

Article

The Recovery of Cu, Co, Zn, and Mn from a Complex Oxide Ore Using an Enhanced Reduction Leaching

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Abstract: The processing of Cu, Co, and Zn at the Boleo project in Mexico involves two-stage (oxidation–reduction) leaching to extract a total of 85–88% Cu in 4 h. The first stage is an oxidation leaching using sulphuric acid (120 kg/tonne ore) at an Eh of 900 mV for 2 h. Then, the reduction stage takes place in 2 h with SO₂ gas sparging for Mn and Co extraction at an Eh of 350–370 mV. The final extraction rates of metal values are 92% of Mn, 80% of Co, and 60% of Co, respectively, after 4 h of leaching at 70 °C. However, the same metal recoveries were obtained within 2 h using an equal amount of sulphuric acid and the addition of 25 kg of SO₂ per tonne of ore in a single stage leaching in this research. In this case, the Fe extracted from the ore as Fe²⁺/Fe³⁺ is believed to have acted as an electrochemical couple contiguously leaching the Cu sulphide and Mn oxides, which also increased the Cu recovery as the Cu mineralised mostly intergrowths in these mineral structure matrices. A significant improvement was made in which the leaching time was halved to 2 h compared to 4 h in the previous plant design and current operation, involving the two-stage oxidation–reduction leaching.

Keywords: Boleo deposit; reduction leaching; copper; cobalt; zinc; manganese



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1. Introduction

The Boleo project is one of the world's largest hydrometallurgical plants processing complex oxide ores, and is located in the middle of Baja California Sur, Mexico. The project is operated by the Mexican company Minera y Metalurúgica del Boleo S.A. de C.V. (MMB). The MMB is owned by Korean companies, led by Korea Resources Corporation, the largest stakeholder, and other companies [1]. The Boleo deposit, containing copper–cobalt–zinc–manganese, is a historic open-pit copper mine that mainly excavated the high-grade sulphide ore, starting in the 1860s, for over 70 years and has recently been re-developed by MMB following an extensive test work [2]. The process developed involves two-stage oxidation–reduction leaching, followed by several stages of solvent extraction to recover Cu, Co, and Zn. The multi-stages of the solvent extraction were based on conventional copper solvent extraction and electrowinning [3], and the patented DSX[®] (Direct Solvent Extraction) process developed by Australian CSIRO (Commonwealth Scientific and Industrial Research Organisation, Australia) to selectively recover the target metal values [4,5]. Mn is not recovered from the proposed process and current plant operation at the Boleo project. Figure 1 shows a schematic of the major stages of the feed preparation and leaching process [2] to produce a pregnant leach solution (PLS) for further Cu, Zn and Co processing.

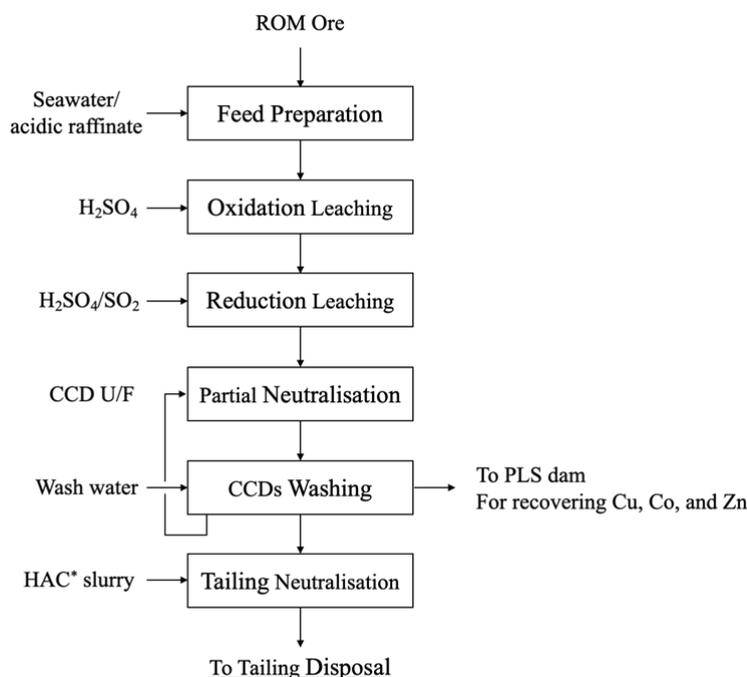


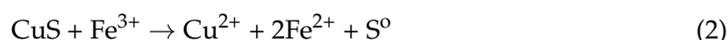
Figure 1. A schematic diagram of the major stages of the feed preparation and the leaching process to produce PLS in the Boleo plant for further processing using the multi-stage solvent extraction (* HAC: high aluminium cement, a low-grade limestone from the mine site).

