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TESIS

EXTRACCIÓN DE COBRE Y MANGANESO MEDIANTE PROCESOS DE LIXIVIACIÓN

*Tecnología y modelización en Ingeniería
Civil, Minera y Ambiental*

Lixiviación agitada de óxidos de cobre en Mantos Blancos, Chile.
Photograph by D.W. Shiers.



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Cartagena 2021

**CONFORMIDAD DE SOLICITUD DE AUTORIZACIÓN DE DEPÓSITO DE
TESIS DOCTORAL POR EL/LA DIRECTOR/A DE LA TESIS**

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EXTRACCIÓN DE COBRE Y MANGANESO MEDIANTE PROCESOS
DE LIXIVIACIÓN

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INFORMA:

Que la referida Tesis Doctoral, ha sido realizada por D/D^a. DAVID TORRES ALBORNOZ, dentro del Programa de Doctorado Tecnología y modelización en Ingeniería Civil, Minera y Ambiental, dando mi conformidad para que sea presentada ante el Comité de Dirección de la Escuela Internacional de Doctorado para ser autorizado su depósito.

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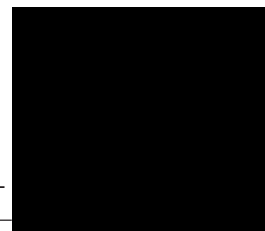
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EXTRACCIÓN DE COBRE Y MANGANESO MEDIANTE PROCESOS
DE LIXIVIACIÓN



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ACUERDA

Autorizar la presentación de la Tesis Doctoral a D. David Antonio Torres Albornoz en la modalidad de “compendio de publicaciones”.

Contra el presente acuerdo, que no agota la vía administrativa, podrá formular recurso de alzada ante el Sr. Rector-Magnífico de la Universidad Politécnica de Cartagena, en el plazo de un mes a partir de la notificación de la presente.

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UNIVERSIDAD POLITÉCNICA DE CARTAGENA

DEPARTAMENTO DE INGENIERÍA MINERA Y CIVIL

**EXTRACCIÓN DE COBRE Y MANGANESO
MEDIANTE PROCESOS DE LIXIVIACIÓN**

**COPPER AND MANGANESE EXTRACTION THROUGH
LEACHING PROCESSES**

Memoria presentada por **David Antonio Torres Albornoz**, Ingeniero Civil
Metalúrgico, Magister en Ciencias de la Ingeniería Mención Metalurgia,
para optar al grado de Doctor por la Universidad Politécnica de Cartagena

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Los artículos que constituyen la tesis son los siguientes:

- **Publicación 1: David Torres**, Luís Ayala, Manuel Saldaña, Manuel Cánovas, Ricardo I. Jeldres, Steven Nieto, Jonathan Castillo, Pedro Robles and Norman Toro. “Leaching Manganese Nodules in an Acid Medium and Room Temperature Comparing the Use of Different Fe Reducing Agents” Q1 ISI WoS Metals Journal, 2019; <https://doi.org/10.3390/met9121316>
- **Publicación 2: David Torres**, Luís Ayala, Ricardo I. Jeldres, Eduardo Cerecedo-Sáenz, Eleazar Salinas-Rodríguez, Pedro Robles and Norman Toro. “Leaching Chalcopyrite with High MnO₂ and Chloride Concentrations” Q1 ISI WoS Metals Journal, 2020; <https://doi.org/10.3390/met10010107>
- **Publicación 3: David Torres**, Kevin Pérez, Emilio Trigueros, Ricardo I. Jeldres, Eleazar Salinas-Rodríguez, Pedro Robles and Norman Toro. “Reducing-Effect of Chloride for the Dissolution of Black Copper” Q1 ISI WoS Metals Journal, 2020 <https://doi.org/10.3390/met10010123>
- **Publicación 4: David Torres**, Emilio Trigueros, Pedro Robles, Williams H. Leiva, Ricardo I. Jeldres, Pedro G. Toledo and Norman Toro “Leaching of Pure Chalcocite with Reject Brine and MnO₂ from Manganese” Q1 ISI WoS Metals Journal, 2020 <https://doi.org/10.3390/met10111426>

