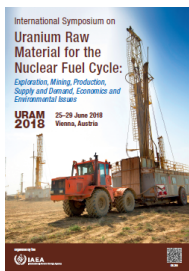


International Symposium on Uranium Raw Material for the Nuclear Fuel Cycle: Exploration, Mining, Production, Supply and Demand, Economics and Environmental Issues (URAM-2018)



Contribution ID: 135

Type: ORAL

The Removal of Radiation and other Impurity from Copper Sulphide Concentrates

Thursday, 28 June 2018 10:00 (20 minutes)

INTRODUCTION

High-grade, copper sulfide concentrates, (typically greater than about 25% w/w Cu), are commonly treated via pyrometallurgical routes, while hydrometallurgical routes are typically favoured for lower grade or impurity bearing concentrates. The processing routes for the treatment of copper concentrates can also be influenced by the presence of minor valuable metals such as silver, gold, uranium, palladium and platinum, as well as deleterious metals such as nickel, cobalt, lead and zinc.

Many copper iron sulfide concentrates contain radioactive uranium and its daughters. Other elements such as zinc, nickel, cobalt and aluminium also add to the impurity load. This paper addresses a process that has been successfully demonstrated to remove very significant levels of the radioactivity whilst at the same time upgrading the concentrate so that it attracts reduced transport and treatment costs at smelters. The upgraded concentrates have demonstrated that they satisfy the IAEA Regulations for the Safe Transport of Radioactive Material (2012) (SSR-6) for the transport, trade and processing thereof.

IMPURITY REMOVAL APPROACH

The objective of radionuclide and impurity removal is to produce a smelter quality copper-iron-sulfide concentrate which can be sold, transported across borders and smelted with zero harm. To minimize the prospect of attention at border crossing or port, the concentrate should contain no more than 0.3 to 0.4 Bq/g for ^{238}U , ^{230}Th and ^{226}Ra and no more than 0.8 to 0.9 for ^{210}Pb and ^{210}Po . The radionuclides removed can be disposed with the concentrator tailings in appropriately lined tailings storage facility.

Impurities are invariably locked within the valuable mineral particles. If not locked, they would typically be separated in the flotation process. It is postulated that where the mother (^{238}U) resides, the daughter products, resulting from decay over long time periods, are in close proximity and so if a pathway can be developed to remove the mother (^{238}U), then the same pathway could be exploited to access the daughters. In addition, the superficially transformed nuclides of ^{210}Pb , ^{210}Bi and ^{210}Po possibly exist in different chemical form to those same nuclides locked in the sulfides minerals.

The concentrate leach in a combined sulfate and chloride lixiviant provides not only the opportunity for radionuclides removal but also the removal of other penalty elements such as nickel, cobalt, lead and zinc. Additionally, the copper concentrate is upgraded resulting in a lower mass "super concentrate" being made and hence this will reduce the concentrate transport costs. In some cases, with this mass loss, silver can be rendered "payable" in the upgrade process. If the removal of radionuclides is not required, then a more targeted concentrate leach in a sulfate lixiviant can be applied.

IMPURITY REMOVAL MECHANISM

Early work was conducted in South Africa [1]. It was recognised at the time that the only way for an upgrade to be effective and majority of the copper and sulfur to remain unleached was to adopt the classical metathesis and hydrothermal approach [2][3][4] employed in some Southern African autoclave systems.

The hydrothermal mechanism is kinetically slower than the preferred metathesis metallurgy. As in the case of the metathesis mechanism, the hydrothermal step also requires a mild oxidant for it to be effective.

Metathesis is an electrochemical process in which the soluble cupric cation exchanges for a more electronegative element in the concentrate. For example in the case of iron, the more electronegative element, is solubilised while the copper cation is received into the concentrate matrix in a reduced form. These two mechanisms create pathways into the mineral structure for the other locked elements to escape.

