TACKLING IMPURITIES IN COPPER CONCENTRATES

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ABSTRACT

Historically, concentrates with higher levels of impurities were sold to smelters with the miner facing penalties that marginally reduced his revenues. The smelters then blended the impurity concentration down to acceptable levels among the various feeds they purchased. When the miner faced unusually high levels of certain impurities, his choice of smelters could be constrained or he was forced to sell his concentrate in small lots to multiple buyers. Today, the relative amount of concentrates with challenging levels of impurities is growing and the proportion of high quality concentrates available for diluting is shrinking. This can create an opportunity for dealing with the problem impurities directly at the mine site which has potential positive environmental and material stewardship outcomes.

In the present paper, case studies are presented for dealing with copper concentrates that contain mercury, bismuth or zinc based on either batch tests or in a fully integrated continuous pilot plant test at Teck's CESL facilities in Richmond, B.C. Extensive test work and positive results for treatment on high arsenic-bearing copper concentrates has been previously discussed. High copper and mercury extractions were confirmed with tennantite/tetrahedrite and cinnabar-bearing concentrates. The generation of a high-grade, compact mercury residue that passed TCLP requirements was demonstrated during piloting. A novel process for leaching bismuth, without leaching any copper, is also discussed. Finally, selective zinc-only leaching test results from copper concentrate are presented. The deciding factor in the success of a particular approach is highly dependent upon the minerals that contain the impurity of interest.

INTRODUCTION

The area of arsenic-challenged copper deposits has been a focal point of CESL's interest in the last few years. Together with Aurubis, Europe's largest copper producer, we have developed a process that efficiently recovers the metal values from these types of deposits and, equally importantly, produces a stable, compact arsenic residue suitable for long term storage (Mayhew et. al. 2011 & Salomon-De-Friedberg et. al. 2014). However, our interest is not limited to arsenic but extends to other impurities found in copper and nickel concentrates as well.

One considers a "typical" copper concentrate as having about 25+% copper and some minor quantity of impurities, preferably rich in precious metals. In practice, smelters purchase all variety of concentrates and blend them to provide a suitable feed for their operations. However, each smelter has differing limitations and this is reflected by the penalties imposed on incoming impurities. In some cases, such as arsenic, the penalty per incremental unit escalates with increasing concentration. Certain smelters may even reject potential feeds outright because of one particularly high impurity. Over the last 10-years, the availability of adequate clean concentrates to act as diluents has reduced and penalties or outright rejection of concentrates has become more common. Table 1 shows some typical limits where penalties begin to be imposed on various impurities and the magnitude of the penalty.

Table 1 - Concentrate Maximum Impurity Levels and Approximate Penalties

Element	Penalty Limit, %	Penalty, $/t per extra 0.1 %
Arsenic	0.2	2
- higher arsenic	>1	>5
Antimony	0.05	15
Bismuth	0.02	25
Cadmium	0.03	30
Fluorine	0.03	15
Lead	1	0.3
Mercury	0.0005	3000
Nickel + Cobalt	0.5	1
Selenium	0.03	15
Zinc	3	0.3

It is to be understood that, if an impurity is penalized, any corresponding metal value is not paid for presenting a "double" opportunity to the concentrate provider. For example, the penalty for excessive nickel may not appear to be high, but the lost nickel value itself can be appreciable. If the metal is lost to the smelter's final discard slag, this also represents a waste of the original resource.

Table 2 shows the approximate compositions of actual concentrates that were sold to smelters that might have benefited from hydrometallurgical pre-treatment assuming further physical separation techniques were not possible. Tonnage, which impacts the economies of scale, was not considered.

Table 2 - Potential Candidates for Hydrometallurgical Pretreatment

Concentrate	Cu,%	As,%	Sb, %	Pb, %	Zn, %	Co + Ni, %
A	28			7		1.5
B	23	3.3	1.6	9	10	
C	25	4.5		6	13	
D	22		0.5	10	7	
E	11					9.5
F	27			10	6	
G	25	0.5	1.1	9	6	
H	24	5.8	5	10	9	
I	19	2.5	2.4	9	8	

While hydrometallurgical processing at the mine reduces the marketing risk associated with impurity-laden concentrates, the technical challenge is to come up with processes that are less costly overall (in terms of capital and operating costs) than the current and forecast future penalties associated with the particular impurities.

