Abstract

Polymetallic Processing within a Circular Economy.

by

P.J. van Staden[1,*] , M. Gericke[1]

(1): Mintek, South Africa.

(*): Corresponding author, petrusv@mintek.co.za

The internationally collaborative IntMet project, funded by the European Commission, is aimed at ensuring long-term access to critical raw materials and the sustainable use thereof.

The project team consists of a multi-national consortium that is devising the technologies required for the exploitation of ‘complex’ ores. Complex is defined here as ores that are of low grade, respond poorly to conventional treatment routes and are polymetallic. Globally a growing proportion of ores that remain to be exploited exhibit these characteristics.

A challenge posed by polymetallic ores is how to best realise the contained value in cases where the production of differential concentrates by physical separation is not an option. Process complexity increases with increasing number of elements to be recovered and with increasing levels of on-site refinement of each product. The selection of the form in which each product is to be produced also needs to take into account the marketability thereof.

A European case study is provided where the contained value is distributed amongst six metals while containing contaminants such as mercury. One distinguishing feature of the proposed process flowsheet is copper and zinc recovery via resin-in-pulp, instead of the more conventional solvent extraction and electrowinning. This was required to overcome challenges of solid-liquid separation and to minimise soluble losses and is also better suited to the low solution tenors encountered.

The Circular Economy ideal strives for maximal utilisation and zero waste. Application thereof to mining presents technical challenges similar to those encountered in polymetallic processing, but of an even higher level of complexity. It requires namely that not only should value be derived from multiple elements in an ore, but from all constituents that are brought to surface.

1 Introduction

The global average grades of various types of ores being processed are degreasing and the remaining ores are becoming more complex in composition. Furthermore, the available data suggest that these trends are not likely to reverse in future, van der Voet et al. (2013).

At the same time the mining industry is constantly pressurised to improve its performance regarding safety and environmental impact. All industrial operations, not only mining, face the challenge of becoming less wasteful in the face of growing demands being made on increasingly constrained resources. But this challenge is particularly relevant to mining since it relies on non-renewable resources.

This paper provides firstly some background on polymetallic ores and companion/by-product metals. A European case study is then provided on the envisaged treatment of ore that is complex in being of low grade, having the contained value distributed amongst six metals and bearing a multitude of contaminants.

The Circular Economy concept represents a next, even higher performance benchmark by striving for zero waste where all obsolete items are re-used/recycled and all constituents derived from an ore and its processing are saleable.

Comment is provided on the manner in which these topics are being investigated and addressed within the European Union.

2 Definitions

In this text, “Polymetallics” refers in the broadest sense to ores from which more than a single value-metal is recovered, regardless of the relative value contributed by each of the metals.

“Companion-metals” are those that occur in a particular ore as by-products, with another metal being the principal contributor to revenue. However the possibility remains for companion-metals to be the principle element being mined in ores elsewhere. For example Mudd et al. (2014) list Ag as a companion-metal occurring in Australian Au ores. However Ag has also been the principle element being mined in North America, Mexico and other parts of the world. Uranium as a companion metal of South African gold ores would be another example. An example of further reading on companion metals is Mudd et al. (2014), who produced a review of companion metals in Australian ores.

The term “By-product metals” is reserved for those metals that are globally produced exclusively as by-products of other “primary” metals, except by rare exception. That is one of the aspects raised in the paper by Nassar et al. (2015), where Co is listed as such an example, being a by-product of copper production in the Democratic Republic of the Congo (DRC) and as a by-product of Ni-laterite processing, (Fisher, 2011).

“Technology metals” refers to those elements that are required in the engineering of the technologies for energy generation from renewable resources, for rechargeable battery manufacture and other high-technology systems. It corresponds more or less to the by-product metals plus lithium and the rare earth elements, (Lifton, 2018).

3 The occurrence and significance of polymetallics, companion-metals and by-product metals

According to the definition provided above, the mining of polymetallic ores is more the rule than the exception. For example gold ores typically contain silver and base metals that report to the bullion (Atmore et al., 1971), and several South African gold mines have produced uranium as a companion of gold. Platinum ores can contain, apart from Platinum Group Metals (PGMs) and Au, also economically significant quantities of Ni, Cu, Co, Ag, Cr, Se and Te, as can be seen from the applications discussed by Jones et al. (2009), Liddell et al. (2011), Ndlovu (2018) and Fisher (2011).