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Resumen

Esta Tesis se centra en la recuperación de Cu y Mn desde cuatro posibles minerales estratégicos para la minería chilena y mundial: los nódulos de manganeso marinos, los óxidos de cobre negros, la calcosina y la calcopirita. Este es uno de los ejes de desarrollo de la industria minera en el sector del cobre que, ante el descenso de leyes y el aumento del consumo, busca nuevas fuentes de abastecimiento, recuperación de otros metales y subproductos y emplear, para los procesos industriales de tratamiento mineral, las sustancias de desecho en otros sectores como el de la desalinización de agua o la industria siderúrgica.

Se analizan las condiciones de disolución de los metales procedentes de estos minerales utilizando la técnica de lixiviación forzada a escala de laboratorio. Se evalúa el uso de diferentes aguas para la solución lixivante, como el agua de mar y la salmuera de descarte en las plantas desalinizadoras, probando el uso de diferentes agentes oxidantes en base al hierro y manganeso.

Bajo las mismas condiciones de trabajo, se obtienen resultados similares para la disolución de Mn desde MnO_2 presente en nódulos de manganeso y cobres negros. Por lo cual, se presume es posible replicar procesos previos en nódulos de manganeso para los minerales de cobre negro que se desechan en la gran minería en Chile, siendo el tiempo de curado un parámetro muy importante a considerar, ya que al trabajar en tiempos prolongados (sobre 48 h) se puede trabajar a bajas concentraciones de NaCl, y a la vez incrementar de forma significativa la extracción de Cu por la previa disolución de MnO_2 .

Por otra parte, la combinación de aditivos entre agua residual de plantas desalinizadoras y MnO_2 en el sistema, se presenta como una alternativa que incrementa la disolución de Cu desde minerales sulfurados a temperatura ambiente en la literatura actual, esto debido a que permite trabajar a altos valores de potencial en el sistema.

Abstract

This Thesis are focused on the recovery of Cu and Mn from four possible strategic minerals for Chilean and worldwide mining: marine manganese nodules, black copper oxides, chalcocite and chalcopyrite. This is one of the main development axes of the mining industry in the copper sector given the decline in grades and increased consumption. Mining enterprises are seeking new sources of supply, recovery of other metals and by-products and also employ waste substances from other sectors for industrial processes of mineral treatment, such as brine from water desalination or the steel industry wastes.

The dissolution conditions of the metals from these minerals are analyzed using the vat leaching technique on a laboratory scale. The use of different waters for the leaching solution is evaluated, such as seawater and waste brine from desalination plants, testing the use of different oxidizing agents based on iron and manganese.

Under the same working conditions, similar results are obtained for the dissolution of Mn from MnO_2 present in manganese nodules and black coppers. Therefore, it is presumed possible to replicate previous processes in manganese nodules for black copper minerals that are discarded in large mining in Chile. Being a very important parameter to consider the curing time, since when working for long times (over 48 h) it is possible to work at low concentrations of NaCl, and at the same time significantly increase the extraction of Cu by the previous dissolution of MnO_2 .

On the other hand, the combination of additives between wastewater from desalination plants and MnO_2 in the system, is presented as the alternative that most increases the dissolution of Cu from sulphide minerals at room temperature in the current literature, this because it allows working at high potential values in the system.

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1. Introducción

Existe una gran diversidad de minerales cupríferos en el territorio chileno, los cuales se ven acompañados de otros elementos de potencial interés comercial, lo que hace que su aprovechamiento constituya una línea de trabajo de especial interés.

Un mineral de suma importancia para el presente y futuro de los procesos extractivos mineros en Chile es la calcopirita. Esto se debe, a que es el mineral de cobre más abundante del mundo [1-7]. Este mineral ha sido trabajado tradicionalmente en la industria por procesos pirometalúrgicos convencionales (flotación, fundición, refinación y electro-refinación), esto debido a las bajas extracciones de cobre y lentas cinéticas de disolución en procesos de lixiviación convencionales [8-12]. Diversos estudios indican que la causa de este comportamiento está en la formación de una capa pasivante en la superficie del mineral, evitando el contacto con los reactantes [13-14]. Por este motivo, este mineral no ha sido posible de trabajar a escala industrial mediante procesos hidrometalúrgicos convencionales, lo cual implica procesar grandes cantidades de este material mediante el uso de técnicas pirometalúrgicas convencionales. Los procesos establecidos para el aprovechamiento por esta vía, provocan excesivas emisiones de dióxido de azufre a la atmósfera y, además, millones de toneladas anuales de relaves por vías de flotación, generando una gran preocupación a la población local por su impacto en el medio ambiente [15-25].