CASE 1 – MERCURY

Mercury has been recognized by the health community as a toxic element that has serious, long-term health implications for humans. A concerted effort by multi-national, governmental bodies over the last 5 years has culminated in the recently signed Minamata Agreement (October 2013). There are currently 128 signatories to this agreement (UNEP website). A key provision of this agreement is the reduction of the supply, demand, trade and atmospheric emission of mercury and its compounds. Although the treaty does not stop the trade of concentrates with naturally occurring mercury, it does encourage the implementation of new process technologies that would reduce overall mercury emissions.

As seen in Table 1, the tolerance for mercury in copper concentrate feeds at most smelters is quite low (5 ppm). This is because the mercury, if uncaptured, preferentially follows the sulphur to the product sulphuric acid which predominantly enters the fertilizer industry. A few copper smelters include mercury scrubbing towers, but the scrubbers are not ubiquitous in the industry.

The leaching of mercury under CESL conditions was explored for two copper concentrates with considerably elevated mercury concentration. The concentrate analysis is shown in Table 3.

Table 3 - Chemical Analysis of Mercury-Bearing Copper Concentrates

Element	Concentrate "A"	Concentrate "B"
	%	%
Cu	26	20
Fe	26	27
S	28	38
As + Sb	0.1	4.1
Zn	0.1	5.5
Hg, ppm	200	430

The principal mineralogy of the two concentrates is shown in Table 4.

Table 4 - Concentrate "A" and "B" Mineralogies

Mineral	Ideal Formula	Conc. "A"	Conc. "B"
		%	%
Chalcopyrite	$CuFeS_2$	72	38
Pyrite	FeS_2	7	33
Tennantite	$(Cu,Fe,Zn)_{12}As_4S_{13}$	0.2	18
Tetrahedrite	$(Cu,Fe,Zn)_{12}Sb_4S_{13}$		1
Sphalerite	ZnS		6.5
Other Cu S=	Cu_2S, CuS, Cu_5FeS_4	1.3	

Concentrate "A" has the sulphides being mostly chalcopyrite and some pyrite and a higher gangue fraction. Concentrate "B" distributes its copper mostly between chalcopyrite and tennantite and has considerably more pyrite.

The mercury mineralogy for the two concentrates was quite different as shown in Table 5:

Table 5 - Mercury Mineralogy of the Concentrates

Mineral	Ideal Formula	Conc. "A"	Conc. "B"
		% of total Hg	% of total Hg
Tennantite	$(Cu,Fe,Zn)_{12}As_4S_{13}$	20	65
Tetrahedrite	$(Cu,Fe,Zn)_{12}Sb_4S_{13}$		5
Sphalerite	ZnS		30
Cinnabar	HgS	80[1]	0

[1] Cinnabar fraction was higher at higher levels of Hg in concentrate

The tennantite grains found in Concentrate "A" were found to contain an average of 3% Hg, while concentrate "B" tennantite grains contained only 0.1% Hg. Mineral grain sampling, in this case, was indicative but not necessarily representative of the concentrates.

One processing approach is a selective leach of mercury from these concentrates. However, because the mercury sulphide mineral is so insoluble and because much of the mercury is tied up within the copper bearing minerals themselves, such an approach is not feasible. Complete mineral oxidation was required.

Bench testing confirmed that a CESL process was capable of achieving greater than 96.5% copper extractions from both concentrates despite the significant presence of refractory copper minerals. Mercury extraction was greater than 90%. A pilot program for Concentrate "A" type material was then initiated. The flowsheet is shown in Figure 1.