Minerally, the mineral metathetic alteration commences as a “rimming” effect in which covellite (CuS) is formed and thereafter further sulfur depletion ensues to form chalcocite/digenite minerals. Depending on the copper activity in the aqueous phase, sulfur depletion (oxidation) and hence final copper in concentrate grade can be influenced.

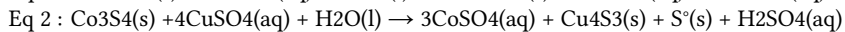
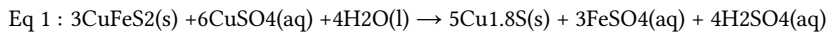
The use of a combined sulfate and chloride lixiviant is suited for the mobilisation and extraction of other elements that have preferred sulfate or chloride lixiviation metallurgy.

The hydrothermal alteration of chalcopyrite is thought to proceed in a different manner. The chalcocite layer once nucleated in the hydrothermal process moves both outwardly and inwardly to convert chalcopyrite to covellite. However, the total conversion to chalcocite may not be economic and consequently, the process is normally terminated with covellite being the dominant mineral in the alteration process [6].

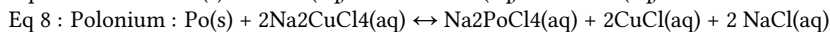
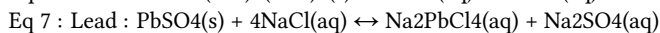
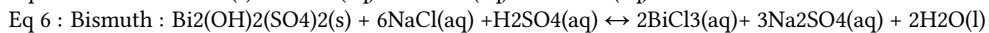
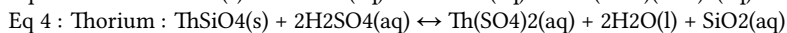
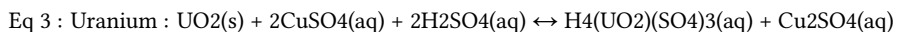
To permit treatment and to maximise the value of a copper concentrate, the levels of impurities in the concentrate needs to be reduced below the limits set by the smelters and in some cases the authorities in the producing and receiving countries. This paper presents a method of impurity (specifically radionuclides) removal for copper concentrates.

CHEMISTRY

Copper concentrates are upgraded via the metathesis process in an autoclaving step called Nonox (a mildly oxidative high temperature environment). Typical chemistry of the upgrade are as shown in equation 1 and 2 below.



The possible chemical reactions for the alteration of other non-sulfide impurities in the concentrate leach are described in equation 3 to 8 below. In sulfate only lixiviant, 238U and 230Th are able to be removed to a level below 1 Bq/g in the copper concentrate. In addition, impurities such as cobalt and nickel are removed. In chloride only lixiviant, there will be no transformation. In sulfate and chloride lixiviant, 238U, 230Th, 226Ra, 210Pb, 210Bi can be removed to a level below 1 Bq/g and to a level below 2Bq/g for 210Po.



FLWSHEET

The principal reagents required in the concentrate treatment flowsheet are a copper ion source, water, sodium chloride (salt) and elevated temperature.

In a typical [5] two stage autoclave flowsheet, the copper concentrate to be upgraded is repulped in recycled brine before it is fed into the Nonox leach autoclave. The copper ions required in Nonox are supplied from a separate close-coupled oxidative Copper Pressure Leach (CPL) autoclave. A portion of the Nonox product is employed in a CPL autoclave which under oxidative conditions is autogenous in temperature. Steam is injected into the Nonox autoclave to control the autoclave at approximately 210°C. Typical conditions in the Nonox autoclave are as follows:

- 2 to 3 hours leach time
- 15-30% w/w concentrate in the autoclave feed slurry
- Greater than 35g/L chloride in Nonox with a Chloride/Sulfate ratio >0.3
- 2500kPa(g)
- 250 to 280 mV and pH of 0.7 to 1.2

The Nonox autoclave discharges into a flash tank. The Nonox discharge slurry is filtered and the filtrate is transferred to the barren liquor treatment circuit for treatment while the filter cake is repulped in clean water.

