

SHORT COMMUNICATION

Leaching of a Mongolian chalcopyrite concentrate

Nicholas J. Welham^{1,2*}, Jadambaa Temuujiin³, Nader Setoudeh^{2,4}¹Principal Technological Consultant, Alexander Mining plc, London, UK²School of Engineering, Edith Cowan University, Joondalup, Western Australia³Institute of Chemistry and Chemical Technology, Mongolian Academy of Sciences, Peace Avenue, 4th Building of MAS, Bayanzurkh district, Ulaanbaatar 13330, Mongolia⁴Materials Engineering Department, Yasouj University, Yasouj, 75918-74831, Iran*Corresponding author: Nicholas.Welham@gmail.com; [ORCID ID:0000-0002-4716-9837](https://orcid.org/0000-0002-4716-9837)

Received: 26 February 2019; revised: 26 February; accepted: 28 February 2019

ABSTRACT

A Mongolian chalcopyrite flotation concentrate was leached using sodium hypochlorite adjusted to different pH using hydrochloric acid. It was found that using a starting pH of below 5.0 resulted in more efficient leaching. The extent of chalcopyrite leaching was determined by the concentration of sodium hypochlorite with > 40% dissolution being achieved. The residue after leaching was found to consist primarily of unreacted chalcopyrite which would be suitable for further leaching or smelting.

Keywords: Chalcopyrite, leaching, sodium hypochlorite

INTRODUCTION

The HyperLeach[®] process is a new proprietary patented process for the extraction of base metals, especially copper, zinc, nickel, cobalt, molybdenum and rhenium from sulphidic ores and concentrates developed by Alexander Mining plc's wholly owned technology company, MetaLeach Limited ('MetaLeach'). The process utilises a chlorine based oxidant to oxidise the sulphide thereby allowing the metals to solubilise [1]. The passivity of chalcopyrite is well known and necessitates the use of high temperature, high pressure, long leach times and/or ultrafine grinding to achieve high extents of leaching [2-5]. Unlike these other processes, HyperLeach[®] operates at ambient temperature and pressure, does not require ultrafine grinding and has a very rapid reaction time. There is significant potential to use HyperLeach[®] for heap leaching due to the absence of any reaction between the reagent and the vast majority of gangue minerals, including pyrite, present in copper sulphide ores. Rather than overcome the passivity by using extreme operating conditions, HyperLeach[®] aims to leach a significant fraction of the copper from the concentrate whilst leaving behind a residue which remains saleable

to copper smelters. By this approach, the capital cost of the leach plant is much lower than processes which aim to completely leach the copper whilst allows for incremental increases in leaching.

HyperLeach[®] differs from previous chlorine based processes in that it does not use chlorine gas, thereby circumventing a number of practical handling and operational issues. Additionally, the process does not require the addition of acid or further chlorine reagent once the reaction has started. The HyperLeach[®] process allows use on existing mine sites as a method for the production of cathode copper from sulphide minerals and concentrates instead of producing concentrates for export or further processing at a remote smelter. This paper examines the use of the HyperLeach[®] process on a Mongolian chalcopyrite concentrate.

EXPERIMENTAL

Approximately 10 kg of chalcopyrite flotation concentrate was provided by a Mongolian mine. The concentrate was dried for 24 h at 70 °C (~1% moisture) then rolled and passed through a 100 µm screen to remove agglomerated lumps. The undersize was used in all leaching runs.

Samples of ore were leached in a stirred reactor for 24 h at a slurry density of 100 g·L⁻¹ of sodium hypochlorite solution adjusted to different starting pH. Intermediate samples were taken periodically but no solution adjustments were made. Iodimetric titrations were performed on all solutions to determine the consumption of hypochlorite.

X-ray diffraction was undertaken on the concentrate and residues over the range of 5 - 70° 2θ with a count time of 0.6 s per 0.02° step. All elemental analyses were performed by SGS Mongolia. The concentrate and residues were subjected to a four acid digest (HNO₃-HCl-HF-HClO₄). The solutions were analysed by AAS for copper and iron and by ICP-OES for all other elements reported.