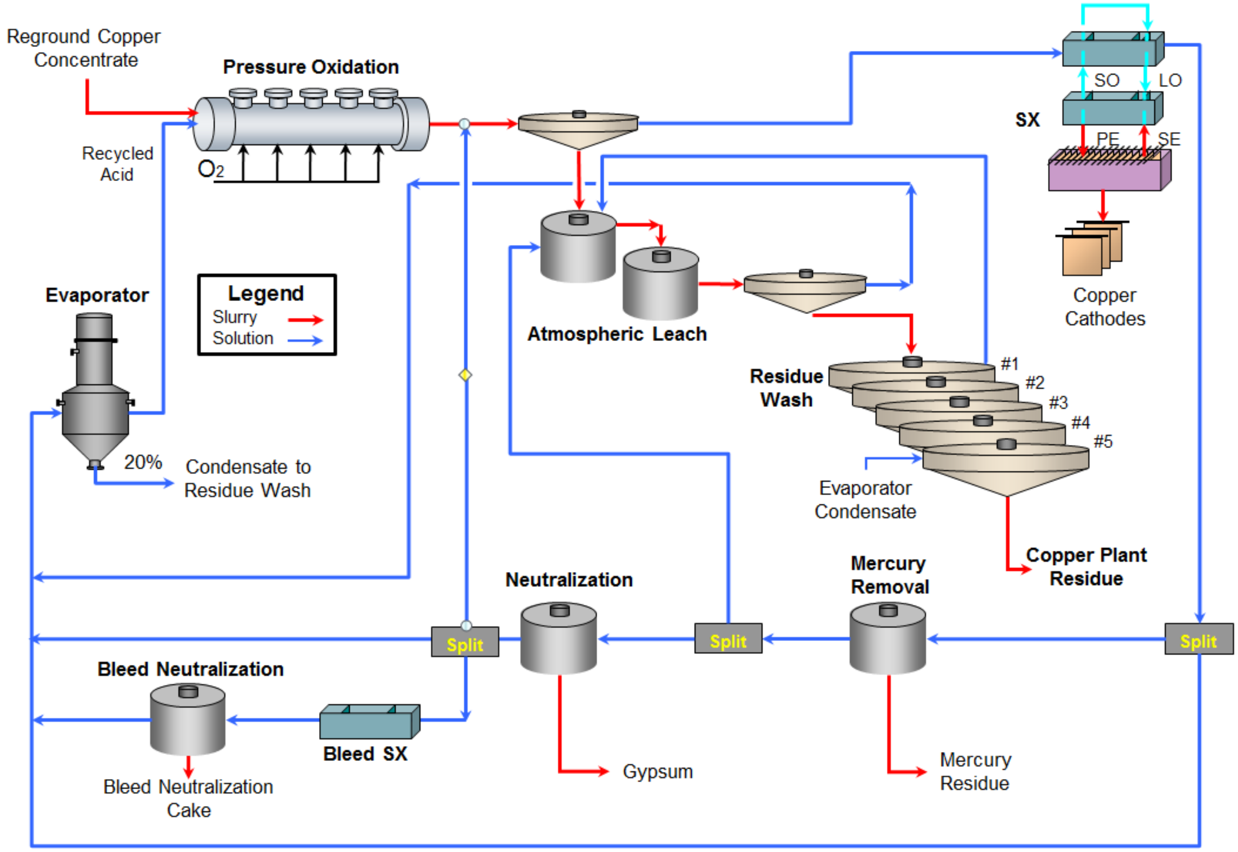

Figure 1 - CESL Flowsheet for Processing Hg-rich Copper Concentrates

Copper and mercury results at the continuous pilot scale confirmed those obtained in batch testing. Gold recovery from the pilot leach residue was also assessed with elemental sulphur flotation of the residue offering 85% recovery of the precious metals to the flotation concentrate and the most favorable net present value (NPV) of the options considered. Besides flotation, the other options investigated included cyanidation, with better but more complex recovery, and gravity concentration.

The work confirmed the technical viability of the CESL Process and further that it is a pragmatic approach to mercury management in mercury-containing copper concentrates. Unlike total oxidative leaching (TOL), where some mercury deports to the flash steam (Krumins et. al.), the presence of chloride in the CESL process liquor appears to complex the solubilized mercury and prevent it from escaping in the autoclave's vent gases. Mercury is captured from solution as a high grade (>20% Hg), low volume, precipitate that is captured separately from the bulk of the residue produced in the autoclave. In the subsequent Toxicity Characteristic Leach Procedure (TCLP) tests, the levels of mercury in these residues were below detection in all of the TCLP leachates. The residue is safe to handle and suitable for long term storage demonstrating a high standard of responsible material stewardship.

CASE 2 – BISMUTH

Bismuth adversely affects the drawability of copper wire, even at low levels, and its concentration in the refined copper must be kept to less than 0.5 ppm. Testwork was performed on two types of a concentrate having up to 25 times the penalty limit of 0.02% Bi in concentrate. The approximate compositions of these select concentrates are listed in Table 6.