In the event where it is economical to recover uranium and thorium as by product, the filtrate from the Nonox discharge filter can be treated through a Continuous Ion Exchange unit where uranium and thorium can be recovered. The barren liquor from the ion exchange is then processed to recover the brine.

A portion of the repulped Nonox product is fed to the CPL autoclave while the remainder is treated in scavenging atmospheric leach (SAL) to further remove 226Ra, 210Pb and 210Po. In the SAL, the concentrate is

treated with a two-stage alkali - acid sodium chloride lixiviant. The product from the scavenging atmospheric leach is filtered to produce the final copper concentrate product and the SAL filtrate is incorporated in the barren liquor treatment circuit.

In the barren liquor treatment circuit, the Nonox filtrate is treated using limestone to precipitate the dissolved iron and radionuclides. The barren liquor treatment discharge slurry is then filtered and the filtrate is recycled to the concentrate repulp. The barren liquor treatment residue contains iron and gypsum and essentially all the impurities including radionuclides that were leached in the Nonox autoclave. The filter cake could be disposed in the concentrator tailings facility.

In a preferred variant of the flowsheet a single stage autoclave can be employed to replace the two stage Nonox plus CPL. In the Single Stage Autoclave, a strong oxidative leach is undertaken on the concentrate in the early compartments of the autoclave to produce the cupric lixiviant and this then passes to a mildly oxidative final section of the vessel. These Single Stage autoclaves have been employed in similar duties in Europe and Africa and are not without precedent.

RESULTS

The copper concentrate treatment process has been able to reduce the radionuclides and other impurities to lower levels. A summary of impurity removal and upgrade results for secondary copper sulfide concentrates was as follows:

- 238U level reduced from 1.4 Bq/g to 0.12 Bq/g.
- 230Th level reduced from 1.5 Bq/g to 0.56 Bq/g.
- 226Ra level reduced from 0.99 Bq/g to 0.73 Bq/g.
- 210Pb level reduced from 6.4 Bq/g to 0.35 Bq/g.
- 210Po level reduced from 7.0 Bq/g to 0.62 Bq/g.
- Copper in the concentrate feed was simultaneously upgraded from 48.6% to 56%.
- The feed concentrate contained the following copper minerals: bornite (39%), chalcocite (32%), chalcopyrite (13%) and pyrite (8%).
- The upgraded concentrate contained predominantly of chalcocite/digenite (64%), covellite (17%), Pyrite (7%).

Primary concentrates displayed a similar trend in radionuclide and other impurity element removal in a Two Stage Leach. However, there was a more significant upgrade in copper in the primary concentrate compared to secondary concentrates:

- Copper was upgraded from 28% to 60% consisting primarily of chalcocite (82%), pyrite (10%) and idaite (7%)
- Chalcopyrite (57%), pyrite (24%) and bornite (14%) were the dominant minerals in the feed concentrate.

In a Single Stage Autoclave Leach a primary concentrate was upgraded as follows:

- Copper from 28% to 59%.
- Silver from 20ppm to 43ppm.
- Gold from 13.5ppm to 25ppm.
- The product concentrate contained predominantly chalcocite (46%), covellite (29%) and pyrite (19%) with a mass loss of approximately 50% and no loss of gold and silver.

DISCUSSION AND CONCLUSION

The concentrate treatment process has the potential to reduce radionuclides 238U, 230Th, 226Ra, 210Pb, 210Bi to a level below 1 Bq/g and to a level below 2Bq/g for 210Po. In addition to radionuclides, other impurities that may attract penalties at the smelters such as nickel, cobalt and lead are also removed in the concentrate treatment process. Economically recoverable uranium can be recovered as by-product employing ion exchange.

Simultaneously, the copper in the final concentrate is raised to 55-60%. This upgrade and hence mass reduction results in reduced transportation and treatment costs. Most importantly, there are minimal copper and silver losses. Gold losses are negligible.

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Country or International Organization

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Session Classification: Tailings and waste management

Track Classification: Track 11. Tailings and waste management