No son los temas medio ambientales el único foco de preocupación de la gran minería en Chile, también el envejecimiento de los yacimientos ha provocado una importante bajada en las leyes de cobre, y en paralelo un aumento en los costos de explotación. Por este motivo, en los últimos años, se ha favorecido el impulso de las líneas de investigación del país encaminadas a fomentar tres focos específicos:

- i) Diversificar la extracción de otros elementos en la minería nacional, y no sólo centrarse en el cobre (un ejemplo, es el enorme crecimiento de la industria del molibdeno, el cual se obtiene como subproducto en los procesos de flotación de cobre).

ii) Conseguir innovadores procesos que optimicen las extracciones de cobre, y en paralelo fomenten la economía circular y disminuyan la contaminación local.

iii) Disminuir el consumo de agua potable en procesos mineros [26].

En relación con la búsqueda de una mayor variedad en el mercado de extracción de elementos metálicos, una alternativa que puede ser atractiva industrialmente es el tratamiento de cobres negros. Estos minerales son recursos que generalmente no se incorporan a los circuitos de extracción o no se tratan, ni como reservas, ni empleando pilas de lixiviación o desechos.

Son estos los denominados “minerales exóticos” y tienen cantidades considerables de Mn y Cu, lo que representa un importante atractivo comercial. Comúnmente se encuentran asociados a minerales como crisocola y atacamita, estando presentes, con frecuencia, de manera masiva en varias mineras del norte de Chile como: Mina Sur en Chuquicamata, Damiana en El Salvador, Huanquintipa en Collahuasi, Lomas Bayas, Spence, etc. [27-33].

A pesar de que existen pocos estudios sobre el tratamiento de cobres negros, se han reportado diversas maneras de extraer el MnO_2 presente en nódulos marinos, los cuales presentan mecanismos de ataque similares para la extracción de manganeso. Para ambos casos (cobre negro y nódulos marinos) es necesario realizar un proceso ácido-reductor que permita bajar el potencial del sistema, favoreciendo la disolución de Mn. Además, en estudios recientes sobre cobres negros, se ha descubierto que al disolver el MnO_2 presente en estos, se favorece de la misma forma la disolución de cobre, permitiendo la extracción con éxito de ambos elementos [34-36].

La escasez de agua dulce en las zonas áridas es un problema económico, medioambiental y social [37-39]. La mayor parte de las grandes Compañías Mineras en Chile, se encuentran en zonas hiperáridas, donde la cantidad de recursos minerales provoca un incremento excesivo de la demanda de agua para el procesamiento, muy por encima de las disponibilidades, lo que ha impulsado el uso de agua de mar como recurso alternativo en los procesos mineros [40-45]. Por este motivo, las autoridades

chilenas han advertido que no se autorizarán proyectos mineros a gran escala que involucren el uso de agua de acuíferos [41,66].

Ante este panorama, en los últimos años se han realizado diversos estudios que involucran el uso de agua de mar en el área de la metalurgia extractiva, ya sea para los procesos de flotación y espesamiento [46-57] como para los de lixiviación [58-65]. El uso de agua de mar ha presentado resultados muy positivos al lixiviar sulfuros secundarios (principalmente calcosina) en la gran minería del cobre. Una alternativa atractiva es el aprovechamiento de aguas residuales de plantas desaladoras. Estas actividades de desalinización producen agua potable para la población, sin embargo, su producto de rechazo contamina los océanos, por ello, es necesario pensar en posibles alternativas para reciclar este material de descarte y al mismo tiempo optimizar los procesos de extracción en la minería local. Es de resaltar además, que en procesos de lixiviación se han logrado mejores resultados al reutilizar aguas residuales de plantas desaladoras que al emplear agua de mar, lo que es debido a sus altos contenidos de cloruro (aproximadamente 40 g/L) [67].