Table 6 - Chemical Analysis of High Bismuth Bearing Concentrates

Concentrate	Bi, %	Cu, %	Fe, %	Cu:Fe
Mid-Grade Cu	0.3	27	22	1.2
High-Grade Cu	0.5	35	17	2

The higher copper grade material with the higher bismuth content was bornite-rich. The associated mineralogy of the two concentrate materials was examined in detail by Process Mineralogical Consulting Ltd. and from this work the bismuth-bearing mineralogy was estimated to be as follows:

Table 7 - Bismuth Mineralogy in Concentrates under Study

Mineral	Formula	Mid-Grade Con	High-Grade Con
		% of total Bi	% of total Bi
Bismuthinite	Bi_2S_3	43	
Bi-Pb Sulphosalts		45	72
"Bi Bornite"	$\sim Cu_{18}Fe_4BiS_{16}$	12	4
Tennantite	$(Cu,Fe)_{12}(As,Sb,Bi)_4S_{13}$		12
Other – Bi Sulphosalt	$\sim Cu_9FeBiS_{11}$		12

The bismuth-bearing sulphosalts in the mid-grade concentrate all appeared to contain lead and were identified as cosalite (Pb_2BiS_5), aikinite ($PbCuBiS_3$) and proudite ($Cu_{0\text{-}1}$,$Pb_{7.5}(Bi)_{9.3\text{-}9.7}(S,Se)_{22}$). In contrast, the high-grade concentrate had no bismuthinite and had most of its bismuth tied up in the Bi-Pb sulphosalt minerals which were at least 9 different mineralogical species in this case. The fraction termed "other" was mostly a bismuth sulphosalt assaying an estimated 17% Bi.

The CESL Option

Leaching of the bismuth-rich concentrates under standard CESL conditions indicated copper extractions approaching 98.5% and complete rejection of the bismuth to the leach residue. Subsequent silver recovery from this residue achieved 96% silver extraction. These favorable technical outcomes led to an economic assessment for this option.

The capital cost of a CESL facility processing 50,000 tpy of high bismuth grade, copper concentrate was estimated to be in excess of $100M with an annual operating cost of $14M/yr. Economics were found to be breakeven for the remote, high-elevation refinery. The option was indistinguishable economically from selling the concentrate and accepting the bismuth penalty. Consequently, efforts were redirected at finding a more attractive, less capital intensive process flowsheet alternative.

Selective leaching

A selective leach that targets the impurity of interest offers the advantage of a simpler, less costly flowsheet that can avoid additional unit operations to recover valuable metals. In the present case, a criterion of maximum bismuth leaching coincident with minimal copper leaching was selected. Seven different leaching agents were screened in 42 tests. An overall summary graph depicting the selectivity of bismuth leaching over copper is shown below:

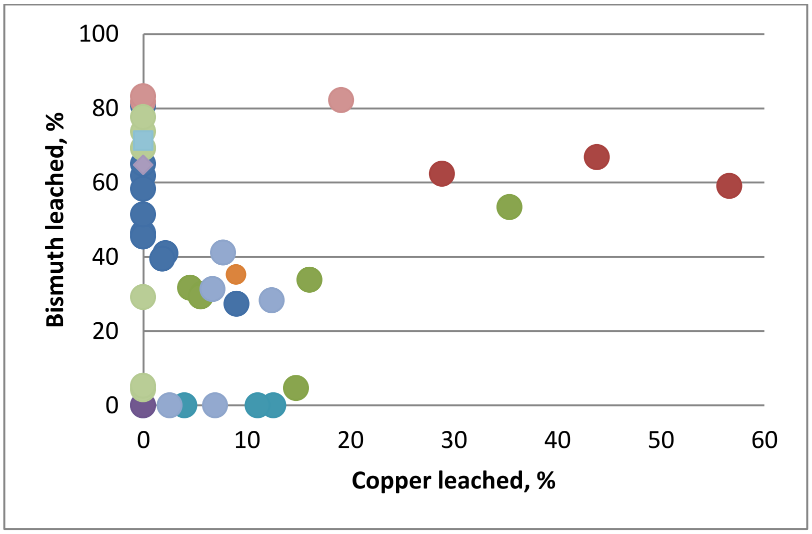

Figure 2 – Selectivity of various leaching agents for dissolving bismuth over copper

Some leaching agents showed good extraction, but poor selectivity over copper while others indicated good selectivity, but poor bismuth extraction. The compromise of maximum bismuth extraction at minimal copper leaching was achieved with 2 leaching agents. However, one of these proved ineffective on the second concentrate being evaluated, reinforcing the importance of understanding initial mineralogy.

