Selective leaching of penalty elements from copper concentrates: A review

Daniel J. Lane [a,b,*], Nigel J. Cook [a,b], Stephen R. Grano [a], Kathy Ehrig [c]

[a] Institute for Minerals and Energy Resources, The University of Adelaide, Adelaide, South Australia 5005, Australia
[b] School of Chemical Engineering, The University of Adelaide, Adelaide, South Australia 5005, Australia
[c] BHP Billiton Olympic Dam, 55 Grenfell Street, Adelaide, South Australia 5000, Australia

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ABSTRACT

Custom copper smelters impose substantial financial penalties for the presence of deleterious impurity elements in copper concentrates and can outright reject concentrates which contain impurity elements in concentrations that exceed specified values. Hence, there is strong motivation to remove penalised impurity elements from copper concentrates at the mine site before shipping to custom smelters. A number of leach systems have been developed for the selective extraction of penalty elements from copper concentrates, including: alkaline sulphide leaching (ASL); hypochlorite leaching; dilute sulphuric acid leaching with aluminium sulphate; and combined pressure oxidation (POX) leaching with copper precipitation leaching. This paper reviews these four systems with emphasis on the leaching behaviour of penalty elements. ASL has previously been employed in industry for the selective extraction of As and Sb from tetrahedrite-rich copper concentrates. Sodium sulphide solution leaches As, Sb, and Hg from a large range of minerals, however, does not leach arsenopyrite, a mineral which often contains a significant portion of the total As in copper concentrates. Hypochlorite leaching extracts As associated with enargite minerals. This leach system benefits from superior rates of As extraction when compared with ASL, and for this reason, has gained recent interest within the research community. Two major issues have been identified with hypochlorite leaching of copper concentrates. These are poor reagent selectivity towards As-bearing minerals and high levels of hypochlorite consumption. Unless these two issues are resolved it is unlikely that hypochlorite leaching will be employed in commercial processes. Dilute sulphuric acid leaching with aluminium sulphate is used to extract F associated with fluorite. This leach system also extracts F associated with apatite and chlorite. Laboratory-scale experiments and extensive operating experience have indicated that fluorite can be substantially leached from copper concentrates without addition of aluminium sulphate provided that the concentration of sulphuric acid in the leach solution is sufficiently high (at least $40 \, g \, L^{-1}$). POX/copper precipitation leach systems have potential to extract a large number of penalty elements from copper sulphide concentrates while simultaneously upgrading the concentration of copper in the concentrate. Two patented POX/copper precipitation leach processes have been specifically developed for the deportment of penalty elements. These two processes are reviewed in detail.

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* Corresponding author at: Institute for Minerals and Energy Resources, The University of Adelaide, Adelaide, South Australia 5005, Australia.
  E-mail address: daniel.lane@adelaide.edu.au (D.J. Lane).

1. Introduction

Some deposits of copper ore contain deleterious impurity elements which occur as inclusions, or are intimately intergrown with the economic copper minerals. Comminution and flotation processes do not always provide complete separation of these elements from copper, and consequently, the impurity elements often report to flotation concentrates during processing. The presence of certain impurity elements adds to the cost of copper concentrate smelting and refining operations, can substantially reduce the market value, and in some cases, even prevent the saleability of copper concentrates.

Refining of copper concentrates at the mine site itself requires significant capital. For this reason most producers of copper concentrate will sell to large custom smelters instead (Fountain et al., 2008), despite the increased costs associated with transport. The majority of custom copper smelters are located in China, Japan, and Europe (Fountain, 2013). These smelters typically impose financial penalties if certain impurity elements are present in the copper concentrate at concentrations which exceed stipulated limits. Financial penalties imposed by a Japanese copper smelter are shown in Table 1 for a range of deleterious impurity elements. There is a general structure for the charging of penalties (Larouche, 2001). Below a certain concentration there is no charge for the impurity element. This threshold value is referred to as the "no charge maximum" (NCM). An incremental charge applies for impurity element concentrations above the NCM. Certain smelters may outright reject the copper concentrate if the concentration of an impurity element exceeds a certain value. The Chinese government has imposed upper limits on several impurity elements in copper concentrates imported into China (Fountain, 2013). These limits are presented in Table 2. Impurity elements which have restrictions or incur financial penalties are collectively referred to as "penalty elements".

Penalty element charges can largely influence the negotiated price for the sale of copper concentrate. In general, the price of copper concentrate will depend on: the market price for London Metal Exchange (LME) Grade A copper cathode; the payable copper content in the concentrate; treatment and refining charges; credits for valuable metals in the concentrate other than Cu (e.g., Au and Ag); and deductions for penalty elements (Hansen, 2013). The payable copper content depends on the grade of copper in the concentrate and is typically 95–97% of the contained copper content for concentrates with copper grades between 20 and 30 wt% (Hansen, 2013; Söderström, 2008). Treatment and refining charges are imposed to account for costs associated with smelting and refining respectively. A typical treatment charge is US$45/dry metric tonne (DMT) of concentrate. A typical refining charge is 4.5US¢/lb of payable copper (Söderström, 2008), which approximately equates to US$23/DMT of concentrate, for concentrate with a Cu grade of ~24 wt%. The average market price for LME grade A copper cathode in June 2016 was US$4630/DMT (London Metal Exchange, http://www.lme.com/metals/non-ferrous/copper/). At this price, it is estimated that copper concentrate with a grade of 24 wt%, would sell for approximately $US990/DMT. Note that this estimate does not take into account credits for payable metals and deductions for penalty elements. This value may be significantly reduced once deductions have been made for penalty elements. For example, if the concentrate contains 4 wt% As and 1 wt% Sb, a penalty of US$140/DMT would be charged according to the penalty element rates presented in Table 1. This deduction reduces the net value of the concentrate to $US850/DMT (14% reduction in price).

Penalty elements bear financial charges for a number of reasons. Some penalty elements are detrimental to the environment and to human health when present in concentrations which are greater than which they occur naturally. Arsenic, Cd, Hg, Pb, and Sb all fit this category (Alloway, 2013). These elements tend to be highly volatile in thermal processes (Fountain, 2013; Larouche, 2001) and risk being emitted into the atmosphere during smelting. Expensive off-gas cleaning measures (e.g., scrubbing for Hg and bag filters or electrostatic precipitators for As, Cd, Pb, and Sb) are needed to prevent their emission. Some penalty elements cause equipment damage. The halogens, F and Cl, for example, are intimately connected with corrosion and fouling problems in smelters and in downstream gas cleaning systems (Fountain, 2013). High concentrations of Zn can reduce the recovery of copper in smelting processes by increasing slag viscosity (Fountain, 2013). Certain penalty elements are difficult to separate during smelting and refining and may be carried through to the final product. This can have an adverse impact on the quality of the produced copper cathode. International standards on the purity of copper cathodes generally require the concentrations of penalty elements to be below certain levels. Upper limits for impurity element concentrations in LME Grade A copper cathode are presented in Table 3. It is noted that the lowest limits are on the concentrations of Bi, Se, and

Table 1
Penalty element charges imposed by a Japanese copper smelter. Data from Fountain (2013).

Element	NCM[a] (wt% or ppm in feed)	Penalty (US$/DMT[b] of concentrate)
As	0.2 wt%	$2.50/0.1% above NCM
Bi	0.05 wt%	$0.30/0.01% above NCM
Cl	0.05 wt%	$0.50/0.01% above NCM
F	330 ppm	$0.10/10 ppm above NCM
Hg	10 ppm	$0.20/1 ppm above NCM
Pb	1 wt%	$1.50/1.0% above NCM
Sb	0.1 wt%	$0.50/0.01% above NCM
Zn	3.0 wt%	$1.50/1.0% above NCM
Ni + Co	0.5 wt%	$0.30/0.1% above NCM

[a] NCM = no charge maximum.
[b] DMT = dry metric tonne.

Table 2
Upper concentration limits on penalty elements for importing copper concentrates into China (Fountain, 2013).

Penalty element	Upper limit, %
Pb	6.0
As	0.5
F	0.1
Cd	0.005
Hg	0.01

Table 3
Impurity element limits for LME Grade A copper cathode (London Metal Exchange, https://www.lme.com/~/media/Files/Branding/Chemicalcomposition/Nonferrous/Chemicalcomposition).