La presente Tesis Doctoral, contribuye en las áreas de ingeniería química y metalúrgica, con un enfoque principal en la lixiviación. Este documento que resume de los trabajos y resultados de investigación, es un compendio de artículos, que incluye cuatro estudios de extracción de cobre y manganeso sobre cuatro tipos de minerales (nódulos de manganeso, cobres negros, calcopirita y calcosina). Cada uno de estos trabajos relacionados aborda determinada problemática que interesa al Sector industrial de la gran minería en Chile.

La línea de trabajo está desarrollada por parte de los equipos de investigación de los directores de la Tesis, habiendo sido leída recientemente por parte de uno de ellos, el Doctor Norman Toro su tesis en esta temática con resultados prometedores y el establecimiento de una metodología que ahora se consolida.

2. Objetivos

Los objetivos que se han establecido para esta Tesis consisten en avanzar en el conocimiento del comportamiento de determinados reactivos y condiciones del proceso de lixiviación para hacer viable el tratamiento de minerales no convencionales, como nódulos de manganeso, cobres negros o calcosina y otros como la calcopirita que no se suelen procesar por esta vía. Se trata de optimizar la recuperación del cobre y otros elementos metálicos de valor asociados a este.

Para la realización de las tareas que desarrollan este objetivo general, se trabaja en pruebas de lixiviación a nivel laboratorio, evaluando los parámetros y aditivos principales que indica la literatura y estudios industriales a nivel local previamente realizados, tratando de reemplazar los aditivos a incorporar en el sistema, ya sea la solución lixivante o el oxidante, por recursos alternativos que son considerados como residuos por la industria.

3. Metodología de trabajo

La primera parte es la parte experimental que se lleva a cabo en 2 etapas: Preparación de la muestra de mineral y Proceso de Lixiviación. Con posterioridad se realiza un tratamiento de los resultados, mediante optimización y/o análisis estadístico ANOVA.

Todas las pruebas experimentales se realizaron en el laboratorio de “Nuevas líneas de investigación”, perteneciente al Departamento de Ingeniería Metalúrgica y Minas, de la Universidad Católica del Norte.

3.1. Preparación del mineral

En los 4 estudios realizados para esta Tesis, se trabajó con nódulos de manganeso, cobres negros, sulfuro secundario (calcosina) y sulfuro primario (calcopirita).

Era fundamental que los minerales a utilizar tuvieran una pureza elevada, para disminuir las desviaciones en los resultados. Con este objetivo fueron reducidos de tamaño con el uso de un mortero, esto para evitar que se contamine debido a las impurezas y polvo que suelen estar presentes en un molino chancador.

La reducción de tamaño del mineral se realiza hasta que el 100% esté a una granulometría -10# (2 mm). Luego se procede a homogenizar el mineral, y se toman 2 muestras representativas de 1 g cada una, para ser enviadas a análisis químico y mineralógico.

Los análisis químicos fueron determinados por espectrometría de emisión atómica de plasma acoplado inductivamente (ICP-AES), mientras que la mineralogía de las muestras se determinó de dos formas: un análisis QEMSCAN, que es un microscopio electrónico de exploración que se modificó tanto en hardware como en software, y/o utilizando un difractómetro de rayos X de la marca Bruker, modelo automático e informatizado de D8. Para la clasificación de tamaños en los diferentes estudios, el material fue molido en el mortero cuidadosamente, y clasificado a través de mallas tamices, hasta llegar a los rangos deseados.

3.2. Proceso de lixiviación

El ácido sulfúrico utilizado para todas las pruebas de lixiviación fue de grado P.A., con una pureza del 95-97%, una densidad de 1.84 kg/L y un peso molecular de 98.80 g/mol.

Las pruebas de lixiviación se llevaron a cabo en un circuito de reactores de vidrio de 50 ml con una relación sólido / líquido de 0,01 (2). A través de los reactores fluye por su revestimiento externo un fluido (agua termostática) a la temperatura de trabajo requerida (1).