The two-stage leaching process relies on the addition of 100–120 kg of sulphuric acid/ton ore during the first 2 h of oxidation leaching. The slurry is then further leached for another 2 h in the presence of sulphur dioxide gas, referred to as reduction leaching [6,7]. Preliminary investigation prior to plant construction has indicated that up to 70% of the Cu oxide minerals could be extracted in the oxidation leaching stage, followed by 10–15% extra Cu dissolved in the reduction leaching stage [1]. Co and Mn can only be extracted in the reduction leaching, whereas most of the Zn could be dissolved during the oxidation leaching [2]. The related chemical reactions for the process currently operated in the Boleo project are discussed below.

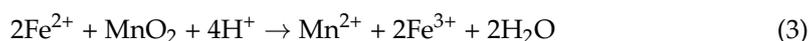
Dissolution of Cu(II) oxide mineral in the ore, for example, atacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$), by sulphuric acid, can be represented by [8]:



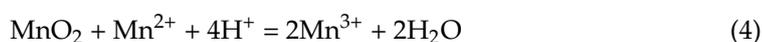
For sulphide minerals, minimal chalcopyrite (CuFeS_2) will not be solubilised until the temperature is $>90^\circ\text{C}$ and under higher than atmospheric pressure [9–17]. Covellite (CuS) or chalcocite (Cu_2S), however, can be leached from ores at mild conditions (70°C) using ferric sulphate [18]:



The Fe^{2+} produced from the leaching of CuS above is then regenerated in the presence of an oxidant such as oxygen [19] or MnO_2 according to the following reaction:



The disproportionation reaction could also take place, producing Mn^{3+} according to the reaction, a process well known during electrolytic Mn production:



The produced Mn^{3+} could then easily oxidise CuS in the same manner as Fe^{3+} shown in Equation (2) above.

The combination of reactions represented by Equations (2) and (3) or (4) is electrochemical in nature, which involves half-cells and electron transfer in which $\text{Fe}^{2+}/\text{Fe}^{3+}$ acts as a redox (electrochemical) catalyst and MnO_2 is the main reagent used for oxidising Cu sulphide minerals.

The remaining unreacted MnO_2 can only be dissolved in the presence of a reductant such as SO_2 (g) or hydrazine [20,21], of which the reaction can be represented as:



(It is noted that although acid is balanced in the net reaction represented by Equation (5), hydrogen ions are required for the two half-reactions involved in the electrochemical reduction of MnO_2).

As the minerals containing Co and Zn could only be identified in intergrowth form in clay minerals due to their low levels in the ores, it is predicted that Zn(II) or Co(II) oxide should be solubilised in acid, whereas Co(III) oxide (generally existing as $\text{CoO}\cdot\text{Co}_2\text{O}_3$, cobaltite) can only be dissolved by reacting with a reductant [22].

The Boleo leaching process could be improved and optimised as the previous study has not dealt with the role of Fe^{3+} and its concentration in the solution. This is vital to re-evaluate the current leaching regimes. This research suggests the optimised leaching condition without a major change in the current design of the plant. The proposed enhanced reduction leaching allows more flexibility in the plant operation strategy and increases the processing capacity. Therefore, the present investigation aims to optimise the leaching conditions (acid and SO_2 consumption, reaction time, temperature, pH, and Eh) for the Boleo project's current plant operation.

2. Experimental

2.1. Materials and Chemicals

A 20 kg ore sample, previously crushed, was obtained from the Boleo plant site. The sample was subdivided into smaller lots for the test work. The material tested has a particle size range of P86 (86% less than) of 75 μm , P30 of 10 μm and a mean diameter d_{50} of 21.9 μm . The chemical composition of the ore sample used for this study is shown in Table 1.

Table 1. Chemical composition of the Boleo ore by ICP-OES (except K by XRF).

Element	Cu	Co	Zn	Mn	Fe	Al	Ca	Mg	K	S	Si
(%)	1.23	0.08	0.48	2.53	8.66	7.16	1.42	2.43	1.25	0.42	22.40

All chemicals used in this study were of analytical grade, supplied by Ducksan Chemical, Korea. Distilled water was used to prepare the diluted chemicals and experiments. Seawater, obtained from South Korea, was used for the leaching test, following the conditions of the field operation in the Beolo plant (Figure 1).