Element	Composition, % maximum
Ag	0.0025
As	0.0005[a]
Bi	0.00020[b]
Cd	–[a]
Co	–[c]
Cr	–[a]
Fe	0.0010[c]
Mn	–[a]
Ni	–[c]
P	–[a]
Pb	0.0005
S	0.0015[d]
Sb	0.0004[a]
Se	0.00020[b]
Si	–[c]
Sn	–[c]
Te	0.00020[b]
Zn	–[c]
Sum of elements listed	0.0065

[a] (As + Cd + Cr + Mn + P + Sb) maximum 0.0015%.
[b] (Bi + Se + Te) maximum 0.0003%, of which (Se + Te) maximum 0.00030%.
[c] (Co + Fe + Ni + Si + Sn + Zn) maximum 0.0020%.
[d] The sulphur content shall be determined on a cast table.

Te. These elements are highly insoluble in copper and consequently even small amounts of these elements make copper cathode brittle (Fountain, 2013). Bismuth can be particularly problematic during electrorefining since it largely dissolves in the electrolyte (Schlesinger et al., 2011). Dissolved Bi can co-deposit with Cu onto the cathode if present in the electrolyte in high enough concentrations (Wang, 2004). Expensive control measures (e.g., bleeding of electrolyte followed by electrowinning) are often required to prevent accumulation of Bi in the electrolyte (Wang, 2004; Wang et al., 2011). Se and Te are generally of lesser concern during electrorefining since typically only a small fraction (~2%) of these elements report to the electrolyte (the majority reports to the anode slimes) (Schlesinger et al., 2011). The low tolerance for Bi in copper cathode and the need to prevent its accumulation in the electrolyte during electrorefining is reflected by the heavy penalty imposed for this element (Fountain, 2013; Larouche, 2001; Zanetell, 2007). Larouche (2001) points out that the NCM for Bi is typically an order of magnitude lower than the NCMs for As and Sb, and two orders of magnitude lower than the NCM for Pb.

An important class of penalty elements which is not shown in Table 1 is the naturally occurring radionuclides. Copper ore deposits with associated uranium, such as the Olympic Dam Cu-U-Au-Ag deposit, South Australia (Ehrig et al., 2012), contain ^{238}U decay series radionuclides. The International Atomic Energy Agency (IAEA) publishes internationally recognised safety protocols for the handling of radioactive materials (IAEA, 2012). Copper concentrates containing ^{238}U decay series radionuclides in secular equilibrium are exempt from regulation if the activity concentrations of ^{238}U and each of its 13 radioactive daughters are less than 1 Bq g^{-1}. If on the other hand, the activity concentrations of the individual radionuclides exceed this threshold value then costly control measures may be needed during shipping for radiation protection. The radionuclides can cause additional handling issues at the site of the smelter. During smelting the radionuclides partition themselves between the various product streams (i.e. matte, slag, flue dust, and off-gas) and can become enriched within a particular stream. ^{210}Pb and ^{210}Po for instance, are known to substantially concentrate in flue dusts (BHP Billiton, 2009; Schreck, 1999; Weiss et al., 1997), particularly when the flue dusts are recycled for

Table 4
Leach systems for the selective extraction of penalty elements from copper concentrates.

Leach system	Penalty elements leached
Alkaline sulphide leach	As, Sb, Hg, Bi[b], Te[b]
Hypochlorite leach	As, Te[b]
Dilute sulphuric acid leach with aluminium sulphate	F
POX[a] leach/copper precipitation leach	Bi, Cd, Co, Ni, Pb, Te, Tl, Zn, ^{238}U, ^{230}Th, ^{226}Ra, ^{210}Pb, ^{210}Po

[a] POX = pressure oxidative.
[b] No leaching data was found for these elements.

recovery of copper (Fountain, 2013). Safe disposal of the radioactivity enriched flue dusts can be both complex and expensive.

It is clear that there is strong motivation to remove penalty elements from copper concentrates at the mine site before shipping to custom smelters. One way to achieve this is to selectively leach penalty elements from the copper concentrate. A number of leach systems have been developed for the selective leaching of penalty elements (see Table 4), however, published literature on these systems tends to focus on the leaching behaviour of just one penalty element from one type of mineral (e.g., the leaching of Sb from tetrahedrite), without considering the behaviour of other penalty elements which may be simultaneously leached from the concentrate. This paper reviews the four leach systems listed in Table 4. It was an aim of the paper to encompass the leaching behaviour of as many penalty elements for which literature is available.

2. Alkaline sulphide leaching

Alkaline sulphide leaching (ASL) is highly selective and for this reason has been the main leach system employed for the extraction of As and Sb from copper concentrates. The behaviour of As and Sb in ASL depends on the mineral speciation of these elements in the concentrate. Sodium sulphide (Na$_2$S) is known to dissolve As when As occurs in the following mineral forms: enargite (Cu$_3$AsS$_4$), tennantite [Cu$_{10}$(Fe,Zn)$_2$As$_4$S$_{13}$], realgar (α-As$_2$S$_2$), orpiment (As$_2$S$_3$), and arsenic trioxide (As$_2$O$_3$) (Anderson et al., 2014; Baláž and Achimovičová, 2006; Delfini et al., 2003). Similarly, sodium sulphide is known to dissolve Sb when Sb occurs in the following mineral forms: tetrahedrite [Cu$_{10}$(Fe,Zn)$_2$Sb$_4$S$_{13}$], stibnite (Sb$_2$S$_3$), and jamesonite (Pb$_4$FeSb$_6$S$_{14}$) (Baláž, 2000b; Baláž and Achimovičová, 2006; Baláž et al., 1998). The chemical reactions which take place between sodium sulphide and these As- and Sb-bearing minerals are presented in Table 5. It can be seen that As and Sb are both converted to sodium thio-anions. A number of studies (Baláž, 2000b; Dayton, 1982; Edwards, 1985; Filippou et al., 2007) have reported that sodium sulphide does not leach As when As occurs in the form of arsenopyrite (FeAsS). The distribution of arsenic between arsenopyrite and soluble forms is thought to place an upper limit on the extraction of As in practical ASL systems (Edwards, 1985). More problematic are cases where the penalty elements do not occur as discrete minerals, but rather incorporated, at concentrations of hundreds or thousands of parts per million into the lattice of common sulphides (e.g., Bi within bornite or chalcocite group phases; Cook et al., 2011).

Many investigators have highlighted that sodium sulphide is also an effective lixivant for the extraction of Hg, however only a few studies (Anderson, 2003; Baláž et al., 1998; Baláž and Dutková, 2009) present data. Baláž and Dutková (2009) reported only minor extraction (<10%) of Hg from a tetrahedrite-rich copper concentrate from Rožňava, Slovakia, in their mechano-chemical leaching process, which involves integrated milling and ASL of the concentrate within the same step (Baláž, 2000b). They attribu-

Table 5
Simplified chemical reactions which take place during ASL of copper concentrates.