The Wheel of Companion Metals, shown in Figure_, represents an effort to represent the association between primary and companion metals. Here the primary metals are considered to be Fe, Al, Au, Pt, Ni, Cu, Zn, Pb, Ti and Sn. In the concentric rings around the core, the companion-metals associated with each primary metal are shown, with an increasing distance away from the core representing a reducing proportion of the companion-metal production being associated with the primary metal.

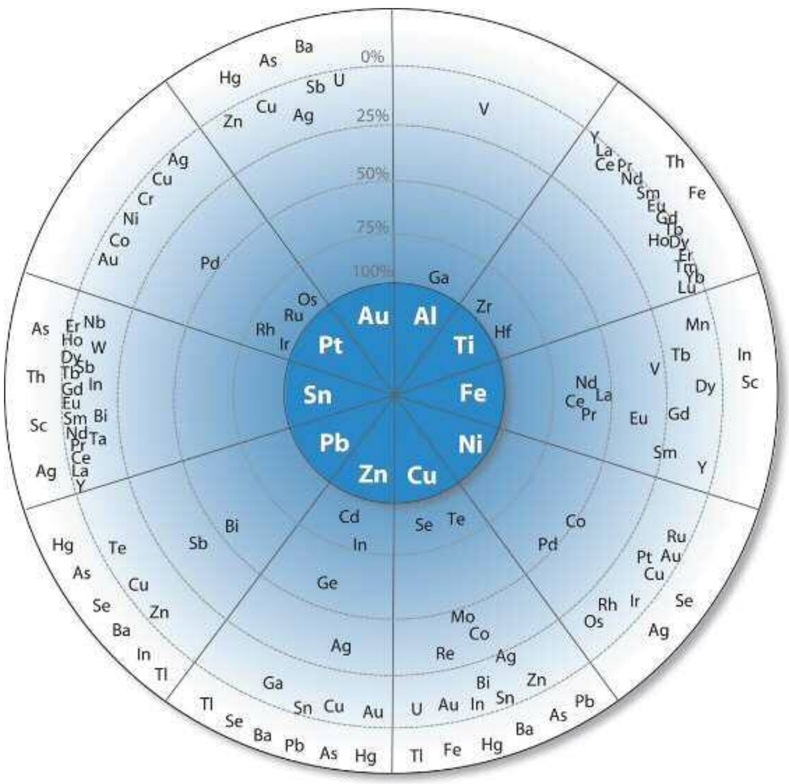

Figure 1. The Wheel of Companion Metals
Reproduced from Nassar et al. (2015)

One reason for the heightened interest in polymetallics in the European Union (EU) (and elsewhere in the world) is the overlap between the technology metals and by-product metals, Moss et al. (2011). The fact that the sourcing of by-product metals relies heavily on access to sources of the primary metals that host them, are viewed as making them more vulnerable to supply constraints.

Examples of regional southern African polymetallic deposits that contain base metals as the primary value-metal include Black Mountain in South Africa (bearing Zn, Pb, Cu and Ag, Coetzee et al. (2018)), Kipushi in the DRC (bearing Zn, Cu, Pb, Co, Ag and Ge, Peters et al. (2016)) and Khoemacau/Boseto on the Botswana Kalahari Copperbelt (bearing Cu and Ag, Cupric Canyon Capital (2018)).

For the purposes of process design and economics it is important to also consider the S content in all sulphide ores, which represents potential for acid and heat production.

4 The processing of polymetallics

From the above it is obvious that 'polymetallics' account for a wide range of ores and no single generic flowsheet or design philosophy could be proposed for its exploitation. What they do have in common is a growing complexity with increasing number of elements to be extracted and with increasing level of on-site refinement.

A good example is what has become known as the "Murrin Murrin flowsheet", (Valle et al., 2017), (Minara Resources, 2018), which is employed at the Ambatovy complex in Madagascar. The primary products are Ni and Co which are produced as metal briquettes after H_2 reduction, other base metals are produced as a mixed sulphide by H_2S precipitation. The complexities involved in the storage and application of these gases in the process cannot be insignificant.