2.2. Experimental Procedures

Accurately weighed ore samples, representing the initial pulp density of 22–33% w/v , were first suspended in 1.2 kg of seawater (at density 1.025) at a temperature range of 40–70 °C. The leaching reaction was carried out using a sealed glass reactor fitted with an agitator and a condenser on a heating mantle. During the oxidation–reduction leaching, sulphuric acid (98%) was introduced at the different predetermined additions of 60–140 g/kg ore, and the acidic oxidation leaching was conducted for 2 h. After this time, sulphurous acid (containing 5% SO_2 w/v) was added to decrease the solution Eh, thus starting the reduction leaching stage for another 2 h. During the single-stage reduction leaching, both sulphuric acid and sulphurous acid were added simultaneously, and the leaching was conducted for 2 h. Samples (2 mL) were taken at different intervals and analysed for Cu, Co, Zn, Mn, and Fe using ICP-OES. These analytical results were then used

to calculate the individual metal recovery (%) based on mass balance and the remaining weight of the leach liquor after each sample was taken. The liquor Eh was measured against a standard calomel electrode (SCE, at 0.244 V vs. SHE, standard hydrogen electrode at 25 °C), and the solution pH was also measured during the experiment. The pH-Eh meter was used by NeoMet pH-220L (iSTEK, Seoul, Korea) coupled with pH and Eh electrodes from the identical manufacturer.

The definition of metal recovery yield in this research is expressed as follows:

$$\text{Metal Recovery (\%)} = \frac{\text{metal content in residue}}{\text{initial metal content in ore}} \times 100$$

2.3. Methods of Analysis

Samples collected at different time intervals during the leaching experiment were analysed using inductively coupled plasma optical emission spectroscopy (ICP-OES) from Genesis FES (Spectro, Kleve, Germany). The ore and leach residue samples were sent to an external laboratory of Bureau Veritas Mineral Laboratories (Perth, WA, Australia) for the mineralogy and petrography by using quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN, FEI Australia, Homebush NSW, Australia) and Quantitative X-ray diffraction (QXRD) analysis using PANalytical XPert Pro PW3040 (Malvern Panalytical, Malvern, UK).

3. Results and Discussion

3.1. Mineralogy

Three different samples were analysed using QEMSCAN and QXRD, including (1) the ore from the Boleo plant site, (2) a sample after oxidation leaching, and (3) a sample after oxidation–reduction leaching. The mineralisation of the Boleo deposit occurred as a widespread stratiform of clay beds as predominated by clay minerals as 40–50% of montmorillonite clay, typically (Figure 2, Feed). Upon the occurrence of the deposit, more than 85% of Cu did not form discrete Cu minerals with a size >10 µm and was finely disseminated in other matrices, such as the clay. A large percentage of Cu was formed as an intergrowth within the structures of chloride, silicate, iron, and Mn oxides (Figure 3). As confirmed in Figure 2, after the oxidation leaching, some Cu minerals still existed together in the Fe and Mn intergrowths in the sample. The subsequent reduction leaching could yield an extra 5–10% Cu extraction as later shown. The presence of Cu as intergrowth within other mineral matrices explains the lower Cu extraction (~80%) in the oxidation leaching, as confirmed by QXRD (Table 2) and leaching results present in a later section. The predominant presence of Mn minerals after acidic oxidation leaching confirms its mineralogy as Mn dioxide (mainly pyrolusite, and jacobsite), pyrosomalite (Mn-silicate), and other Mn intergrowths (Figure 3a), which requires reduction for its extraction. Zn and Co also existed as intergrowth with the structure of clay minerals and some others (Figure 3c,d).

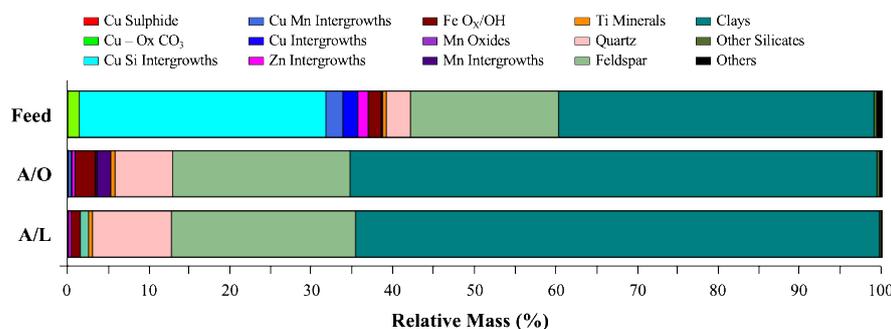


Figure 2. Mineral abundance chart (relative mass, wt.%, not absolute value) classified by QEMSCAN (feed: the original ore; A/O: after oxidation leaching samples; A/L: after oxidation and reduction leaching samples).