Se mantuvo en suspensión un total de 200 mg de mineral de dióxido de manganeso con el uso de un agitador magnético de cinco posiciones (IKA ROS, CEP 13087-534, Campinas, Brasil) a una velocidad de 600 rpm (5).

Las pruebas en general se realizaron a una temperatura ambiente de 25 ° C, mientras que para otras se varió la temperatura (de 25 a 90 °C) evitando la evaporación de agua con el uso de un refrigerante de vidrio conectado a la parte superior de los reactores (3). Los tubos refrigerantes, son alimentados por una manguera conectada a la llave de agua potable, de este modo al pasar el chorro de agua a temperatura ambiente y hacer contacto con el gas caliente que sale del reactor hace que éste se condense y vuelva al mismo (4). (ver Figura 1).

Las pruebas se realizaron por duplicado y las mediciones (o análisis) se realizaron en muestras de 5 ml sin diluir utilizando espectrometría de absorción atómica con un coeficiente de variación $\leq 5\%$ y un error relativo entre 5 y 10%.

Las mediciones del pH y el potencial de oxidación-reducción (ORP) de las soluciones de lixiviación se realizaron con un medidor de pH-ORP (HANNA HI-4222 (instrumentos HANNA, Woonsocket, Rhode Island, EE. UU.)). La solución ORP se midió en una celda de electrodo de combinación ORP compuesta de un electrodo de trabajo de platino y un electrodo de referencia de Ag/AgCl saturado.

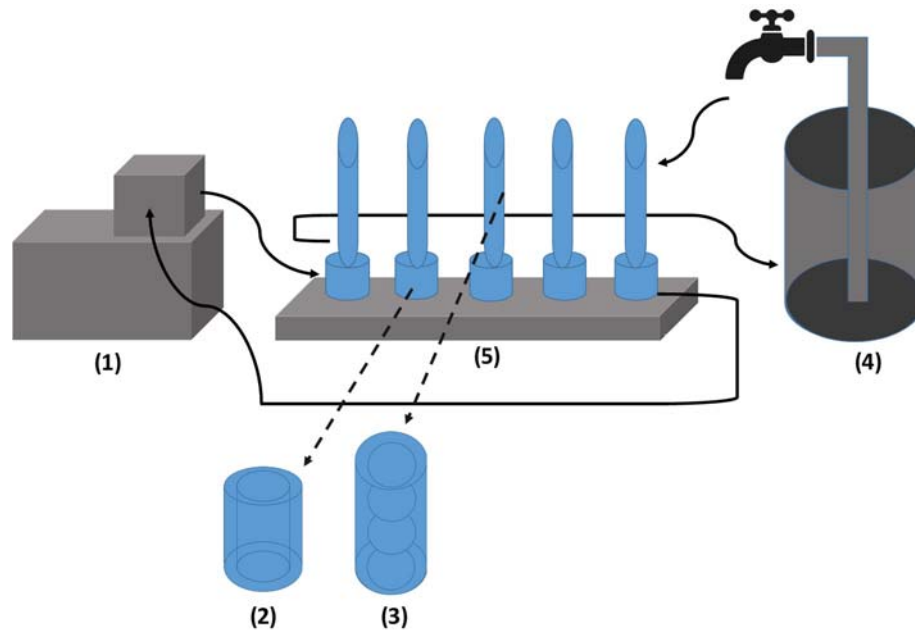


Figura 1. Esquema del circuito de reactores en serie utilizado en el laboratorio.

3.3. Preparación del mineral

Una vez obtenidos los resultados se han realizado dos tipos de tratamientos sobre estos datos, generalmente relacionados con el porcentaje de recuperación obtenido, como paso previo a la obtención de conclusiones:

- Un análisis de sensibilidad, al variar alguno de los factores intervinientes en el proceso y dejar el resto en valores medios de su rango de variación.
- Un análisis estadístico de varianzas ANOVA, para obtener la relación entre los factores y el resultado. El modelado previo de los experimentos se realizó con programas adecuados a este tipo de experiencias (Minitab 18).