Base metal production flowsheets inevitably require pH control/adjustment steps, which calls for careful selection of neutralising agents. Limestone and lime are relatively inexpensive but produce gypsum which is intolerable in a unit operation such as solvent extraction (SX) and dilutes the product in a hydroxide-precipitate production step. Alkali-metal or Mg-hydroxides/carbonates are effective and produce no precipitate but are more expensive and the cation needs to be bled from the circuit to prevent its uncontrolled accumulation in solution. In the Murrin Murrin flowsheet, NH_3 is used at several pH control/adjustments steps. The manner in which this is bled from the circuit is to crystallise $(NH_4)_2SO_4$ to be sold as fertilizer.

The challenge of sourcing the necessary expertise in order to manage the technology risk, pointed out by Benz (2017), can be assumed to become more difficult with the increasing process complexity that polymetallics require.

Another feature of polymetallic processing is the number of possible process combinations from which the optimal configuration needs to be selected. For example Swartz et al. (2009) list 8 combinations of precipitation agents and Co-products to consider for the production of Co-precipitates as by-product of copper production. That is apart from possibilities such as Co-electrowinning (EW) which in turn could follow the conventional route or could be done by direct electrowinning as per Mulaudzi and Kotze (2013). Each additional metal to be produced could add a similar number of possibilities for its production, leading to a proliferation of total possible over-all flowsheet combinations across all metals to be produced. The large number of options does not represent flexibility, since once the flowsheet configuration has been built, changing it would involve additional expenditure and disruption of production. The challenge it poses is to select the balance between production rate and marketability of the selected product types that optimises the economic model over the life of the project.

5 A European case study

5.1 Characterisation

The IntMet research project, funded by the European Union (EU), aims to establish technologies for facilitating on-site recovery of all value-metals from ores and concentrates that are of low grade, polymetallic and/or complex in any other way.

In total, four such ores/concentrates from various locations in Europe are being studied for their amenability to processes based upon either atmospheric leaching, pressure leaching or bioleaching as the primary extraction step. Downstream processing details depend on the characteristics of each individual feedstock which will not be elaborated on in this text.

The focus will be on the example of an ore sample originating from the Bor district in Serbia. Its complexity comprises of being of relatively low grade in value-metals, having the contained value distributed amongst six elements and bearing relatively high concentrations of iron, sulphide-sulphur and the toxic contaminants Hg and As. Attempts at producing selective concentrates of each value metal, or even a bulk concentrate of all value-metals by physical means, has proven unfeasible. Therefore the entire ore needs to be treated with its mineralogical and chemical analyses appearing in Table 1.

Table 1 Mineralogical and chemical composition of the BOR polymetallic ore

Species	**Content, %**
Mineralogical	
Sphalerite	7 - 8
Chalcopyrite	0 – 1.5
Covellite	2 – 3
Galena	5 – 7.5
Pyrite	45-50
Balance	34- 36
Chemical	
Zn	5
Cu	1.8
Pb	4.5
Ba	15
Au	1.4 ppm
Ag	115 ppm
Fe	25
S (as sulphide)	31
Hg	500 ppm
As	0.42

Balance	18

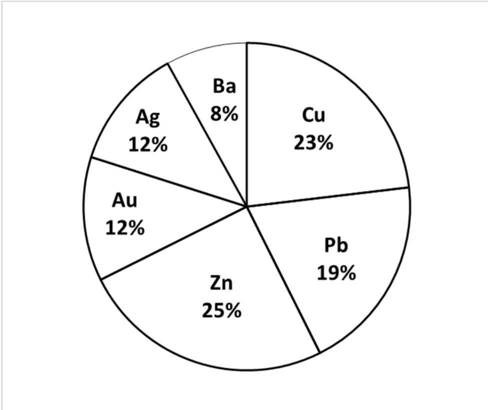

Figure 2. Value distribution amongst metals in Bor ore.