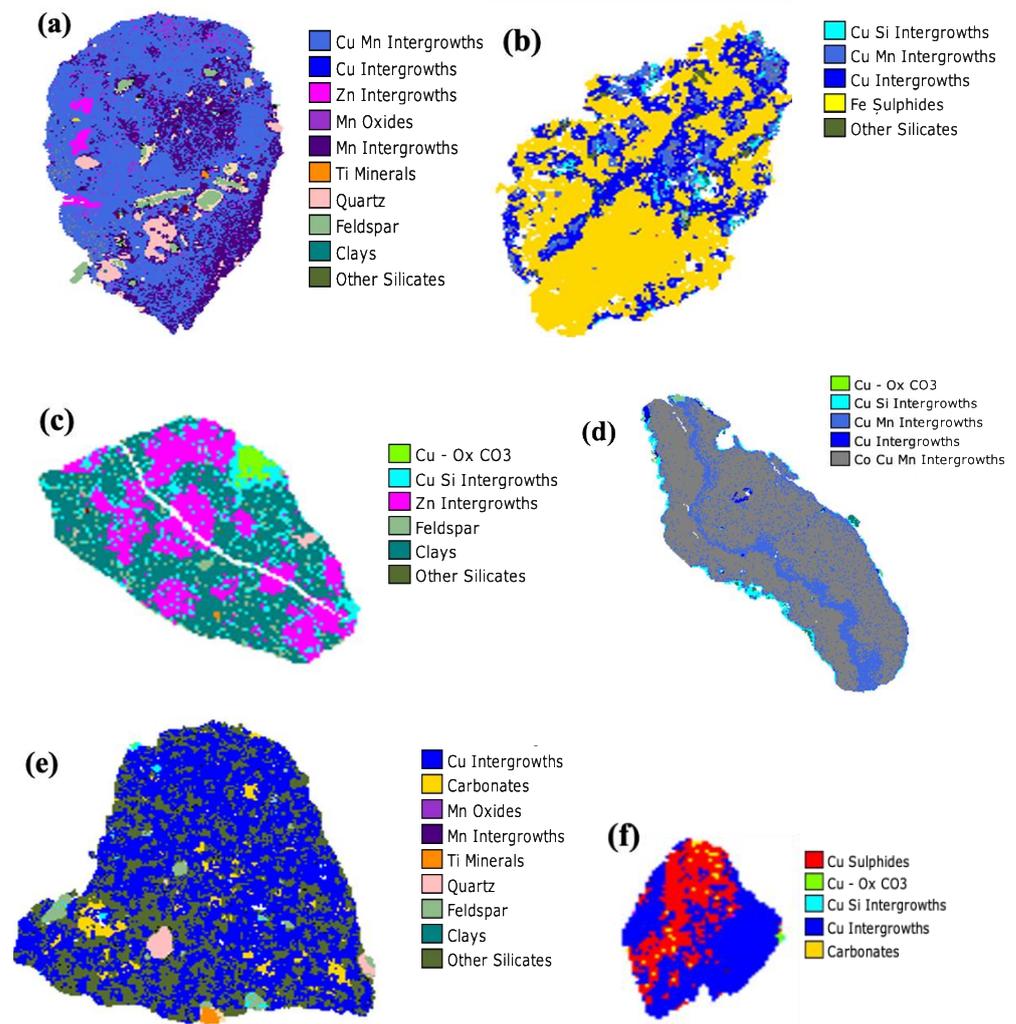


Figure 3. QEMSCAN image for the ore samples: (a) Cu, Mn, and Zn intergrowths; (b) Fe sulphide with Cu intergrowths; (c) Cu oxides and carbonate with Zn intergrowth in clays; (d) Co, Cu, and Mn intergrowths; (e) Cu intergrowth with carbonates, quartz, and silicates; and (f) Cu sulphide and intergrowths.

Table 2. QXRD analysis results for samples before and after acidic oxidation leaching.

Minerals	Formula	Sample		
		Feed	A/O	A/L
Quartz	SiO ₂	1.4	1.6	2.0
Smectite group ⁽¹⁾	X _{0.3} Y ₂₋₃ Z ₄ O ₁₀ (OH) ₂ ·nH ₂ O	73.9	68.4	69.0
Plagioclase	NaAlSi ₃ O ₆ -CaAl ₂ Si ₂ O ₈	14.3	18.4	18.0
Gypsum	CaSO ₄ ·2(H ₂ O) ₂	0.0	0.4	0.7
Bassanite	CaSO ₄ ·0.5(H ₂ O) ₂	0.0	0.0	0.6
K-Feldspar	KAlSi ₃ O ₈	5.1	3.9	7.1
Calcite	CaCO ₃	0.0	0.0	0.0
Goethite	FeO(OH)	5.3	7.2	2.6
Maghemite	Fe ₂ O ₃	0.0	0.0	0.0
Unassigned Peak	-	Tr	Tr	Tr
Total		100	100	100

⁽¹⁾ Smectite group, where X (exchangeable cations) = Ca^{0.5}, Li, Na; Y = Al, Cr³⁺, Cu²⁺, Fe²⁺, Fe³⁺, Li, Mg, Ni, Zn; Z = Al, Si. Montmorillonite was used for the QXRD refinements. Tr: trace, i.e., the mineral that gives rise to the peak is assumed to be present in trace amount.