4. Estado del arte

4.1 Recursos de manganeso

Existe un agotamiento en los recursos minerales de la zona más superficial de la corteza terrestre [68-70]. A pesar de que el manganeso es uno de los 12 elementos más abundantes, ya que constituye aproximadamente el 0.1% de los elementos constituyentes del subsuelo [71], este metal se encuentra muy diseminado, y son escasos los depósitos de alta ley. El Mn se puede asociar en diferentes formas, entre las cuales tenemos, por orden de abundancia, los óxidos, sulfuros, carbonatos y silicatos [72]. Además, también es posible hallar manganeso en las profundidades del mar, en forma de nódulos, micro concreciones, recubrimientos y costras [73]. [74,75].

Los últimos datos de consumo nos indican que la demanda de Manganeso a nivel mundial está en aumento. A esto se suma el agotamiento gradual de menas de alta ley de manganeso [76]. Este metal tiene una gran importancia en varios mercados como: aleación para la producción de acero, preparación de aditivos dietéticos, fertilizantes, células, productos químicos finos y algunos reactivos químicos [77-84]. La fabricación de acero, incluido su componente de fabricación de hierro, representa la mayor parte de la demanda interna de manganeso, actualmente en el rango del 85% al 90% del total [74], [85].

Se han hecho grandes esfuerzos para recuperar el manganeso desde minerales de pirolusita de baja ley, sin embargo, esto es insuficiente para satisfacer los niveles de producción requeridos [76].

4.2. Nódulos de manganeso

Se estima que, en los fondos marinos, se encuentra las más grandes reservas de cobalto, níquel y manganeso en el mundo [86]. Existen tres grandes recursos ricos en minerales en las profundidades del océano: nódulos marinos, costras de ferromanganeso y sulfuros polimetálicos [87,88]. Son particularmente los nódulos marinos una atractiva opción debido a sus altos contenidos de manganeso (entre un 16 y 24 %) [89-91].



Figura 2. Nódulo de manganeso utilizado.

Los nódulos marinos, también conocidos como nódulos de manganeso, son concreciones de roca formadas por capas concéntricas de hidróxidos de Fe y Mn [92]. Estos recursos minerales, están compuestos principalmente por óxido δ -MnO₂ hidrogenético, 10 Å manganato diagenético, conteniendo mayoritariamente Todorokita, formada por diagénesis óxica, y Vernardita formada por precipitación hidrogénica [89]. Su formación se produce en llanuras abisales cubiertas de sedimentos a profundidades de agua de 4,000–6,500 m, donde las tasas de acumulación de sedimentos son bajas [93-94].

Estos depósitos abisales de nódulos marinos cubren el 50% de grandes áreas del fondo marino del Pacífico y la cuenca del Océano Índico central [95-96].

4.3. Cobres negros

Los yacimientos de cobre están sometidos a los agentes geológicos, que producen de forma lenta la oxidación de algunos minerales presentes en el pórfido encajante, como pirita. Ésta, al reaccionar con el agua, genera ácido sulfúrico, ocasionando la movilidad de metales, como el cobre que, bajo ciertas condiciones de potencial y pH,

pueden ser transportadas logrando precipitar aguas abajo y formando los yacimientos secundarios denominados “Exóticos” [27].

La mineralización existente en estas zonas de precipitación en la parte superior del depósito de sulfuros, incorpora distintas especies de minerales de cobre tales como, crisocola atacamita, copper pitch y copper wad [29], estos últimos definidos como mineraloides, debido a que cristalizan de manera amorfa [30,33]. También son denominados silicatoides ricos en Si-Fe-Cu-Mn [31].

Los minerales “copper pitch” y “copper wad” se caracterizan por tener altas concentraciones de MnO₂. Este óxido los vuelve minerales refractarios (quiere decir que no se pueden procesar por procesos convencionales) lo cual conlleva a que sean comúnmente desechados y almacenados en botaderos de escombros de las plantas mineras [97].



Figura 3. Mineral de cobre negro utilizado.