According to metal prices prevailing at the time of writing, the Bor ore contains a total value of USD 428 USD per tonne distributed amongst the metals appearing in Figure 2. The proportional contributions to the total contained value is shown as percentages. The relative even distribution of value between the various metals (with the exception of Ba that contributes <10%) makes it hard to discard any one of the metals without sacrificing an unacceptable proportion of the total contained value.

5.2 Leach optimisation

While other members of the consortium consider other leaching alternatives, the bioleaching option has been explored at the Mintek laboratories. The selection of the bioleach configuration requires identification of the combination of the following parameters that optimise the process economics:

- Operating temperature, choosing between either around 30^{o}C (mesophiles), around 45^{o}C (moderate thermophiles) or around 70^{o}C (extreme thermophiles). Higher temperature obviously enhances reaction kinetics, provided the corresponding bacterial culture tolerates the solution conditions.
- Feed solids concentration. A higher concentration reduces reactor volume, but leads to higher solution tenors (which could be inhibiting to the cultures) and higher oxygen mass transfer intensity.
- Acidity regime. It is desirable to allow a pH value as close as possible to that resulting from the naturally occurring reactions of the available minerals, with only sufficient control to maintain bacterial activity.
- Particle size. Regrinding to the 20µm size range is typically required.
- Retention time and reactor configuration. By default 6 days total retention time is selected, but this could be reduced if the specific case permits. A minimum of 3, but preferably 4 mixed reactors are placed in series to approach plug flow, i.e. minimising the effect of by-passing.

Of the combinations evaluated, the optimal conditions were identified as:

- Feed concentration of *
- Reground to 80% < 20µm
- Temperature of 45oC, utilising Mintek's moderately thermophilic cultures
- Retention time of 6 days in total across 4 reactors in series.

The progression of extraction achieved along the four stages after achievement of steady state is illustrated in Figure_. An unusual observation made is that the Zn extraction (from sphalerite) occurs more slowly than the Cu extraction (from chalcopyrite). Other consortium members reported similar observations on other feed materials with high Hg content.

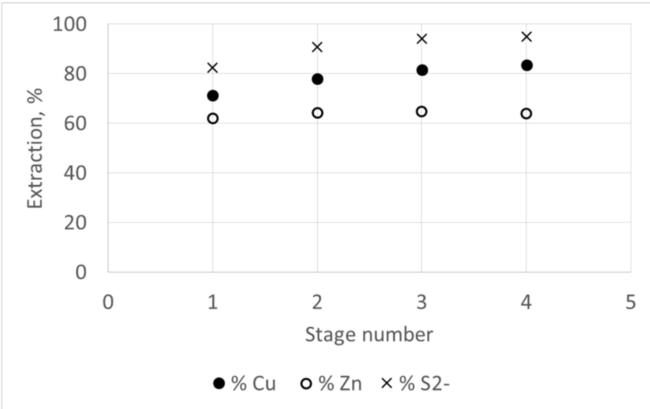

Figure 3. Extents of bioleaching extraction per stage

5.3 Metals recovery from solution

The major cations appearing in the leach solution are Fe, Cu and Zn. A conventional hydrometallurgical approach would be to separate the liquid and solids from the bioleach step and win the Cu from solution by solvent extraction (SX). This could be preceded by a bulk-Fe removal step. The Cu-SX raffinate would be subjected to a complete Fe removal step followed by Zn recovery by either precipitation or SXEW.

This approach failed when attempted on the bioleach pulp produced from the Bor ore. Firstly the fine nature of the solid phase prevented a sharp solid-liquid separation and reduced the washing efficiency of the solid phase. Secondly the Fe concentration was very high due to the high pyrite content of the feed, compared to very low concentrations of Cu and Zn due to the low head grades in these metals. This created the potential for relatively large losses of Cu and Zn by co-precipitation with the Fe.

These considerations led to adoption of the flowsheet shown in Figure 4, where the bulk Fe removal step is followed by a MinRIP™ resin-in-pulp stage. This aims to adsorb both Cu and Zn from solution and to desorb from the precipitated solids any Cu and Zn that might have co-precipitated during Fe removal. The MinRIP stage is deliberately kept separate from the bulk Fe removal step to prevent soluble Fe from competing with Cu and Zn for adsorption.