3.2. Oxidation–Reduction Leaching

The acidic oxidation–reduction leaching was conducted to replicate the conditions used in the plant at the Boleo project. Concentrated sulphuric acid (98% *w/v*) was added at different levels of consumptions (60–140 kg acid/tonne ore) in the temperature range 40–70 °C. The leach liquor pH was generally at pH < 1, whereas during the first 2 h of leaching, the Eh was generally at >900 mV (vs. SCE). The high Eh (>900 mV vs. SCE, or >1.14 V vs. SHE) of the liquor, observed just by adding sulphuric acid alone, indicates other predominant soluble species exist in the solution (such as more oxidising Mn^{3+} or Co^{3+}), apart from Fe^{3+} , which has a lower standard reduction potential (E°) of 0.77 V (vs. SHE). After 2 h, sulphurous acid was added at 25 kg/tonne ore to start the reduction stage, upon which the liquor Eh dropped instantly to 350–370 mV (vs. SCE). The typical liquor Eh and pH measured at 40, 50, and 70 °C are shown in Figure 4.

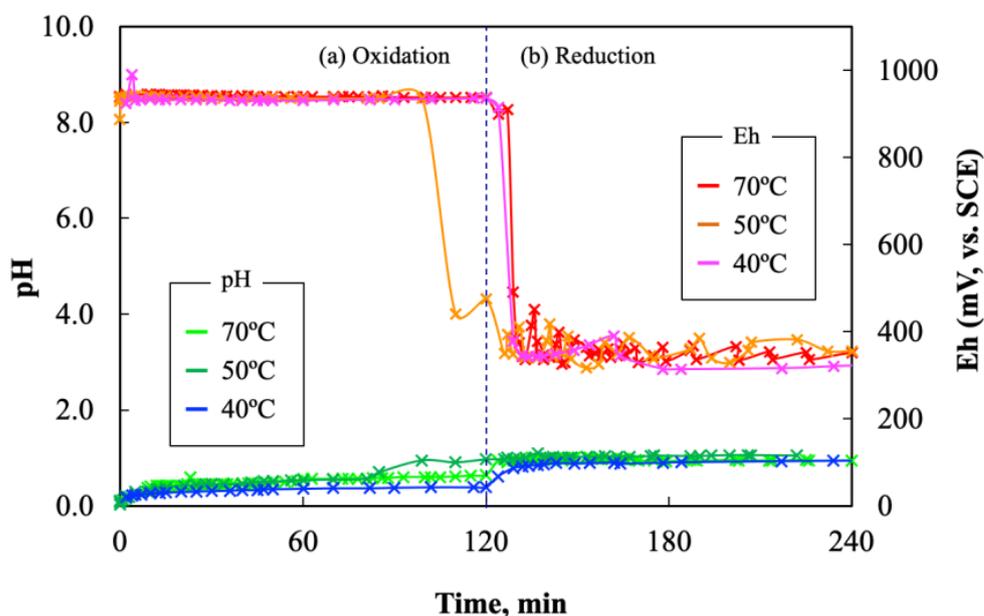


Figure 4. Variation of Eh and pH with time during leaching at different temperatures (40, 50, and 70 °C); (a) oxidation stage (first 120 min): 120 kg H_2SO_4 /tonne ore at 34.5 g/L, and 33% *w/v* pulp density; (b) reduction stage (from 120 to 240 min): 25 kg H_2SO_3 /tonne ore at 7.5 g/L, and 20% *w/v* pulp density.

The presence of MnO_2 in the slurry at this stage, although having a high standard reduction potential for the redox couple MnO_2/Mn^{2+} of 1.23 V, is not believed to be the redox half-cell imparting the high Eh potential measured during the oxidation leaching.

As shown in Figure 5, the leaching recovery of Cu was in the range of 70–80% after 2 h acidic oxidation leaching using sulphuric acid alone, upon the addition of 120 kg acid/tonne ore (equivalent to 34.5 g/L H_2SO_4). This result confirms the finding of QEM-SCAN that some Cu minerals are not leachable at a high Eh (>900 mV vs. SCE). After the oxidation leaching stage, SO_2 (as sulphurous acid) was added at 25 kg/tonne ore (7.5 g/L SO_2) to conduct the reduction leaching for 2 h. Only when the liquor Eh was decreased to 350–370 mV (vs. SCE) by adding SO_2 was it that a further 5–10% Cu could be extracted into the solution. This indicates that either Cu from minor copper sulphide minerals or Cu associated with Fe_2O_3 or MnO_2 minerals is further extracted during reduction leaching.