Host mineral	Reaction(s)		Reference
As-bearing minerals			
Enargite (Cu_3AsS_4)	$2Cu_3AsS_4(s) + 3Na_2S(aq) \rightarrow 3Cu_2S(s) + 2Na_3AsS_4(aq)$	(1)	Baláž and Achimovičová (2006)
Realgar (AsS)	$2AsS(s) + Na_2S(aq) \rightarrow Na_2As_2S_3(aq)$	(2)	(Delfini et al. (2003)
Orpiment (As_2S_3)	$As_2S_3(s) + Na_2S(aq) \rightarrow 2NaAsS_2(aq)$	(3)	(Anderson et al. (2014)
	$NaAsS_2(aq) + Na_2S(aq) \rightarrow Na_3AsS_3(aq)$	(4)	Anderson et al. (2014)
Arsenic trioxide (As_2O_3)	$As_2O_3(s) + 4Na_2S(aq) + 3H_2O \rightarrow 2NaAsS_2(aq) + 6NaOH(aq)$	(5)	Anderson et al. (2014)
	$NaAsS_2(aq) + Na_2S(aq) \rightarrow Na_3AsS_3(aq)$	(6)	Anderson et al. (2014)
Sb-bearing minerals			
Tetrahedrite [$Cu_{10}(Fe,Zn)_2Sb_4S_{13}$]	$Cu_{12}Sb_4S_{13}(s) + 2Na_2S(aq) \rightarrow 5Cu_2S(s) + 2CuS(s) + 4NaSbS_2(aq)$	(7)	Awe et al. (2013)
	$NaSbS_2(aq) + Na_2S(aq) \rightarrow Na_3SbS_3(aq)$	(8)	Awe et al. (2013)
Stibnite (Sb_2S_3)	$Sb_2S_3(s) + 2Na_2S(aq) \rightarrow Na_4Sb_2S_5(aq)$	(9)	Baláž (2000b)
	$Sb_2S_3(s) + 2Na_2S(aq) \rightarrow 2Na_3SbS_3(aq)$	(10)	Baláž (2000b)
Jamesonite ($Pb_4FeSb_6S_{14}$)	$FePb_4Sb_6S_{14}(s) + 3Na_2S(aq) \rightarrow FeS(s) + 4PbS(s) + 6NaSbS_2(aq)$	(11)	Baláž and Achimovičová (2006)
Hg-bearing minerals			
Cinnabar (HgS)	$HgS(s) + Na_2S(aq) \rightarrow Na_2[HgS_2](aq)$	(12)	Baláž et al. (1998)

ted the low extraction of Hg to electrochemical effects caused by interactions between the iron balls used for milling and the process feed (Baláž and Dutková, 2009). Mercury was substantially extracted (>90%) from the concentrate when the same leaching process was applied to the concentrate but without milling (Baláž and Dutková, 2009). This result is consistent with a separate study by Anderson (2003), who reported 95% extraction of Hg after 12 h of ASL. According to Anderson (2003) the Hg in the copper ore deposit at Rožňava, Slovakia is associated with the copper sulphide mineral, tetrahedrite. A number of elements, including Hg, are stable in the crystal structure of tetrahedrite (King, 2001). The general chemical formula for tetrahedrite-tennantite type minerals is $A_{10}B_2C_4$, where A = Cu or Ag, B = Fe, Zn, Mn, Cd, Cu, or Hg, and C = As, Sb, Bi, or Te (Awe, 2010; Hobson et al., 2006). Mercury can also occur separately to Cu in copper concentrates such as in the minerals cinnabar and metacinnabar (HgS) (Anderson, 2003). According to Baláž et al. (1998), Hg is leached from cinnabar according to Reaction 12 (see Table 5). The product of this reaction, $Na_2[HgS_2]$, is a complex salt that requires a base such as sodium hydroxide (NaOH) to prevent its precipitation (Baláž et al., 1998). Sodium hydroxide is added to most practical ASL processes in order to prevent the hydrolysis of sodium sulphide to sodium hydrosulphide (NaHS), which is understood to inhibit the dissolution Sb (Anderson and Krys, 1993).

Anderson (2005) reported extractions for various metals after leaching a range of As- and Sb-containing materials in an alkaline sulphide solution for 6 h at 105 °C. The leach media was prepared by adding elemental sulphur and sodium hydroxide to water (100 g of S and 25 g of OH^- per litre). The added S reacts with sodium hydroxide to form sodium sulphides (including Na_2S) and sodium thiosulphate ($Na_2S_2O_3$) (Anderson et al., 1991). Extractions of Sb and As were >95% for all materials tested. Gold was partially extracted from all materials, including an enargite-rich copper concentrate (14% extraction). Anderson (2016) proposed that the leaching of Au is a result of polysulphide oxidation and sulphide complexation. Extractions were negligible (<1%) for the following metals: Ag, Co, Cu, Cd, Fe, Pb, Ni, and Zn. It has been reported that ASL is effective for the extraction of Bi (Ruiz et al., 2013) and Te (Anderson et al., 2014), however, no data has been found for these two elements.
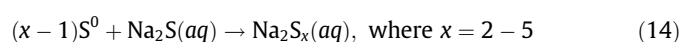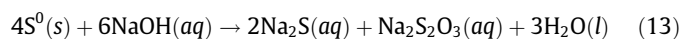
In most studies on the ASL of copper concentrates (e.g., Anderson, 2003; Torres, 2011) Cu is more or less completely retained (>99%) in the solid leach residue. Chalcopyrite ($CuFeS_2$) has been shown to be inert in ASL systems (Awe and Sandström, 2010). The Cu associated with enargite, tennantite, and tetrahedrite is predominantly converted to covellite (CuS) and chalcocite (Cu_2S) (see Table 5), however, can also be transformed to

new species of copper sulphide such as $Cu_{1.5}S$ (Awe and Sandström, 2010; Curreli et al., 2009).

A number of ASL technologies have been developed for the treatment of industrial copper concentrates. Three of the most established technologies are: the Sunshine process, the Equity process, and the Melt process. These technologies are reviewed below.
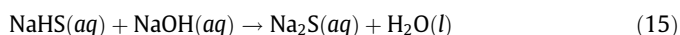
2.1. The Sunshine process

The longest standing industrial application of ASL was at the Sunshine Mine in Idaho, USA. The Sunshine process is based on patented technology by Holmes (1943). It was designed to leach Sb from a tetrahedrite-rich copper concentrate containing approximately 19 wt% Sb so that the Sb content was reduced to below 1 wt%. The leach solution consisted of: elemental sulphur; sodium hydroxide; sodium carbonate; and an alkaline-sulphide-rich electrolyte solution, which was recycled from a downstream electrowinning circuit used to recover Sb from the leach solution. Elemental sulphur was used as a reagent since it was in ready supply from a downstream silver refinery. The sulphur reacts with sodium hydroxide to form sodium sulphide, sodium polysulphide (Na_2S_x, where x = 2–5), and sodium thiosulphate ($Na_2S_2O_3$) according to Reactions 13 and 14 (Anderson, 2012). Anderson and Krys (1993) reported results from an experimental investigation into the influence of the initial concentrations of these species on the extraction of Sb in the Sunshine process. Increasing the concentration of sulphide from 75 to 150 g L^{-1} enhanced both the rate and extent of leaching of Sb. Increasing the concentration of thiosulphate from 0 to 100 g L^{-1} also enhanced the rate and extent of leaching of Sb. The rate of leaching of Sb decreased with increasing polysulphide concentration. The total extent of leaching reached a maximum when polysulphide accounted for 20% of the initial sulphide content in the leach solution. Increasing the proportion of polysulphide above this value caused substantial reductions in the extent of leaching of Sb.

$$4S^0(s) + 6NaOH(aq) \rightarrow 2Na_2S(aq) + Na_2S_2O_3(aq) + 3H_2O(l) \quad (13)$$

$$(x-1)S^0 + Na_2S(aq) \rightarrow Na_2S_x(aq), \text{ where } x = 2-5 \quad (14)$$

2.2. The Equity process

Equity Silver Mines Ltd. developed their own ASL process in British Columbia, Canada, in order to leach Sb and As from a concentrate rich in Cu, Au, and Ag. The Equity process was initially operated to reduce the As and Sb contents in the concentrate from around 7 wt% Sb and 4 wt% As to 0.3 wt% Sb and 1.5 wt% As

(Dayton, 1982). In-house tests on the Equity process showed a non-linear correlation between the extent of leaching of Sb and reagent consumption (Edwards, 1985). According to Edwards (1985), reductions in the residual content of Sb below 0.5 wt% required exponentially increasing amounts of reagent. The targets for Sb and As extraction were later relaxed to 0.8 wt% Sb and 2 wt% As in order to reduce reagent consumption (Edwards, 1985). The potential for extraction of As in the Equity process was largely limited by the amount of insoluble arsenopyrite in the concentrate feed (Edwards, 1985). Sodium hydrosulphide and sodium hydroxide were used as reagents in the Equity process. Sodium hydrosulphide reacts with sodium hydroxide to form sodium sulphide according to Reaction 15. Attempts to recycle sodium sulphide from a downstream arsenic precipitation circuit were unsuccessful (Edwards, 1985). Instead, sodium sulphide was oxidised and crystallised to form high purity sodium sulphate (Na_2SO_4) (Edwards, 1985, 1991) which was sold to paper mills (Filippou et al., 2007).