RESULT

Sample characterisation: Table 1 shows the major elements present in the concentrate. Clearly, the ore is primarily a copper iron sulphide with lesser amounts of gangue. The molar ratio of Fe/Cu is 1.04, slightly above the 1.00 ratio for CuFeS₂ suggesting that there is probably a small quantity of pyrite present in addition to the predominant chalcopyrite. From this data, the mass fraction of chalcopyrite can be calculated to be ~82%, pyrite ~2%, the remaining ~16% is assumed to be primarily quartz as the other common gangue elements are low. The level of arsenic is reasonably low for a copper concentrate and is most probably due to the presence of low levels of tennantite and/or enargite. The elevated level of Mo indicates the concentrate was most probably from a porphyry deposit.

Table 1. Composition of the concentrate.

Element	Analysis	Units
Al	1.22	%
Cu	28.14	%
Fe	25.81	%
As	1980	ppm
Mo	420	ppm

X-ray diffraction showed that there were three major phases present, chalcopyrite, pyrite and quartz which correlates extremely well with the analytical data. No attempt was made to identify the minor phases as XRD is not especially good at identifying phases with low abundance.

Leaching Results: The dissolution of copper as a function of time for the three runs is shown in Figure 1. From this data it is clear that the reaction is rapid, with the majority of copper leaching in the initial 30 mins. The optimum leaching time appears to be 4-6 h, beyond which there is loss of copper from solution. Starting the leaching at a pH of 4-5 seems to be more effective than starting at pH 6.

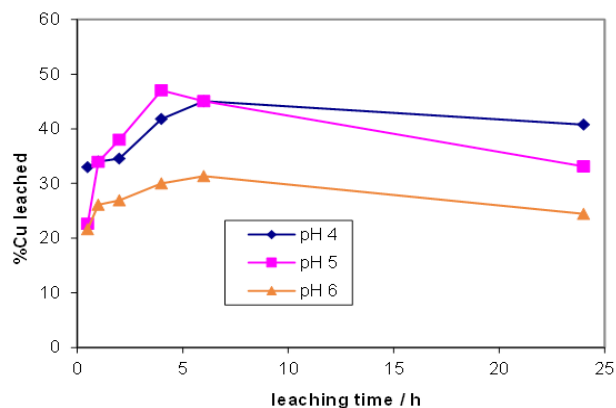
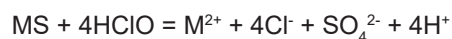


Fig. 1. Copper leaching as a function of time

The low extent of leaching is due to the low concentration of sodium hypochlorite in the starting solution. Iodimetric titration of the starting solution indicated a concentration of around 40 g NaClO/L, substantially lower than the 125 g·L⁻¹ which is the maximum commercially available. The iodimetry also showed that essentially all of the starting hypochlorite was consumed in the initial 1 h, although leaching continued for several hours after the hypochlorite had been consumed, indicating a secondary oxidant was also present. The pH of the solutions decreased to ~2 within the initial 30 mins, this is entirely expected since the oxidation of sulphide minerals leads to production of protons thereby reducing the pH.



The apparent stability of the pH suggests that the oxidation reaction was largely completed in the initial 30 mins.

Figure 2 shows the iron dissolution as a function of time for the three different starting pH. The iron would seem to be precipitating beyond 4-6 h, which is roughly the same time for maximum copper leaching. Thus it would appear that the additional oxidant was ferric ions. The

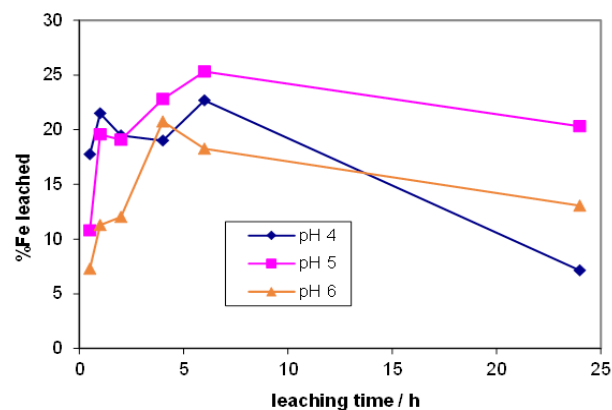


Fig. 2. Iron leaching as a function of time

initial reaction between chalcopyrite and hypochlorite led to the production of ferric ions, which then oxidised the copper phase more slowly. The decrease after 4 h can only be due to precipitation of an iron(III) phase as iron(II) is soluble up to pH 5-6. Thus, it can be reasonably assumed that the aerial oxidation of iron(II) ions results in the precipitation. At shorter times, any iron(III) present is reduced to iron(II) by reaction with the chalcopyrite essentially preventing precipitation. Only once the reaction between iron(III) and chalcopyrite has slowed is the iron(III) precipitated.

