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# Selective leaching of penalty elements from copper concentrates: A review

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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.



**Contents**



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## 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".

**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 |

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