$$NaHS(aq) + NaOH(aq) \rightarrow Na_2S(aq) + H_2O(l) \qquad (15)$$

2.3. The Melt process

The Melt (mechano-chemical leaching of tetrahedrites) process was developed at pilot scale in Krompachy, Slovakia, in order to leach Sb and As from a tetrahedrite-rich copper concentrate from the Maria Rožňava Mine. In the Melt process milling of concentrate particles and ASL are integrated into one step (Baláž, 2000b). During milling crystal structures become temporarily disordered and are theoretically more susceptible to leaching (Baláž and Achimovičová, 2006). These effects are not always stable and can have short relaxation times (<10 s) (Baláž and Achimovičová, 2006). The concept behind mechano-chemical leaching is that leaching occurs immediately after milling, before the crystals have time to relax from their disordered state (Baláž and Achimovičová, 2006). Experiments have shown mechano-chemical leaching to substantially improve the kinetics of Sb and As leaching from tetrahedrite-tennantite group minerals (Baláž, 2000a). Maximum extraction of Sb and As is achieved within 30–40 min in the Melt process (Baláž, 2000a).

The operating parameters used in the Sunshine process, Equity process, and Melt process are compared in Table 6. All three processes operate at atmospheric pressure and close to the boiling temperature of the slurry. The residence time in the Melt process

is an order of magnitude lower than the retention times in the Sunshine process and Equity process. This can be attributed to superior leaching kinetics in the Melt process. Reagent consumption in the Sunshine process is lower than that in the Melt process. The difference in reagent requirements is likely due to recycle of sulphide-rich electrolyte solution (produced in an electrowinning circuit used to recover Sb) in the Sunshine process.

The Sunshine process and Equity process are no longer used in industry. The Melt process was only ever operated at pilot scale. Indophil Resources NL recently reported the use of an ASL process to selectively extract As from a copper-gold concentrate in a pre-feasibility study on the mining of copper and gold at the Tampakan mine in the Philippines (Indophil Resources NL, http://www.indophil.com). Details of this process were not released.

3. Hypochlorite leaching

Hypochlorite leaching is another leach system developed for the selective extraction of As from copper concentrates (Curreli et al., 2005; Mihajlovic et al., 2007; Viñals et al., 2003). In most studies hypochlorite leaching is carried out at atmospheric pressure, at relatively low temperatures (20–60 °C), and at alkaline pH (pH 12–12.5). Sodium hydroxide is generally added to the leach solution to maintain alkaline conditions (Viñals et al., 2003).

The majority of research on hypochlorite leaching of copper concentrates has focused on the extraction of As from enargite-group minerals (Mihajlovic et al., 2007; Musu et al., 2009; Viñals et al., 2003), or from enargite-rich copper concentrates (Curreli et al., 2005; Mitovski et al., 2015). There is general consensus in the literature that sodium hypochlorite (NaClO) reacts with enargite according to Reaction 16. X-ray diffraction (XRD) and scanning electron microscopy/energy dispersive spectrometry (SEM/EDS) analyses of enargite leach residues have confirmed the formation of insoluble tenorite (CuO) (Curreli et al., 2005; Mihajlovic et al., 2007; Musu et al., 2009). Laboratory-scale experiments (Viñals et al., 2003) have shown high conversions of enargite (>95%) within less than 1 h of leaching at reaction temperatures in the range 40–60 °C. In these experiments the concentrations of hypochlorite and hydroxide were maintained at 0.13 M and 0.03 M, respectively (Viñals et al., 2003). According to Curreli et al. (2005) the optimum pH for the extraction of As from enargite is 12.5. The rate of extraction of As is reduced at lower values of pH

Table 6
Summary of operating parameters used in ASL technologies.
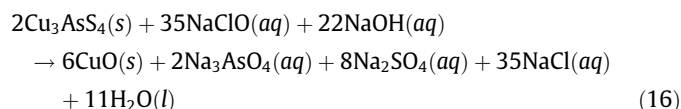
	Sunshine process Ackerman et al. (1993), Anderson et al. (1991)	Equity process Dayton (1982), Edwards (1985, 1991)	Melt process Baláž (2000b, 2003), Baláž and Achimovičová (2006), Baláž and Dutková (2009)
Commercial (C)/pilot plant (PP)	C (1940s–2001)	C (1981–1994)	PP (1990s)
Mode of operation	Batch	Batch	Continuous
Production	20 tonne day^{-1}	90 tonne day^{-1}	0.5 tonne day^{-1}
Retention/residence time	8–12 h	8 h	1 h
Temperature	104 °C	107 °C	88–105 °C
Pressure	Atmospheric	Atmospheric	Atmospheric
Minerals in feed	Tetrahedrite, pyrite, galena, bornite	Tetrahedrite, tennantite, chalcopyrite, pyrite, sphalerite, galena, arsenopyrite	Tetrahedrite, pyrite, chalcopyrite, siderite, quartz
Slurry density	200 g L^{-1}	Up to ~600 g L^{-1}	300 g L^{-1}
Initial particle size	70% <200 mesh	nd[a]	60% <200 mesh
Reagent additions:	Na$_2$S: 100 g L^{-1} (equivalent)[b]	NaHS[c]	Na$_2$S: 300 g L^{-1}
	NaOH: 15 g L^{-1}	NaOH: nd	NaOH: 50 g L^{-1}
	Na$_2$CO$_3$: 25 g L^{-1}		

[a] nd = no data.
[b] Elemental sulphur is dissolved in NaOH to produce Na$_2$S.
[c] Addition of NaHS is adjusted according to the concentrations of Sb and As in the feed. The molar ratio of S^{2-}/(Sb + As) was set to ~2.

(Curreli et al., 2005). At higher values of pH, sodium hypochlorite rapidly decomposes (Curreli et al., 2005).

$$2Cu_3AsS_4(s) + 35NaClO(aq) + 22NaOH(aq)$$
$$\rightarrow 6CuO(s) + 2Na_3AsO_4(aq) + 8Na_2SO_4(aq) + 35NaCl(aq)$$
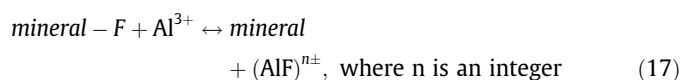$$+ 11H_2O(l) \tag{16}$$

Studies which address hypochlorite leaching of penalty elements from minerals other than enargite are scarce. According to Filippou et al. (2007), As associated with realgar, orpiment, tennantite, and luzonite (Cu_3AsS_4) are readily dissolved during hypochlorite leaching. It has also been reported that Te associated with gold tellurides is extracted (Filippou et al., 2007) and that Sb is not extracted to any appreciable extent during hypochlorite leaching of copper concentrates (Ruiz et al., 2013), however no published data has been found to support these claims. Mihajlovic et al. (2007) studied the selectivity of hypochlorite leaching by individually leaching the following copper sulphide minerals in a solution containing 0.3 M of NaClO and 5 g L^{-1} of NaOH: enargite, realgar, covellite, chalcocite, and chalcopyrite. Analysis of the leach residues indicated that 99% of the enargite, 97% of the realgar, 32% of the covellite, 5% of the chalcocite, and 16% of the chalcopyrite had reacted. This result implies poor selectivity of hypochlorite for As-bearing minerals.

When compared with ASL, hypochlorite leaching is typically much faster. Rates of extraction of As in hypochlorite leaching processes are generally an order of magnitude higher than rates of extraction of As in ASL processes. Nevertheless, hypochlorite leaching has been largely limited to laboratory-scale studies and unlike ASL, has not been employed on an industrial scale. Two key issues have been identified with the use of hypochlorite leaching for the treatment of industrial copper concentrates:

(1) Sodium hypochlorite has relatively poor selectivity for As. Copper sulphide minerals which do not contain As, particularly covellite, react to a significant extent during hypochlorite leaching (Filippou et al., 2007; Mihajlovic et al., 2007).
(2) High additions of hypochlorite (typically 250–740 g ClO$^-$ per kg of concentrate (Filippou et al., 2007)) are needed for effective extraction of As. This may partially be attributed to the poor selectivity of hypochlorite for As but also to reaction stoichiometry. Complete conversion of one mole of enargite requires 17.5 mol of sodium hypochlorite (see Reaction 16).