The precipitation of the iron explains the lower than expected mass losses, 9.2, 12.5 and 0.6% for starting pH of 4, 5 and 6 respectively. Previous runs have given similar mass losses to the extent of copper leached as the Cu, Fe and S all remained in solution at lower pH. Iodimetric titration of the solutions was used to determine the consumption of reagent by difference.

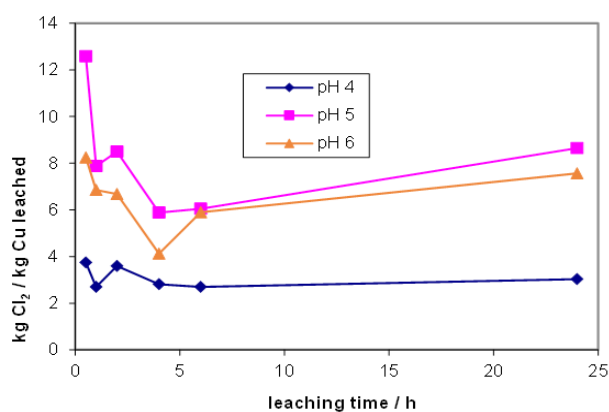


Fig. 3. Chlorine-equivalent consumption as a function of time

In all three runs, the hypochlorite was essentially all consumed within the initial 30 mins, although copper leaching continued for up to ~6 h. Figure 3 shows the specific reagent consumption, in terms of chlorine, with time for each of the runs. As can be seen, the consumption for pH 5 and 6 was similar and notably higher than for pH 4. The decrease from 0.4-6 h is due to the ongoing copper leaching reaction between the chalcopyrite and ferric ions since all hypochlorite had been consumed very rapidly. The increase beyond 6 h is due to precipitation of copper, as shown in Figure 1. The consumptions after 6 h (i.e. before the copper starts to precipitate) were ~2.7, 6.0 and 5.9 kg Cl₂ / kg Cu for starting pH of 4, 5 and 6 respectively.

X-ray diffraction of the residues showed the phases present after leaching were much the same as those present in the feed. Atacamite, a copper chloride hydroxide, was present as a very minor phase in the residues from pH 4 and 6. This is presumed to be one of the phases precipitated during the leaching time from 6 - 24 h. No new iron phases were identified in any residue by XRD. This was not entirely unexpected

as the phase needs to be crystalline to be detected by XRD and at low temperatures iron(III) tends to form polymeric gels rather than phases such as akaganeite, goethite etc. The poor filterability of the residue supports the formation of a gelatinous precipitate.

Table 2. The major element analyses of the residues

Element	Concentrate	pH 4	pH 5	pH 6	Unit
Al	1.22	1.34	1.39	1.36	%
Cu	28.14	19.5	20.73	21.45	%
Fe	25.81	25.11	26.68	26.73	%
As	1980	1800	1830	1900	ppm
Mo	420	408	396	432	ppm

Comparison with the data for the concentrate, Table 2, shows that copper was the major metal leached during the runs. Iron, arsenic and molybdenum all remained much the same, suggesting the extent of leaching was similar to the mass losses. The concentration of aluminium increased in accordance with the decrease in mass due to Cu leaching. Also leached were Ca and Mg, although these were only present at very low levels in the feed. It is expected that had the runs been stopped after 4-6 h, the iron precipitation would not have occurred and the level of iron in the residue would have been somewhat lower, leading to a higher Cu concentration in the residue.

If the iron is ignored for now, the composition of the residue is very similar to the feed concentrate, other than the decreased Cu content. This being the case, the residue from leaching would be suitable as a feed for the same smelter as the concentrate since the composition is largely the same.