A single resin is used for the simultaneous adsorption of both Cu and Zn, the two metals are separated into two eluates by selective elution steps. Options remain open for the types of marketable Cu and Zn products to be ultimately recovered from the eluates.

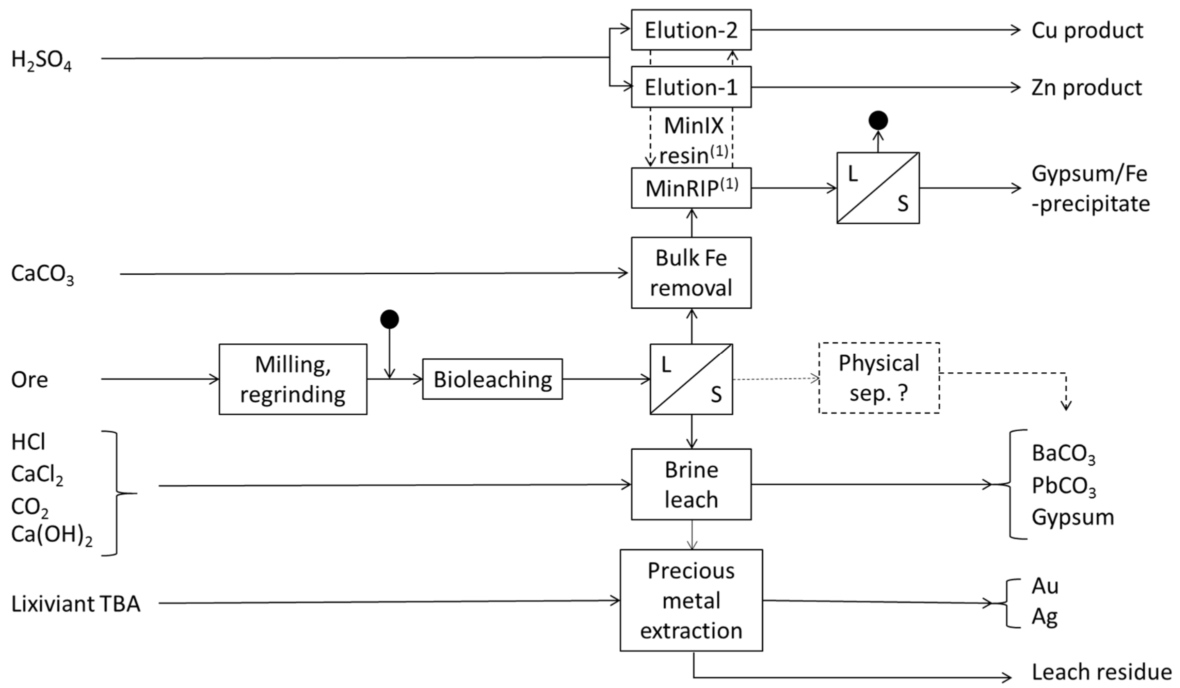

Figure 4. Proposed flowsheet for BOR polymetallic ore treatment

(1)MinRIP™ is a trade-marked resin-in-pulp technology of Mintek, utilising the MinIX™ resin, Mintek Hydrometallurgy (2018)

5.4 Metals recovery from bioleach residue

The solid residue emanating from the bioleaching step contains Au, Ag, Pb and Ba as valuable elements. As a first avenue, the residue has been subjected to a number of physical separation techniques to establish whether marketable concentrates of one or more of these elements could be produced. However no appreciable concentration of any of these elements could be achieved.

As a hydrometallurgical alternative, brine leaching of the residue is being tested for extracting Ba and Pb, to be followed by selective precipitation thereof.

An alternative lixiviant to cyanide is required for extraction of the Au and Ag, bench-scale tests have already proven thiosulphate with ethylenediamine (EDA) to yield virtually complete extraction. However the reagent suite selection is yet to be finalised.

5.5 Tailings stabilisation

Due care is required in devising the final treatment and disposal means of the solid residue. A separate team within the consortium is dedicated entirely towards value creation from, and purification/stabilisation of effluents. In the particular case of the Bor ore, the relatively high mercury content would need to be either captured for safe storage (assuming little marketing prospect for it), or would need to be suitably stabilised if allowed to report to the residue.