4. Dilute sulphuric acid leaching with aluminium sulphate

Fluorine is selectively extracted from metal ore concentrates by leaching with sulphuric acid (H_2SO_4) in the presence of aluminium sulphate ($Al_2(SO_4)_3$). Jomoto and Hughes (1995) present a general equation for this leach system (Reaction 17). According to these two authors and to Torrisi (2001), two soluble species of aluminium fluoride are formed, AlF^{2+} and AlF_2^+, as well as several species of aluminium fluoride which are either insoluble or are only sparingly soluble, including AlF_3, AlF_4^-, AlF_5^{2-}, and AlF_6^{3-}. Leaching is typically carried out at atmospheric pressure and at ambient to slightly elevated temperatures ($\sim$60 °C).

$$mineral - F + Al^{3+} \leftrightarrow mineral$$
$$+ (AlF)^{n\pm}, \text{ where n is an integer} \tag{17}$$

The role of sulphuric acid is to control the pH of the leach solution. The optimum pH for the extraction of F is thought to be somewhere between pH 3.0 and 4.3 (Jomoto and Hughes, 1995; Torrisi, 2001). Below this range, fluoride ions react with hydrogen ions to form undissociated hydrogen fluoride, which reduces the availability of fluoride ions for reaction with Al^{3+} and may slow the rate of
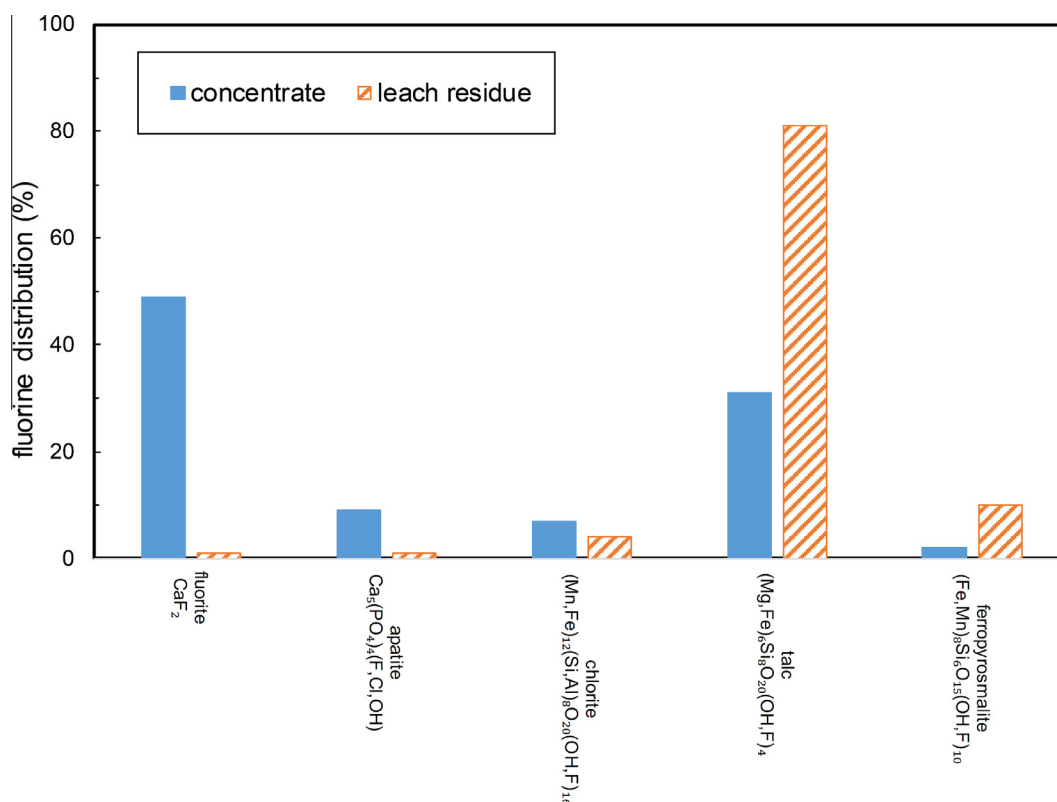

Fig. 1. Distribution of F between different mineral forms before and after leaching a zinc concentrate with dilute sulphuric acid and aluminium sulphate. All data from Torrisi (2001).

Table 7
Operating parameters recommended for sulphuric acid leaching of flotation concentrates with aluminium sulphate. All data from Jomoto and Hughes (1995).

Reagents	$Al_2(SO_4)_3$, H_2SO_4
Particle size	90% < 37 μm
Al:F ratio (molar)	At least 1:1
Solids density	20–60%
pH	2.8–3.8
Oxidation redox potential	−200 to +100 mV
Temperature	25–60 °C
Residence time	2 h

extraction of F from the concentrate (Jomoto and Hughes, 1995). Above this range, aluminium precipitates from solution as aluminium hydroxide (Torrisi, 2001).

The zinc and lead concentrates produced at South32's Cannington mine in Queensland are acid leached with aluminium sulphate at atmospheric pressure in order to remove F (Torrisi, 2001). Torrisi (2001) compared the distribution of F among the main F-bearing minerals in the zinc concentrate with that in the leach residue. The results from the analyses are presented in Fig. 1. The F in the zinc concentrate was found to be associated with fluorite, apatite, and various silicate minerals including: talc, chlorite, and ferropyrosmalite. Fluorine associated with fluorite and apatite was more or less completely leached. Fluorine associated with chlorite was partially leached. Fluorine associated with talc and ferropyrosmalite was insoluble. The majority of the residual F was associated with these two silicate minerals.

The zinc concentrate produced at Cannington is leached with an Al:F ratio (molar) of 0.5–1.0 (Torrisi, 2001). This range is just above the theoretical minimum amount of Al needed for complete dissolution of F in fluorite, the main F-bearing mineral in the concentrate (see Fig. 1). According to Torrisi (2001), the theoretical minimum Al:F ratio is 0.5. Maximum extraction of F from fluorite is approached within 2 h of leaching in the Cannington process (Torrisi, 2001). The kinetics of leaching of chlorite has not been formally investigated in the Cannington process. Bench-scale leaching experiments by Tan et al. (2009) have indicated that chlorite is leached by different mechanism to fluorite.

Although there are no known cases in industry where sulphuric acid leaching with aluminium sulphate has been used for the treatment of copper concentrates, the process is considered suitable for the selective extraction of F from copper concentrates according to international patent WO 95/01460 (Jomoto and Hughes, 1995). The operating parameters recommended in this patent are summarised in Table 7.

Copper concentrate produced at BHP Billiton's Olympic Dam mine in South Australia is leached in dilute sulphuric acid without addition of aluminium sulphate. Ragozzini et al. (1986) studied the extraction of F in this process. The principal F-bearing mineral in the copper ore deposit at Olympic Dam is fluorite (Reeve et al., 1990). Fluorite enriched regions can contain as much as 1–2 wt% F (Reeve et al., 1990). High extractions of F (>90%) were reported after leaching for 24 h at temperatures in the range 30–60 °C and with an initial sulphuric acid concentration in the range 40–98 g L^{-1}. The extent of extraction of F decreased to around 15–20% when the initial concentration of sulphuric acid was reduced to 9.8 g L^{-1}. Importantly, leaching with dilute sulphuric acid (<98 g L^{-1}) did not extract appreciable quantities of copper from the concentrate. The results from this study demonstrate that fluorite can be effectively leached from copper concentrate without addition of aluminium sulphate provided that the concentration of sulphuric acid is sufficiently high (above 40 g L^{-1}). It is noted that the amount of sulphuric acid needed to extract F in the

absence of aluminium sulphate is greater than that needed in the presence of aluminium sulphate.
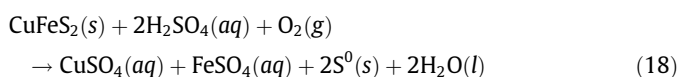
Dilute sulphuric acid is also an effective lixivant for the extraction of U. The Commonwealth Scientific and Industrial Research Organisation (CSIRO) studied the extraction of U in dilute sulphuric acid from copper concentrates with two distinct types of copper mineralogy: bornite-chalcopyrite mineralogy (Ragozzini et al., 1986); and chalcocite-bornite mineralogy (Ragozzini and Sparrow, 1987). Uraninite (UO_2) was the principal U-bearing mineral in both concentrates. High extractions of U (>90%) were reported for both types of concentrate after leaching for 24 h at initial sulphuric acid concentrations above 40 g L^{-1}. The authors concluded that the differences in copper mineralogy had little effect on the extraction of U.

