe</th>
<th>Si</th>
<th>Mg</th>
<th>Mn</th>
<th>Cu</th>
<th>Zn</th>
<th>Ca</th>
<th>Al</th>
<th>Cr</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed* (mass %)</td>
<td>1.60</td>
<td>0.15</td>
<td>37</td>
<td>7.2</td>
<td>6.9</td>
<td>0.80</td>
<td>0.01</td>
<td>0.05</td>
<td>0.10</td>
<td>2.1</td>
<td>1.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Tailings* (mass %)</td>
<td>0.31</td>
<td>0.06</td>
<td>41</td>
<td>9.8</td>
<td>5.4</td>
<td>0.85</td>
<td>0.01</td>
<td>0.03</td>
<td>0.09</td>
<td>2.2</td>
<td>1.7</td>
<td>0.23</td>
</tr>
</tbody>
</table>


Table 2
Advantages and issues of concern in the Caron process

<table>
<thead>
<tr>
<th>Issues</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>High energy consumption in the drying and roasting stages, compared to direct atmospheric or pressure leaching nickel laterites (Xavier and Ciminelli, 2008)</td>
</tr>
<tr>
<td>Iron removal</td>
<td>Easily leachable Fe$_3$O$_4$ in tailings compared to Fe$_2$O$_3$ in pressure leaching</td>
</tr>
<tr>
<td>Recycling reagents</td>
<td>Recovery and re-use of NH$_3$ and CO$_2$ (main reagents) despite the high cost of distillation (Muir and Ho, 2006)</td>
</tr>
<tr>
<td>Slow kinetics</td>
<td>Up to 8 h leaching in anaerobic and aerobic tanks as well as in CCD circuit in Fig. 1a (compared to rapid leaching in high-pressure autoclave)</td>
</tr>
<tr>
<td>Low Ni-Co recovery</td>
<td>82% Ni and 60% Co (Yabulu plant) 82% Ni and 40% Co (Punta Gorda plant; Borjas, 2004)</td>
</tr>
<tr>
<td>Environment</td>
<td>Pollution caused by heavy metals in tailings (Table 1) and roaster emissions</td>
</tr>
</tbody>
</table>

Table 3
Experimental conditions used during aeration/oxidation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value / unit</th>
<th>Solubility limits*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of solution</td>
<td>800 mL</td>
<td></td>
</tr>
<tr>
<td>Temperature (unless stated otherwise)</td>
<td>40 °C</td>
<td></td>
</tr>
<tr>
<td>Impeller speed</td>
<td>800 rpm</td>
<td></td>
</tr>
<tr>
<td>Ammonia/ammonium (as carbonate)</td>
<td>5.3 M (total)</td>
<td></td>
</tr>
<tr>
<td>Carbonate</td>
<td>1.5 M</td>
<td></td>
</tr>
<tr>
<td>Initial Co(II) concentration</td>
<td>1.0 g L$^{-1}$, 20 g L$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Air flow rate</td>
<td>1.2 L min$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Initial Fe(II) concentration</td>
<td>2.0 g L$^{-1}$, 3.5 g L$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Initial Mn(II) concentration</td>
<td>Varied (0.025-1.25 mg L$^{-1}$), 40 mg L$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>9.5</td>
<td></td>
</tr>
</tbody>
</table>

a. Solubility limits in solutions containing 5.3 M NH$_3$ and 1.5 M CO$_2$ at a NH$_3$/CO$_2$ mass ratio of 1.4 (Benjamin, 2003).
Table 4
Solids formed in laboratory aeration experiments and Yabulu refinery

<table>
<thead>
<tr>
<th>Metal ions in initial SAC solution</th>
<th>Solid precipitated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(II)</td>
<td>None</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>FeOOH</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>MnCO$_3$ (at high Mn(II) concentrations)</td>
</tr>
<tr>
<td>Fe(II)+Mn(II)</td>
<td>FeOOH (some Fe$_3$O$_4$ initially)</td>
</tr>
<tr>
<td>Co(II)+Mn(II)</td>
<td>None</td>
</tr>
<tr>
<td>Co(II)+Fe(II)</td>
<td>FeOOH</td>
</tr>
<tr>
<td>Co(II)+Fe(II)+Mn(II)</td>
<td>FeOOH</td>
</tr>
<tr>
<td>Aerator of Yabulu refinery</td>
<td>NiFe$_2$O$_4$, Fe$_3$O$_4$, Mg$_2$SiO$_4$, SiO$_2$, Fe$_2$O$_3$, MgFe$_2$O$_4$</td>
</tr>
</tbody>
</table>

(See Figures 6-8)
Highlights

- A brief review of current understanding of cobalt and nickel losses in the Caron process
- The aeration/oxidation results of synthetic solutions of Fe(II)+Co(II)+Mn(II)+NH₃+NH₄HCO₃
- Oxidized/precipitated species of iron/manganese catalyse the oxidation of Co(II) to Co(III)
- Solids from laboratory tests/plant residues confirm co-precipitation of Co(II) during aeration
Figure 1

(a) 

Dried Ore → Herreshoff Roaster → Ore Cooler → Roasted Ore (CD) → Quench Slurry (QS) 

Quench Liquor → A1 → A2 → A3 → A4 (Integrated Leaching Train) → Compressed Air → Vent Gas 

Leach Slurry → Overflow Liquor → CCD Thickeners → Product Liquor 

Underflow Slurry → Product to Extract Ni and Co 

Raffinate from Solvent Extraction 

Washed Solids to Tailings (after steam stripping to recover NH₃ and CO₂) 

(b) 

As in Fig 1a → Proposed 

1 → 2 → 3 → 4
Figure 3

(a) Fraction of Residual Co(II) vs. Time/hours

(b) log([C]/[C₀]) for Co(II) vs. Time/hours

Equation: y = -0.1811x

R² = 0.9964
Figure 4

Graph showing the relationship between time (hours) and the log of the concentration ratio ($[C_t/C_o]$) of Co(II) at different temperatures:

- **25 °C**:
  - Equation: $y = -0.0314x$
  - $R^2 = 0.9826$

- **35 °C**:  
  - Equation: $y = -0.1254x$
  - $R^2 = 0.9998$

- **45 °C**:
  - Equation: $y = -0.0741x$
  - $R^2 = 0.9835$

The graph indicates a decrease in concentration with increasing time for each temperature.
Figure 6

(a) Fraction Residual Mn vs. Time/hours

(b) X-ray diffraction pattern

- Intensity vs. 2 Theta

- Triangles represent Rhodochrosite
Figure 9

(a) Fraction of Residual Species

(b) Fraction of Residual Co(II)

Time/hours
Figure 11