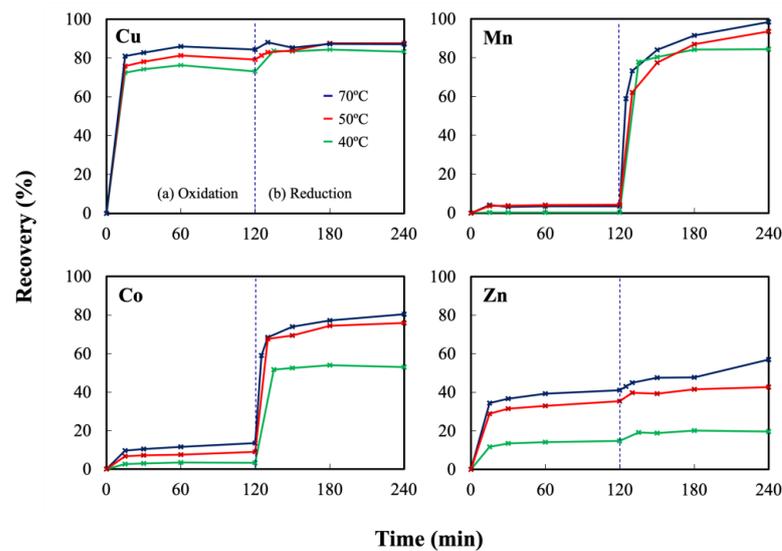


Figure 5. Metal recovery from oxidation–reduction leaching at different temperatures (40, 50, and 70 °C); (a) oxidation stage (first 120 min): 120 kg H₂SO₄/tonne ore at 34.5 g/L, and 33% *w/v* pulp density; (b) reduction stage (from 120 to 240 min): 25 kg H₂SO₃/tonne ore at 7.5 g/L, and 20% *w/v* pulp density.

The recoveries of Co and Mn are less than 15% and 10%, respectively, whereas <60% Zn is extracted at 70 °C. While there seems to be little improvement in Cu or Zn extraction, the recovery of Mn and Co at 70 °C increased significantly, reaching 80% and 95% for Co and Mn, respectively. Table 3 lists the maximum concentrations (g/L and mol/L) of all metals of interest achieved after 4 h of total leaching (oxidation–reduction) at different temperatures. The overall two-stage leaching also yields concentrations within the range of 3.5–5.5 g/L for Cu and Mn. Concentrations of <0.1–0.8 g/L were obtained for Co, Zn, and Fe, similar to those found for the Boleo plant operations. On a molar basis, the amount of Fe leached is ~20% that of Cu and MnO₂ availability is 1.5 times that of Cu.

Table 3. Maximum concentration ranges of Cu, Mn, Co, Zn, and Fe after oxidation–reduction leaching at different temperatures (40, 50, and 70 °C), 120 kg sulphuric acid/tonne ore with 25 kg/t SO₂.

Component	Concentration, g/L (mol/L)		
	40 °C	50 °C	70 °C
Cu	3.57 (0.056)	4.00 (0.063)	4.55 (0.071)
Mn	5.27 (0.096)	5.07 (0.092)	5.43 (0.098)
Co	0.089 (0.0015)	0.103 (0.0017)	0.119 (0.002)
Zn	0.205 (0.003)	0.294 (0.004)	0.387 (0.005)
Fe	0.477 (0.008)	0.673 (0.012)	0.730 (0.013)

3.3. Reduction Leaching

3.3.1. Comparison between Leaching Regimes Using Oxidation–Reduction and Reduction Only

The slight improvement in Cu recovery during reduction leaching implied that most copper had been extracted, and the Cu associated with the silicate, Mn, and Fe oxide intergrowths identified by QEMSCAN analysis contributed to a further 5–10% extra extraction. In this context, although not much MnO₂ is dissolved during the oxidation stage, the Mn³⁺/Mn²⁺ and Fe³⁺/Fe²⁺ could act as redox catalysts for the leaching process. The leaching circuit in the Boleo plant is designed to bypass each reaction stage without modification. It is possible to bypass the oxidation stage and start the leaching by adding sulphurous acid (or reductant, SO₃ in the field) directly to the leaching at the beginning, together with sulphuric acid. The Eh and pH monitored at 3 different temperatures (40, 50,

and 70 °C) show a similar range of Eh (350–370mV (vs. SCE)) and pH 0.8–1.2, compared to the two-stage leaching (Figure 6). Figure 7 compares the performance of the reduction leaching to that of oxidation–reduction at the same conditions. Under these conditions, the Eh was immediately set at 350–370mV (vs. SCE) as soon as the sulphurous acid was added. Copper extraction reached ~85% in less than 30 min, at 50 °C, whereas Mn took up to 2 h to reach ~92%. The extraction of Co and Zn was the same as in the two-stage leaching. The significant improvement for plant operation is that the leaching time can be halved to 2 h rather than the total 4 h for the combined oxidation–reduction leaching.