The extraction of U in dilute sulphuric acid may reduce the level of radioactivity (associated with the ^{238}U decay series) in the upgraded copper concentrate. In order to effectively remove radioactivity from copper concentrates only the moderate- to long-lived radionuclides in the ^{238}U decay series (^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Pb, and ^{210}Po) need to be leached. The short-lived radionuclides with half-lives smaller than a few days (e.g., ^{234}Pa) will decay to negligible levels within a small period of time. Published literature on the behaviour of the moderate- to long-lived radionuclides in copper concentrate leaching processes is scarce. It may be that some radionuclides are located in the same sites in the copper concentrate as the parent uranium and that these species are extracted along with U during leaching. Fundamental research is needed to firstly understand the occurrence modes (both spatial distribution and chemical bonding) of these radionuclides in copper concentrates, and then, to determine the partitioning of these species between the different product streams in dilute sulphuric acid leaching processes, as well as in other selective leaching processes used to treat copper concentrates with high levels of radioactivity. In the case that the radionuclides are leached to different extents, concentrate shipping and handling procedures may need to be revised since different regulations apply for radioactive materials which are not in secular equilibrium.
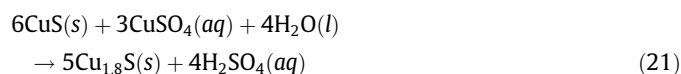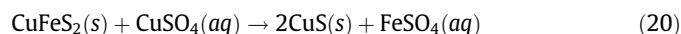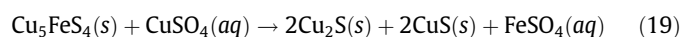
5. Pressure oxidation/copper precipitation leaching

There are a large number of patented processes (e.g., Collier et al., 2004; Dunn and Bartsch, 2008; Dunn et al., 2014; McGauley et al., 1951; McKay and Parker, 1977) which are based on the combination of pressure oxidation (POX) leaching and copper precipitation leaching of chalcopyrite-rich copper concentrates.

POX leaching is used to remove gangue material (e.g., pyrite) but also to partially dissolve copper sulphide minerals, including chalcopyrite. The dissolved copper plays an important role in copper precipitation leaching. Chalcopyrite is generally refractory at ambient temperatures and at atmospheric pressure (Schlesinger et al., 2011). Elevated temperatures and pressures are needed to release copper from this mineral into solution. POX leaching is usually carried out in sulphuric acid media (Abed, 1999) but can also be carried out in other acids such as HCl (Habashi and Toor, 1979; Mizoguchi and Habashi, 1981). An oxygen-bearing gas (e.g., air) is generally used to create oxidising conditions but sometimes a chemical oxidant (e.g., ferric iron) is used instead. The general equation for POX leaching of chalcopyrite in sulphuric acid media is shown below (Reaction 18) (Harvey and Yen, 1998). The Cu and Fe in chalcopyrite are converted to soluble sulphates. The S is converted to elemental form.

$$CuFeS_2(s) + 2H_2SO_4(aq) + O_2(g)$$
$$\rightarrow CuSO_4(aq) + FeSO_4(aq) + 2S^0(s) + 2H_2O(l) \quad (18)$$

Copper precipitation leaching of Cu-Fe-sulphides involves the exchange of Fe and S in the Cu-Fe-sulphide minerals for copper ions dissolved in the leach solution. During this exchange dissolved copper ions are precipitated and Fe and some S are dissolved. The exchange reactions are referred to as "metathesis reactions" and occur in both non-oxidising and reducing environments. Under non-oxidising conditions bornite is converted to covellite and to chalcocite according to Reaction 19 (Abed, 1999). Chalcopyrite is converted to covellite according to Reaction 20 (Abed, 1999). The formed covellite may further react to form digenite ($Cu_{1.8}S$) according to Reaction 21 (Abed, 1999). Similar reactions describe the conversion of chalcopyrite to Fe- and S-depleted copper sulphides under reducing conditions (Dreisinger and Abed, 2002; Hiskey and Wadsworth, 1975). Chemical metathesis results in enrichment of copper in the concentrate by rejection of Fe and S from copper sulphide minerals as well as recovery of dissolved Cu (generated during POX leaching) from the leach solution.

$$Cu_5FeS_4(s) + CuSO_4(aq) \rightarrow 2Cu_2S(s) + 2CuS(s) + FeSO_4(aq) \quad (19)$$

$$CuFeS_2(s) + CuSO_4(aq) \rightarrow 2CuS(s) + FeSO_4(aq) \quad (20)$$

$$6CuS(s) + 3CuSO_4(aq) + 4H_2O(l)$$
$$\rightarrow 5Cu_{1.8}S(s) + 4H_2SO_4(aq) \quad (21)$$

POX/copper precipitation leaching processes tend to be optimised for the enrichment of copper rather than for the deportment of penalty elements. Many studies have focused on the behaviour of Cu in both POX leaching (Dreisinger, 2006; Hackl et al., 1995; McDonald and Muir, 2007a, 2007b) and in copper precipitation leaching (Bartlett, 1992; Dreisinger and Abed, 2002; Fuentes et al., 2009a; Sequeira et al., 2008). Much less research has been done to understand the leaching behaviour of penalty elements in these processes.

Fuentes et al. (2009b) studied the influence of leaching temperature and concentration of Cu^{2+} ions on the extraction of ten penalty elements (As, Bi, Cd, Hg, Mo, Pb, Sb, Te, Tl, Zn) during copper precipitation leaching of copper concentrates produced at the Chuquicamata mine in Chile. Possible host sites for the penalty elements were enargite, sphalerite (ZnS), galena (PbS), and molybdenite (MoS_2). These minerals were identified in XRD, reflected-light microscopy, and SEM/EDS analyses of the concentrate samples. The following elements were substantially extracted (~80%) at a reaction temperature of 225 °C: Bi, Cd, Tl, and Zn. Extractions were moderate (40–70%) for Pb and Te and were the lowest (20–40%) for As, Hg, Mo, and Sb. Decreasing the reaction temperature significantly reduced extractions for all penalty elements over the range 150–225 °C. The concentration of Cu^{2+} ions had negligible effect on the extraction of penalty elements over the range 1–85 g L^{-1}.

Viñals et al. (2004) studied the dissolution of pure sphalerite in acidic solutions containing different concentrations of copper sulphate. The concentration of soluble Cu^{2+} ions had minimal impact on the rate of dissolution of Zn over the range 1–10 g L^{-1}. This finding is consistent with results reported by Fuentes et al. (2009b). SEM/EDS analyses of partially reacted sphalerite particles revealed the formation of an outer layer of copper-sulphide around a shrinking core of sphalerite. Based on these results Viñals et al. (2004) proposed that the rate of sphalerite dissolution during copper precipitation leaching is controlled by diffusion of Cu^{2+} and Zn^{2+} ions through the layer of solid copper sulphide.