4.3. Minerales convencionales de cobre

Dentro de los minerales de cobre, los sulfuros son mucho más abundantes que los óxidos, existiendo además un agotamiento de estos últimos. A causa de esto, la mayor parte de la producción de cobre (~80%) en el planeta, se realiza por procesos

pirometalúrgicos que involucran etapas de flotación y posteriormente fundición, mientras que un menor porcentaje (~25%) se trabaja mediante procesos hidrometalúrgicos [98-99].

Chile es el principal productor de cobre a nivel mundial con una participación de aproximadamente 28% en la venta de esta materia prima (commodity). Actualmente, se tiene como estrategia país el aumentar los niveles de producción, para lo cual, se ha planificado que para el año 2027, en Chile el 80% de la producción de cobre se realizará mediante procesos de flotación [17]. Sin embargo, esto generará una enorme cantidad de relaves estériles (por cada tonelada de cobre obtenida mediante procesos de flotación se generan 151 toneladas de relaves) que son pasivos ambientales cuya gestión genera incertidumbres y preocupación en la población local [18].

Por este motivo, se continúa investigando constantemente alternativas hidrometalúrgicas que permitan disolver de manera rentable sulfuros primarios, debido a que es un proceso menos contaminante.

4.4. Calcopirita

La calcopirita es el mineral de cobre más abundante en el planeta, siendo además un mineral de baja ley de cobre (34,6%) que es refractario a los procesos de lixiviación convencionales, y que por lo tanto, ha sido tratado históricamente por procesos de flotación [101]. En cuanto a su apariencia, es de color amarillo latón con reflejos verdes y posee brillo metálico, encontrándose comúnmente asociada a pirita.



Figura 4. Mineral de calcopirita utilizado.

Se han realizado estudios recientes para la disolución de CuFeS_2 utilizando para ello aguas de descarte procedentes de las desalinizadoras [3,60,67]. A pesar de que no se han logrado todavía escalar a planta piloto estos procesos, se ha logrado demostrar que el agua residual de plantas desalinizadoras presenta mejores resultados que el agua de mar, que es la que se aplica actualmente en la industria.

4.5. Calcosina

La calcosina es el sulfuro secundario de cobre más abundante, con el mayor contenido de cobre y de más fácil tratamiento por procesos hidrometalúrgicos, lo que lo hace un mineral muy rentable para su extracción [67,102-105]. En cuanto a su apariencia, es de color gris oscuro y se encuentra comúnmente en el ambiente supergénico enriquecido debajo de la zona oxidada de los depósitos de pórfido de cobre [106].

Se han realizado diversos estudios para la disolución de Cu_2S con el uso de múltiples aditivos y en diferentes medios como: biolixiviación [107], solución de sulfato férrico [108-109], medios clorurados [110-111], medios alcalinos [112] y calcosina sintética (metal blanco) [113-114]. De todos ellos, el más utilizado es el medio clorurado, siendo aplicado a nivel industrial en procesos de lixiviación en pilas, aprovechando los iones cloruro presente en el agua de mar como un agente complejante que ayuda a catalizar el proceso [115-116].



Figura 5. Mineral de calcosina utilizado

4.6. Lixiviación de minerales

Existen diferentes métodos para lixiviar, que corresponden a la forma en que se contactan las soluciones lixiviantes con las menas (Figura 6). Los métodos más comunes son [11]:

a) Lixiviación In Situ: Se realiza en yacimientos de bajas leyes que no se pueden explotar de forma convencional por razones técnicas o económicas regando directamente el yacimiento. La recuperación requiere largos períodos de ataque (del orden de años) y las recuperaciones son muy variables. Además, existe el riesgo de que las soluciones ácidas contaminen las aguas subterráneas y superficiales lo que exige infraestructuras para el control de sus flujos.