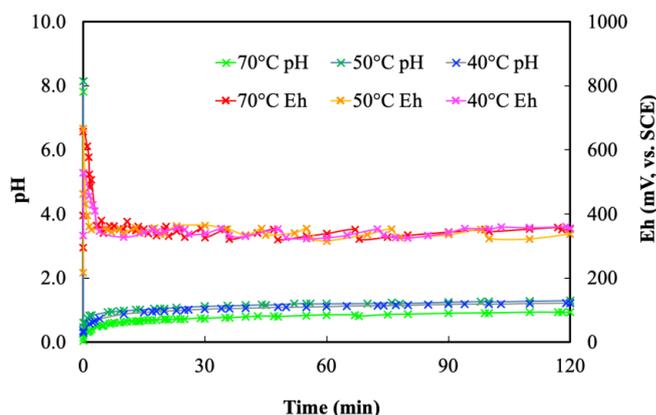


Figure 6. Variation of Eh and pH with time during the enhanced reduction leaching at different temperatures (40, 50, and 70 °C), 100 kg H₂SO₄/tonne ore at 28.7 g/L initial concentration, 25 kg H₂SO₃/tonne ore at 7.5 g/L initial concentration, and pulp density: 20% w/v.

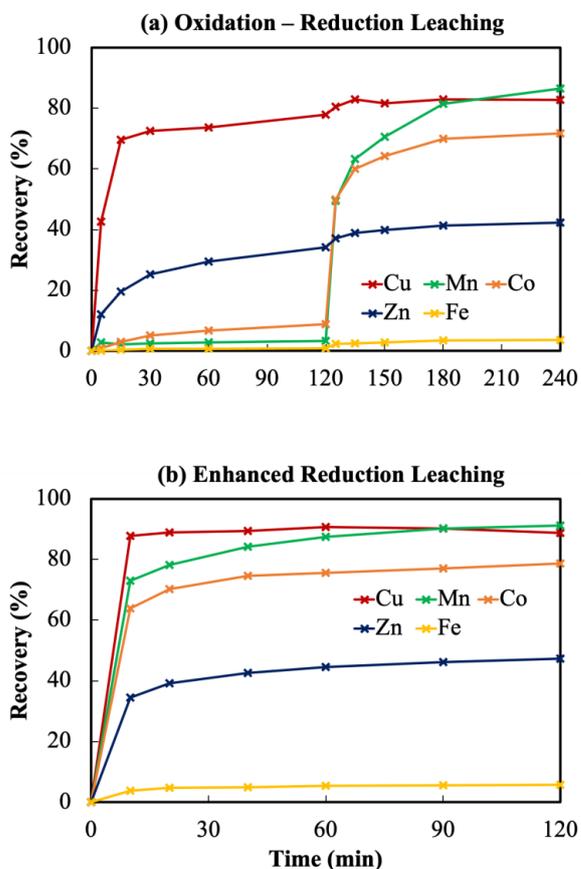


Figure 7. Comparison of Metal recovery of (a) the two-step leaching and (b) the enhanced reduction leaching (condition: 100 kg H₂SO₄/tonne ore at 28.7 g/L initial concentration and 25 kg H₂SO₃/tonne ore at 7.5 g/L initial concentration, 20% w/v pulp density, and temperature at 50 °C).

A Cu extraction of 85–88% during single stage reduction also implies that Cu sulphide minerals and/or Cu is associated with Mn(IV) dioxide or Fe(III) oxide intergrowths in the ore and can be leached using the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple as a catalyst in 2 h, together with Mn, Zn, and Co.

3.3.2. Effect of Temperature

At different temperatures (40, 50, and 70 °C), extractions of 90–92% were observed for Mn within 2 h of leaching using sulphurous acid reductant and 100 kg/tonne ore acid addition, as shown in Figure 8. Under the same conditions, the extraction of Cu also increased to within the range of 85–90% as the temperature was increased. The maximum Zn and Co extraction are 60% and 80%, respectively, similar to those found in the two-stage oxidation–reduction leaching.