6 Towards the circular economy ideal

The '*restorative use of resources*', to quote the Ellen MacArthur Foundation (2015), requires in the first instance re-using/recycling goods/materials after their useful life. However it also aims to maximise the utility and value derived from of any material at any given point in its life-cycle. Translated for application to minerals extraction, it means the maximum net value to be derived from a resource that bears multiple value-elements. In the ideal case it aims for zero waste production by deriving valuable products from all constituents of an ore.

The circular economy ideal therefore addresses similar challenges to those encountered during polymetallic processing, namely of deriving value from a large number of constituents in the ore. However it raises the bar to yet a higher level in aiming to derive value, not from a multitude of elements, but from all elements contained in the ore. That would add to the magnitude of the challenges of planning, design, forecasting, management and skills acquisition that are encountered in polymetallic processing.

This ideal may at first glance seem unachievable for economic reasons, but the counter-argument of the Circular Economy reasoning is that all prices should reflect real costs, i.e. they should include the long-term actuarial cost of environmental and other consequences of resource exploitation, incomplete utilisation and waste disposal.

A particular challenge is posed to mining by the toxic elements in an ore which have little prospect of being marketed in the quantities at which they are brought to surface. Examples are As and Cd, the content of which in copper ores is reportedly on average globally increasing, the same applies to Hg where it occurs.

A principle being suggested by this reasoning is that it should be aimed to only bring the marketable elements to surface, leaving the balance underground, undisturbed. Of course it has always been strived to mine as selectively as possible, and in-situ solution-mining has served as an example of implementation of this principle in very specific cases. The implementation of this principle can be expected to continue expanding gradually, rather than to abruptly become the new norm.

Referring to the Bor flowsheet in Figure 4, value-addition to effluent streams such as the gypsum and Fe-bearing residues is also being investigated by a separate part of the research consortium. Specific aims were to produce gypsum of suitable purity and morphology for plasterboard, and an Fe-bearing product that could be utilised in steel smelting.

Furthermore, multiple avenues for the recovery of residual metal values as well as sulphide-sulphur from tailings are being investigated. Similarly, the purification of mining-impacted water, to yield water suitable for irrigation plus potentially saleable mineral/chemical products, is being investigated.

7 The EU research model

The European Commission serves as the executive of the European Union (EU) and is tasked with the pursuit of a number of medium and long-term priorities for the EU. Not surprisingly employment, growth and investment ranks high on the list amongst other priorities such as energy and migration. As a sub-set of these high-level priorities appear access to critical raw materials and sustainable use thereof. The Horizon-2020 (H2020) research and innovation programme has been launched to fund and manage the establishment of projects towards the achievement of the set objectives, including (amongst many others) the IntMet project that comprises the topic of discussion in this article, (H2020, 2018).

Although the research serves EU objectives, participation in the projects is open to any person or institution globally. Multi-national consortia, consisting of experts in their fields from across the world, conduct the research under the coordination of European administrators. In this manner, the best globally available resources are combined to address the challenges. Web-based facilities for application, reporting and communication minimise administrative effort while synchronising the work of the various research teams operating in various parts of the world.

Therefore ultimately the outcomes of the research benefit not only the EU, but also the rest of the world who share the same challenges as those existing in the EU.

8 Acknowledgements

The paper is published with the permission Mintek.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 689515.

9 References

Atmore, R.B., Howat, D.D., Jochens, P.R., 1971. The effects of slag and gold bullion composition on the removal of copper from mine bullion by oxygen injection. Journal of the South African Institute of Mining and Metallurgy, pp. 5-11.

Benz, M., 2017. Processing expertise: managing hydrometallurgical project risk, ALTA 2017, Pan Pacific Hotel, Perth, Australia, pp. 2-30.

Coetzee, S., Boucher, H., Kihn, C., 2018. General information on Black Mountain Mining. http://www.aggeneys.com/business/black-mountain-mining.

Cupric Canyon Capital, 2018. Developing a premier construction ready high-grade copper project. https://www.cupriccanyon.com/.