Good leaching results were obtained from the different runs with all showing > 30% copper leaching. However, the starting hypochlorite was somewhat old and had decomposed over time to around one third of the initial concentration. The initial slurry density was based around the expected fresh hypochlorite, so leaching of ~30% of the copper is entirely reasonable since only around one third of the expected hypochlorite was present. On this basis, higher extents of dissolution should be achieved by using the more concentrated hypochlorite or by reducing the slurry density to better suit the available hypochlorite concentration. The solution leach tenor is excellent with > 10g·L⁻¹ Cu being achieved in the PLS.

The lower than expected extent of leaching also led to a higher than expected solution pH, since fewer protons were produced by oxidation of the sulphide. This resulted in the precipitation of both iron and copper at longer leach times. Suitable adjustment of the leaching conditions would eliminate this effect.

The stability of the hypochlorite leaching solution is good over a time period of a few weeks. This allows it to be considered as a potential reagent for a heap

leach for chalcopyrite ores. The intrinsic selectivity for sulphide minerals would reduce the consumption of reagent by preventing reaction with gangue minerals. Thus, the reagent consumptions are not expected to be significantly different between tank and heap leaching. The proposed solution treatment route is solvent extraction to extract copper, which is then passed to a cell house for electrowinning into cathodes. Care needs to be taken to prevent transfer of chloride into the cell house by thoroughly washing the loaded organic. The copperfree solution is then mixed with lime to raise the pH of the solution to around pH 7 to precipitate the iron and other elements, the residue is sent to tailings. The remaining solution, which is primarily NaCl, can then be passed to an electrolysis unit where the hypochlorite is regenerated and recycled back to the leach. The leach residue is sold as a feed to a smelter.

CONCLUSIONS

The HyperLeach® process uses hypochlorite solution adjusted to a specific pH to perform the leaching of sulphide minerals. For concentrates, the slurry density needs to be matched to the hypochlorite concentration in order to ensure maximum extent of leaching. The leach is highly selective for sulphides, with no clear oxidative reaction with the gangue minerals. The protons generated during oxidation reduce the pH such that the metals remain in solution, allowing the ferric ions to also act as secondary oxidants for the chalcopyrite.

High extents of copper extraction can be achieved under optimum conditions, leading to the production of cathode copper on a mine site which presently produces a flotation concentrate. The lower grade ore which is not economically viable to concentrate by flotation can also potentially be treated in a heap leach using the same chemistry.

ACKNOWLEDGEMENTS

NS would like to thank Yasouj University for the opportunity to visit Edith Cowan University in Perth, Western Australia as part of a sabbatical year. NS would also like to thank Edith Cowan University for hosting his sabbatical. All authors would like to thank Alexander Mining plc for funding the research work and for permission to publish the work.

REFERENCES

1. Welham N.J., Johnston G.M., and Sutcliffe M.L. (2016) Method of oxidative leaching of sulfide ores and/or concentrates. Mongolian patent 3671,
2. McDonald R.G., Muir D.M. (2007) Pressure oxidation leaching of chalcopyrite. Part I. Comparison of high and low temperature reaction kinetics and products. *Hydrometallurgy* **86**(3-4), 191-205 [doi:10.1016/j.hydromet.2006.11.015](https://doi.org/10.1016/j.hydromet.2006.11.015)
3. Watling, H.R. (2013) Chalcopyrite hydrometallurgy at atmospheric pressure: 1. Review of acidic sulfate, sulfate-chloride and sulfate-nitrate process options, *Hydrometallurgy*, **140**, 163-180 [doi:10.1016/j.hydromet.2013.09.013](https://doi.org/10.1016/j.hydromet.2013.09.013)
4. Watling H.R. (2014) Chalcopyrite hydrometallurgy at atmospheric pressure: 2. Review of acidic chloride process options. *Hydrometallurgy*, **146**, 96-110 [doi:10.1016/j.hydromet.2014.03.013](https://doi.org/10.1016/j.hydromet.2014.03.013)
5. Dixon D.G., Mayne D.D., Baxter K.G. (2008) Galvanox™ - A novel galvanically-assisted atmospheric leaching technology for copper concentrates, *Canadian Metallurgical Quarterly* **47**(3), 327-336 [doi:10.1179/cmqr.2008.47.3.327](https://doi.org/10.1179/cmqr.2008.47.3.327)