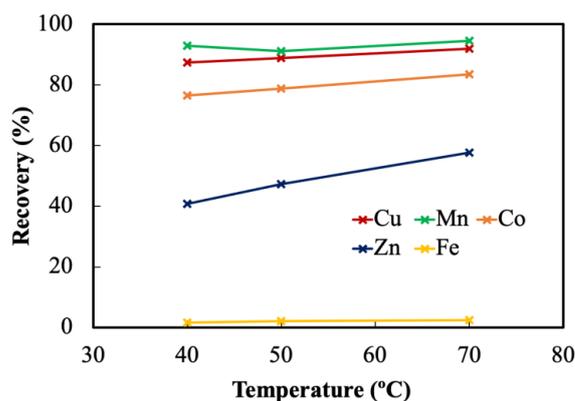


Figure 8. Metal recovery at different temperatures using the enhanced reduction leaching (conditions: 100 kg H_2SO_4 /tonne ore at 28.7 g/L initial concentration and 25 kg H_2SO_3 /tonne ore at 7.5 g/L initial concentration, pulp density: 20% *w/v*).

3.3.3. Effect of Acid Additions

A minimum acid addition at 100 kg sulphuric acid/tonne ore is required to extract ~90% Cu and Mn from the ore at 70 °C. Cobalt also was extracted at 82% and seemed to be only slightly sensitive to acid addition. Zn, on the other hand, was more sensitive to acid addition, increasing in the range 46–62% as acid addition increased from 100 to 140 kg/tonne ore (Figure 9).

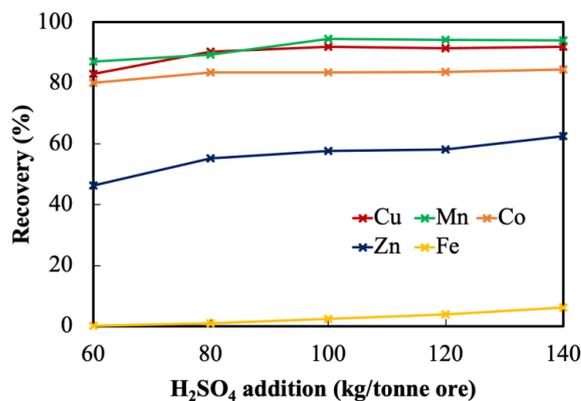


Figure 9. Metal recovery at different acid conditions using the enhanced reduction leaching (Conditions: 25 kg/tonne ore at 7.5 g/L initial concentration, 20% *w/v* pulp density, and temperature at 70 °C).

3.4. Economical Aspect on the Proposed Process

A current operation in the Boleo plant involves two-stage oxidation–reduction leaching using multiple cascade leaching reactors for at least 4 h reaction time. However, this is

the only process for leaching in the plant from the original design, limiting the operating time when maintenance issues are raised. Furthermore, the plant uses hot leaching, which means the reliability of equipment and sensors is lower than that of a standard temperature operation. These underlying conditions are directly connected with operation costs. The enhanced reduction leaching proposed in this research allows better reliability in operation and maintenance to the plant. Moreover, two lines of the leaching process not only increase the plant operation time, but also extend the processing capacity by at least 20 to 30% from the current design of the Boleo plant.

4. Conclusions

In summary, the enhanced reduction leaching to optimise the current leaching condition in the Boleo plant for recovering Cu, Co, Zn, and Mn was investigated.

- (a) The leaching operation at the Boleo process is currently conducted through two stages, with the addition of 100–120 kg sulphuric acid/tonne ore. This study confirms that under these two-stage leaching regimes, a total of 85–88% Cu was extracted in 4 h, first at an oxidising condition with Eh of ~900 mV (vs. SCE), followed by the addition of SO₂ as sulphurous acid to reduce the Eh to 350–370 mV (vs. SCE). The extractions of Mn, Co, and Zn reached 92%, 80%, and 60%, respectively, after 4 h of combined oxidation–reduction leaching at 70 °C.
- (b) However, using a 25 kg addition of SO₂/tonne ore (equivalent to 7.5 g/L SO₂ added as sulphurous acid) together with 100–120kg sulphuric acid/tonne ore in a single-stage reduction leaching, similar metal recoveries of 85%, 80%, 60%, and 92% for Cu, Co, Zn, and Mn, respectively, were reached within only 2 h (at Eh of 350–370 mV (vs. SCE) and pH 0.8–1.2).
- (c) The dissolution of Cu sulphides and oxides of Mn(IV) or Fe(III) under reduction conditions by sulphurous acid further released Cu simultaneously with the leaching of Cu oxide minerals by sulphuric acid.

A significant improvement was achieved in which the leaching time was halved from 4 to 2 h, compared to the previous plant design and current operation involving the two-stage oxidation–reduction leaching. Furthermore, the current plant design could be modified into two multiple leaching process lines, resulting in better reliability in operation and maintenance without major shut down of the plant.

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Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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