Ellen MacArthur Foundation, 2015. Towards a circular economy: Business rationale for an accelerated transition, 20 pp. https://www.ellenmacarthurfoundation.org/publications/towards-a-circular-economy-business-rationale-for-an-accelerated-transition.

Fisher, K.G., 2011. Cobalt processing developments, Base Metals Conference 2011, Hans Merensky Hotel & Spa, Phalaborwa, South Africa.

H2020, 2018. Horizon 2020 statistics. https://ec.europa.eu/programmes/horizon2020/en/horizon-2020-statistics.

Jones, R.T., Geldenhuys, I.J., Reynolds, Q.G., 2009. Recovery of base metals and PGMs in a DC alloy-smelting furnace. Journal of the Southern African Institute of Mining and Metallurgy vol. 109, pp. 595-600.

Liddell, K., Newton, T., Adams, M., Muller, B., 2011. Energy consumption for Kell hydrometallurgical refining versus conventional pyrometallurgical smelting and refining of PGM concentrates. Journal of the Southern African Institute of Mining and Metallurgy vol. 111, pp. 127-132.

Lifton, J., 2018. Technology Metals Research (TMR). http://www.techmetalsresearch.com/about-us/jack-lifton/.

Minara Resources, 2018. Murrin Murrin process and technology flow chart. http://www.minara.com.au/files/docs/411_Murrin_Murrin_Process_and_Tech_Flow_Chart_FINAL_-_8_August_2011.pdf.

Mintek Hydrometallurgy, 2018. http://www.mintek.co.za/technical-divisions/hydrometallurgy-hmd/services/processes-group/.

Moss, R.L., Tzimas, E., Kara, H., Willis, P., Kooroshy, J., 2011. Critical metals in strategic energy technologies, assessing rare metals as supply-chain bottlenecks in low-carbon energy technologies, JRC Scientific and Technical Reports, 159 pp. https://setis.ec.europa.eu/sites/default/files/reports/JRC-report-Critical-Metals-Energy-Sector.pdf.
Mudd, G.M., Yellishetty, M., Reck, B.K., Graedel, T.T., 2014. Quantifying the recoverable resources of companion metals: A preliminary study of Australian mineral resources. Resources vol. 3, pp. 657-671. https://pdfs.semanticscholar.org/5d38/fe9117451a8bf6b4d2385345016893d99890.pdf
Mulaudzi, N., Kotze, M., 2013. Direct cobalt electrowinning as an alternative to intermediate cobalt mixed hydroxide product, Base Metals 2013 Conference Southern African Institute of Mining and Metallurgy, Ingwenyama Conference & Sports Resort, Mpumalanga, South Africa.
Nassar, N.T., Graedel, T.E., Harper, E.M., 2015. By-product metals are technologically essential but have problematic supply. Science Advances No. 3, vol. 1, 10 pp. http://advances.sciencemag.org/content/advances/1/3/e1400180.full.pdf
Ndlovu, J., 2018. Overview of PGM processing. http://www.angloamericanplatinum.com/~/media/Files/A/Anglo-American-Platinum/investor-presentation/standardbankconference-anglo-american-platinum-processing-111114.pdf.
Peters, B., Robertson, M., Witley, J., 2016. Kipushi 2016 Preliminary economic assessment, Ivanhoe Mines, 298 pp. https://www.ivanhoemines.com/site/assets/files/1868/kipushi-project-pea-may-2016.pdf.
Swartz, B., Donegan, S., Amos, S., 2009. Processing considerations for cobalt recovery from Congolese copperbelt ores, Hydrometallurgy Conference 2009, Misty Hills, Gauteng, South Africa.
Valle, L., Dickson, P., Curtis, A., 2017. The HPAL plants that SNC-Lavalin built: Where are they now?, ALTA 2017, Pan Pacific hotel, Perth, Australia, pp. 410-436.
van der Voet, E., Salminen, R., Eckelman, M., Mudd, G., Norgate, T., Hischier, R., 2013. Environmental Risks and Challenges of Anthropogenic Metals Flows and Cycles, A report of the working group on the global metal flows to the International Resource Panel., UNEP. http://orbit.dtu.dk/files/54666484/Environmental_Challenges_Metals_Full_Report.pdf.