The eventual flowsheet that resulted (Figure 3) included a two stage counter-current atmospheric leach, a selective bismuth precipitation step to recover the bismuth from solution, and a bleed neutralization step that handled other impurities that dissolved and would otherwise compromise the flowsheet if left uncontrolled.

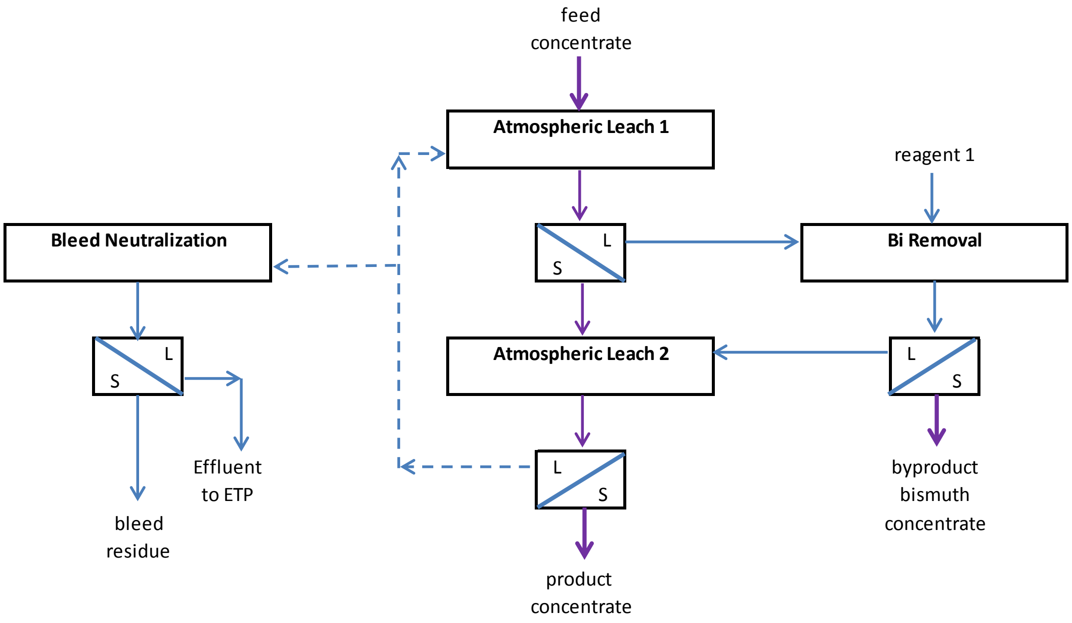

Figure 3 - Atmospheric leach for selectively dissolving bismuth from copper concentrate

Economics

The selective bismuth leach was evaluated on a throughput of 200,000 tpy of concentrate. An "Order of Magnitude" capital cost of the plant was estimated at $65M. The estimate included factoring indirects at 67% of the direct costs and adding a 50% contingency on the sum of directs plus indirects. Use was made of existing concentrate filtration capacity and an existing effluent treatment facility at the target site. The capital intensity translates to ~$325 per annual tonne of concentrate which compares quite favorably with base metal leaching refineries that typically see capital intensity costs in the range of $1,000 to $2,000 per annual tonne of concentrate.

In the present case study, the operating costs of the proposed leach plant (~$40/t of concentrate) were found to be virtually equal to the revenue generated by the sale of the bismuth byproduct recovered which was 400 tonnes per year (tpy) of contained bismuth (2000 ppm Bi from the original concentrate). This left the savings in bismuth penalties on the concentrate being sold, estimated at $13M/yr, to recover the capital cost of the plant. A breakdown of the operating costs is shown in the Table 8.

Table 8 - Selective Bismuth Leach Operating Cost Breakdown

Operating Cost Element	$/t concentrate	% of Total
Labour	12.7	31
Power	8.6	21
Reagents	13	31
Consumables	7.2	17
Totals	**42**	**100**

The key driver in the process economics for the selective bismuth removal process is the bismuth grade of the starting concentrate and the extent to which it is recovered. Both factors influence potential added revenue and the size of smelter penalty being avoided. A technical opportunity remains in this particular instance. Bismuth extraction during leaching from the mid-grade concentrate (0.3% Bi) approached 80% whereas only about 40% was achieved from the high-grade concentrate (0.5% Bi). The reasons are attributable to differences in mineralogy between the two samples.