Harvey and Yen (1998) studied the extraction of zinc from artificial concentrate samples during POX leaching in sulphuric acid media. A high extraction (>90%) of Zn was reported from pure sphalerite after 240 min of leaching at a reaction temperature of 210 °C and at an oxygen partial pressure of 689 kPa. Lowering

the reaction temperature and oxygen partial pressure significantly reduced the extraction of Zn. The influence of mineralogical composition on the extraction of Zn was studied by leaching concentrate mixtures with varying proportions of sphalerite (0–100%), chalcopyrite (0–75%), pyrite (0–75%), and galena (0–75%). Pyrite additions up to 10% improved selectivity by increasing the extraction of zinc and reducing the extraction of copper. The reduced extraction of copper was attributed to the formation of ferrous sulphate, which retards the dissolution of chalcopyrite. Pyrite additions above 10% had the opposite effect on selectivity. The increased dissolution of copper at pyrite additions above 10% was attributed to the formation of high levels of free acid. The addition of galena inhibited the extraction of Zn. According to Harvey and Yen (1998), galena competes with sphalerite for oxygen, and can therefore reduce the extent of oxidation of sphalerite to soluble zinc sulphate. The formation of insoluble, zinc-bearing plumbojarosites is also thought to account for the reduced extraction of zinc (Harvey and Yen, 1998).

Anode slimes produced during the electrorefining of copper often contain commercial quantities of Cu, Au, Ag, Se, and Te (Cooper, 1990), and are sometimes subject to POX leaching in sulphuric acid media in order to recover the Cu and Te. Former mining company, Noranda Mines Ltd., claimed virtually complete extraction of copper and at least 75% extraction of Te from anode slimes in their POX process (Morrison, 1977). Newmont Mining also claimed substantial extraction of Cu, however, claimed a lower extraction for Te (30%) in their POX process (Yannopoulos and Borham, 1978).

There are two patented processes which deal specifically with the deportment of penalty elements in combined POX/copper precipitation leaching processes. One of these processes (McKay and Parker, 1977) was patented by former mining company Cominco Ltd. and the other (Dunn et al., 2014) by metallurgy consulting company Orway Minerals Consultants (OMC). These two processes (hereafter referred to as the "Cominco process" and the "OMC process") are reviewed below.

5.1. The Cominco process

The Cominco process was developed to separate Co, Ni, Zn, and Pb from chalcopyrite-rich copper concentrates (McKay and Parker, 1977). Cobalt, Ni, and Zn are all dissolved in the Cominco process. Lead is not dissolved but is converted to a form (lead sulphate) which facilitates its separation from Cu by flotation. Leaching is carried out in two consecutive stages: POX leaching and then copper precipitation leaching. The products (both solid and liquid) from the copper precipitation leach are subject to differential flotation in order to separate the formed lead sulphate from copper sulphides.

A schematic of the Cominco process is shown in Fig. 2. Impure copper concentrate is fed to the POX reactor with sulphuric acid, copper sulphate ($CuSO_4$), and an oxygen-bearing gas. Lead contained in galena reacts to form insoluble lead sulphate, presumably according to Reaction 22 (Harvey and Yen, 1998). Cobalt, Ni, and Zn which are present as sulphides are primarily converted to soluble sulphates. Covellite, chalcocite, and bornite dissolve, forming soluble copper sulphate. Chalcopyrite dissolves only to a minor extent. The concentration of free sulphuric acid is carefully controlled (10–70 g L^{-1}) in order to minimise the dissolution of chalcopyrite. It is claimed that no more than 20% of the total Cu reacts during POX leaching (McKay and Parker, 1977). A small portion of the Cu, Zn, Fe, and Pb in the concentrate react to form insoluble jarosites.
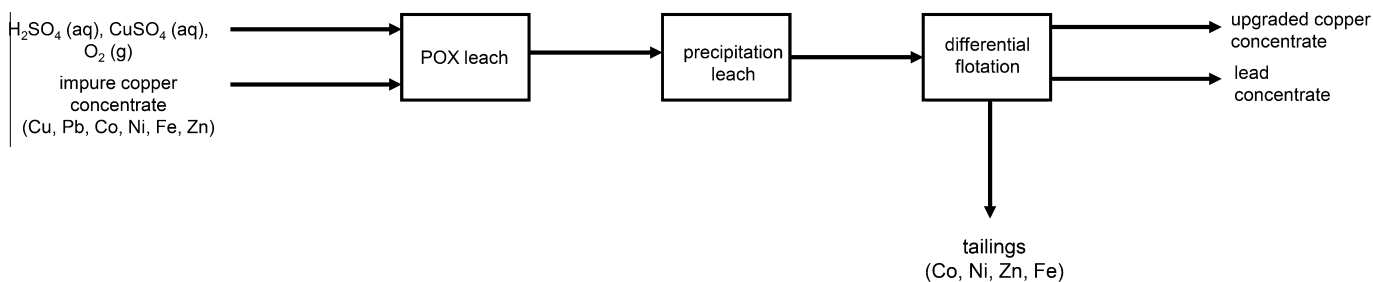
$$PbS(s) + H_2SO_4(aq) + \frac{1}{2}O_2 \rightarrow PbSO_4(s) + S^0(s) + H_2O(l) \quad (22)$$

H₂SO₄ (aq), CuSO₄ (aq), O₂ (g)

impure copper concentrate (Cu, Pb, Co, Ni, Fe, Zn)

Fig. 2. Simplified schematic of the Cominco process.

H₂SO₄ (aq), O₂ (g)

POX leach

impure copper concentrate (Cu, Fe, radionuclides)

precipitation leach

liquor neutralisation and solids to tailings (Fe, radionuclides)

S/L

(L)   (S)
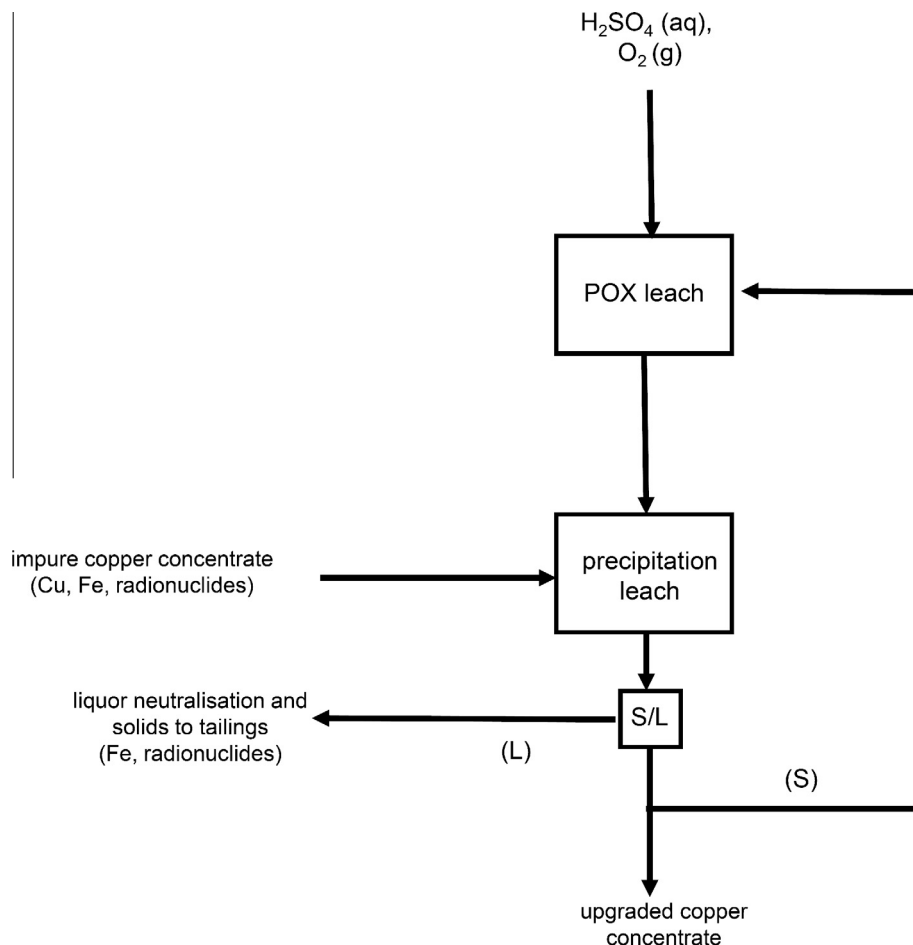
upgraded copper concentrate

Fig. 3. Simplified schematic of the OMC process.