A simple and viable solution was identified for dealing with a high bismuth-bearing concentrate that focused on leaching only the impurity of interest and recovering it to a saleable product that contained nearly 50% Bi. Besides the real economic benefit of eliminating Bi penalties on concentrate sales and producing a saleable Bi product, an added benefit of a selective leach for bismuth from these concentrates is the increased marketability of during periods of concentrate oversupply.

OTHER OPPORTUNITIES

CESL Technology has been successfully proven on high fluoride-containing copper concentrate where the element precipitates to the leach residue leaving no free flouride (<30 ppm) in solution. We have also explored the selective leaching of zinc from copper concentrates, but this work is still in its early stages. Hydrothermal upgrading of copper concentrates, both with and without oxygen, has been known for quite some time and has received recent attention (Muszer et al., (2013), Fuentes et al., (2009)). A related approach was pursued to selectively remove zinc from a copper concentrate (Harvey et al. 1992). The range of Cu-Zn separations possible from this particular concentrate during leaching is shown in Figure 4.

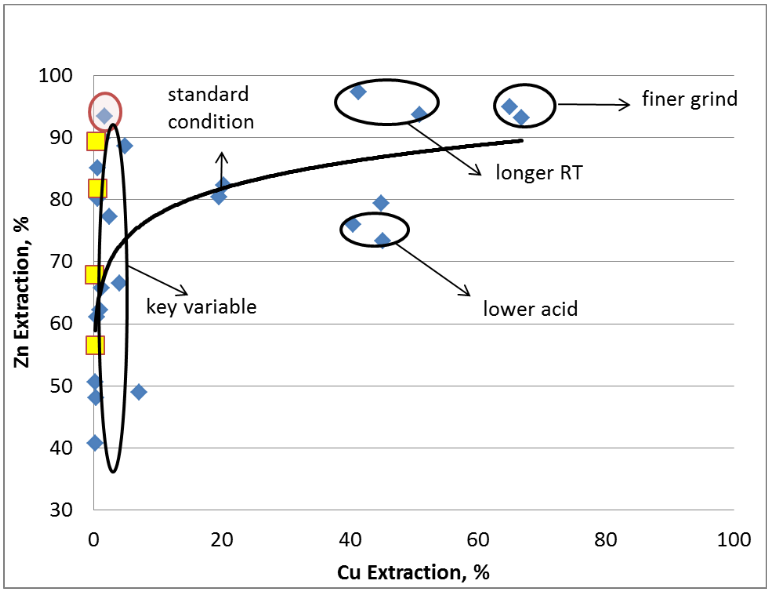

Figure 1 - Selective zinc leaching over copper

Because some iron is dissolved, as well as zinc, the concentrate mass is reduced and its copper grade increased, which would reduce downstream shipping and smelting costs as well as providing an opportunity for zinc recovery. As an example, one concentrate's copper grade, under optimal conditions, was increased from 26% to 34% Cu while the zinc grade was reduced from 5% to 1% Zn.

CONCLUSIONS

Copper concentrates contain many impurities at concentrations that may cause significant challenges to the miner that produces and markets them and ultimately to the smelter that purchases and processes them. On occasion, an opportunity may exist for the miner to remove and/or recover the impurity at the mine site thereby upgrading the concentrate product. However, there are factors to be considered.

- Because an impurity may be present in numerous minerals with highly varying chemical characteristics, the success of a particular approach on a given concentrate is not assured. It is highly dependent on the mineralogy of the concentrate.
- The target mineral/metal being recovered by the mine must possess chemically inert characteristics relative to the impurity being targeted for selective leaching to be successful.
- The field of geometallurgical study provides an invaluable tool for better understanding the reasons behind the particular success of a given approach. However, a geometallurgical model does not yet exist for many mining operations and the lack of a comprehensive model reduces the miner's confidence in the assessment of the scope and severity of the problem element. For geometallurgy, the challenge is accentuated because the products of leaching can often be very fine in size, have amorphous components, and contain low, but still significant concentrations of the impurities of interest.
- Selective leaching of impurities, if feasible, is important because it allows the miner to capture greater value from his concentrate. Furthermore, precious metals will invariably deport preferentially to the upgraded product.
- Selective impurity leaching processes are challenged by the fact that concentrate impurity mineralogy and impurity concentration may shift appreciably over the life of the mine. However, ever tightening environmental constraints will favor its advancement.

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