The products from the POX leach are fed directly to the copper precipitation leach. Copper precipitation leaching is carried out at a higher temperature than used in the POX leach, in an oxygen-free gas atmosphere, and at autogenous pressure. Insoluble jarosite compounds formed in the POX leach decompose. The lead and copper associated with jarosites are converted to insoluble lead sulphate and insoluble copper sulphides. Dissolved copper sulphate reacts with part of the residual chalcopyrite to form insoluble copper sulphides and aqueous ferrous sulphate (see Reactions 20 and 21). These reactions lead to rejection of Fe from chalcopyrite and therefore result in an upgrade in the copper content of the concentrate. Virtually all of the copper is recovered (>99%) in the leach residue. The Co, Ni, and Zn remain dissolved in the leach medium. It is claimed that 85–95% of the total Co and Ni are extracted in the Cominco process. No claims are made regarding the extraction of Zn.

5.2. The OMC process

The OMC process was developed for the removal of radionuclides from the ^{238}U decay series, specifically ^{238}U, ^{230}Th, ^{226}Ra, ^{210}Pb, and ^{210}Po, from copper sulphide concentrates which contain export limiting levels of radioactivity. According to the inventors (Dunn et al., 2014), Co, Ni, and Zn are also removed in the OMC process, however, no claims are made regarding the deportment of these elements. A simplified schematic of the OMC process is shown in Fig. 3. The impure copper concentrate is first fed to the copper precipitation leach rather than to the POX leach. The product from the copper sulphate leach is separated by physical processes (including, but not limited to sedimentation and filtration) into a predominately liquid phase stream and a concentrated slurry which contains the upgraded copper concentrate. An unspecified portion of the upgraded copper concentrate is washed

Table 8

Operating parameters specified for the Cominco process (McKay and Parker, 1977) and OMC process (Dunn et al., 2014). Simplified schematics of the Cominco process and OMC process are provided in Figs. 2 and 3, respectively.

	Cominco process	OMC process
Feed properties		
Slurry density (g L^{-1})	670	ns[a]
Feed particle size	d$_{90}$ < 44 μm	ns
Reagents:	H$_2$SO$_4$: 10–70 g L^{-1}	H$_2$SO$_4$: 1–50 g L^{-1}
	CuSO$_4$: 20–80 g L^{-1}	Cl$^-$: ns
Pressure oxidation (POX) leach		
Temperature (°C)	90–115	140–180
Partial pressure of O$_2$ (kPa)	689–1379	200–1000
Retention time (h)	1–5	0.25–6
Copper precipitation leach		
Temperature (°C)	150–180	160–240
Total pressure (kPa)	Autogenous	0.5–3.5
Oxidising redox potential (mV, Ag/AgCl 3.8 M KCl)	Non-oxidising[b]	200–450
Retention time (h)	1–5	0.5–8

[a] ns = not specified.
[b] Precise values are not specified.

with freshwater and then recycled to the POX reactor. Controlled additions of sulphuric acid are made to the POX reactor so that the free acid concentration is maintained within the range 1–50 g L^{-1}. The product from the POX reactor is fed directly into the copper precipitation leach reactor without cooling. The oxidation-redox potential is controlled (200–450 mV, Ag/AgCl 3.8 M KCl) during copper precipitation leaching by limiting the feed of oxygen-bearing gas to the reactor or by adding small quantities of chemical oxidants. It is reported that the lixivant used in the copper precipitation leach contains chloride ions. It is not clear what role the chloride ions play in the copper precipitation leach or where and in what quantities the chloride ions are introduced to the process.

It is claimed that there is above 90% extraction of U and Th, and at least 30% extraction of Ra, Pb, and Po in the OMC process (Dunn et al., 2014). No claims are made regarding the recovery of Cu in the OMC process other than that the product from the copper precipitation leach contains no more than 50 g L^{-1} of soluble copper.

The OMC process is more complex than the Cominco process in that it involves recycle of solids between the POX leach and copper precipitation leach. The operating parameters used in the OMC process are compared with those used in the Cominco process in Table 8. It is difficult to compare sulphuric acid consumption in the two processes since such a broad range of acid additions (1–50 g L^{-1}) has been specified for the OMC process. Copper sulphate solution is added to the Cominco process (20–80 g L^{-1}) but not to the OMC process. The reason for adding copper sulphate in the Cominco process is to enhance the dissolution of Co and Ni during POX leaching. It is reported that the total extraction of these two penalty elements increases from 70–85% to 85–95% with the addition of copper sulphate (McKay and Parker, 1977). The ranges of operating temperatures used in the OMC process are higher than those used in the Cominco process for both the POX and copper precipitation leach. Ranges of retention times specified for the OMC process and Cominco process are similar for both the POX leach and the copper precipitation leach.

6. Conclusions

Several leach systems have been developed for the selective extraction of penalty elements from copper concentrates.

Alkaline sulphide leaching (ASL) has previously been employed in industry for the extraction of As and Sb from tetrahedrite-rich copper concentrates. This leach system is characterised by almost complete recovery of Cu into the solid leach residues. Most research into ASL has focused on the leaching behaviour of As and Sb. A large number of As- and Sb-bearing minerals dissolve, including: enargite, tennantite, realgar, orpiment, arsenic trioxide, tetrahedrite, stibnite, and jamesonite. Arsenopyrite is highly insoluble in ASL. The extent of extraction of As in industrial ASL processes is limited to the distribution of As between arsenopyrite and soluble forms. Experimental investigations have shown ASL to extract Hg associated with tetrahedrite-tennantite type minerals. Other penalty elements may also be extracted from copper concentrates during ASL, including Bi and Te, however further research is needed to better understand the behaviour of these elements.

Arsenic associated with enargite minerals is extracted from copper concentrates by leaching with sodium hypochlorite. The rate of As leaching is generally much higher in hypochlorite leaching processes than in ASL processes. The leaching characteristics of penalty elements associated with minerals other than enargite during hypochlorite leaching are not well understood. Two main drawbacks have been identified with hypochlorite leaching of copper concentrates: poor selectivity of the reagent for As (i.e. minerals which do not contain As also react to an appreciable extent) and high reagent consumption for effective extraction of As. Applications of hypochlorite leaching have so far been limited to laboratory-scale studies.

Dilute sulphuric acid leaching with aluminium sulphate is used in industry for the extraction of F from zinc and lead concentrates. Fluorine associated with fluorite, apatite, and chlorite is soluble in this leach system. Mineralogical analyses of leach residues indicate that F associated with talc and ferropyrosmalite is refractory. Laboratory experiments and operating experience have shown that it is possible to selectively leach fluorite from copper concentrates without addition of aluminium sulphate to the leach medium, provided that the concentration of sulphuric acid is sufficiently high (at least 40 g L^{-1}).

Leaching processes based on the combination of pressure oxidation (POX) leaching and copper precipitation leaching have received a large amount of commercial interest. Such leach systems not only extract penalty elements from copper concentrates but also result in significant upgrade in the copper content of the concentrate by dissolving major gangue minerals and rejecting Fe and S from Cu-Fe-sulphide minerals. Two POX/copper precipitation leaching processes have been developed specifically for the deportment of penalty elements from copper sulphide concentrates. One of these processes was patented by Cominco Ltd. and the other by Orway Mineral Consultants (OMC). In the Cominco process, Co, Ni, and Zn are leached from a chalcopyrite-rich copper concentrate. Lead is not leached in the Cominco process but is converted to a form which facilitates its separation from copper sulphides in flotation processes. In the OMC process, radionuclides from the ^{238}U decay series are leached from a copper sulphide concentrate which contains export limiting levels of radioactivity. High extractions are claimed for U and Th (minimum of 90%). Lower minimum extractions (30%) are claimed for Ra, Pb, and Po. Other separation techniques may be needed to reduce the activity concentrations of ^{226}Ra, ^{210}Pb, and ^{210}Po to acceptable levels.

The performance of a given leach system, in terms of its ability to selectively remove penalty elements from a copper concentrate, is largely determined by the chemical and physical properties of the concentrate, especially the concentrations and mineral speciation of the penalty elements. The feasibility of employing the reviewed leach systems in commercial processes will ultimately depend not only on their performance but also on a number of

external factors, such as: charge rates and restrictions on penalty elements; the availability and price of reagents; and the economic potential of recovering valuable elements from the leachate.

Acknowledgements

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