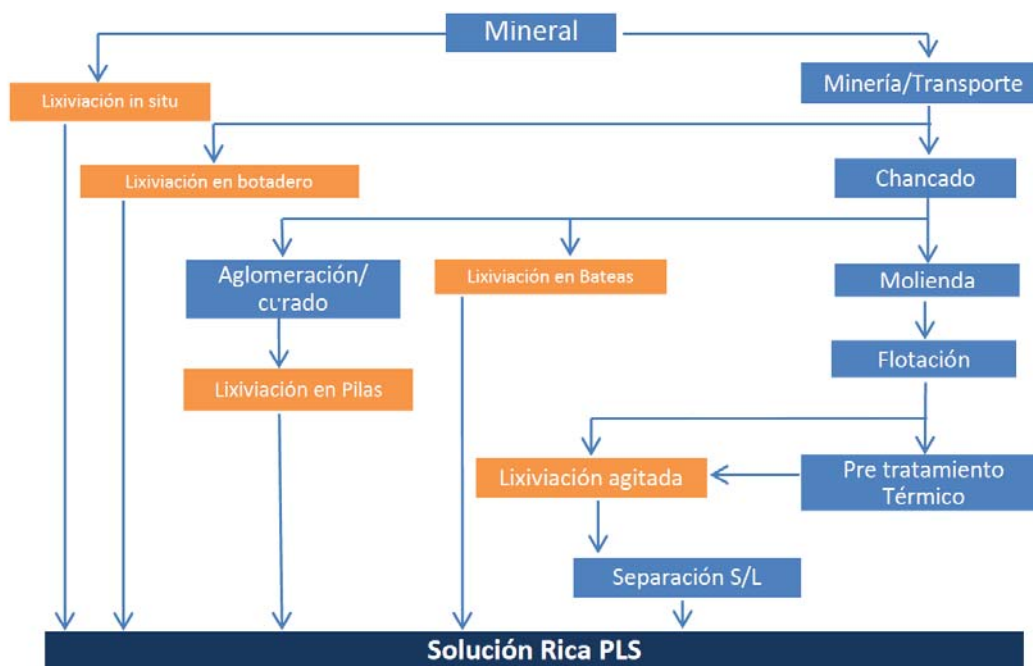


Figura 6. Alternativas de lixiviación de minerales (Modificado desde: [12])

b) Lixiviación en vacíos (botaderos; dump leaching): Se aplica a materiales de desmonte y recubrimiento de baja ley (menor a 0,4% para Cu). No tiene costos asociados a transporte y las recuperaciones fluctúan entre 40 y 60% para el caso del cobre en un plazo de unos 3 años.

c) Lixiviación por percolación o en bateas: Se aplica para mineral con granulometría de entre 10 y 20 mm (triturado). Consiste en llenar unos depósitos de hormigón con mineral. Se inunda con soluciones de lixiviación que se van

extrayendo por el fondo y recirculando a otras bateas para ir concentrando. Este método está prácticamente obsoleto para el cobre [118].

d) Lixiviación en pilas química y bacteriana (heap leaching): Cuando el mineral tiene una mayor ley, de manera que justifica recurrir un tratamiento más complejo que requiere una planta de molienda (chancado). El mineral puede ser óxido, mixto o sulfuro y puede recibir pre-tratamientos de lixiviación como curado férrico, curado ácido y/o aglomeración.

Se amontona en pilas de 2 a 12 m y se riega con la solución lixivante. La solución rica de lixiviación conocida como PLS –del inglés Pregnant Leach Solution- tiene una concentración de 3 a 10 g/L de Cu. La recuperación varía desde 75% a 90%, en un período de 2 a 3 meses en el caso de óxidos y sobre 12 meses en el caso de sulfuros [120].

Para el caso de lixiviación bacteriana de minerales sulfurados, las bacterias se pueden reproducir de forma natural en las pilas, dependiendo de las condiciones en las que se encuentren, así como también es posible controlar su reproducción en reactores y ser transportadas a la pila como solución lixivante. Es importante considerar que ciertas especies son tóxicas para las bacterias como cloruros y nitratos, pero con tiempo estas se pueden acondicionar para tolerar especies tóxicas en concentraciones de hasta 2 a 3 g/L [120].

e) Lixiviación por agitación: Para aplicar este método se requiere que el mineral esté finamente molido, por esta razón se aplica a minerales con leyes muy altas, que por su mayor valor contenido justifican la molienda húmeda, a cambio de mayores recuperaciones y menos tiempos de procesos. Se puede realizar por medios mecánicos o bien con aire. Una particularidad de este método es que es adecuado para la aplicación de factores aceleradores de la cinética como velocidad de agitación, temperatura, presión, uso de reactivos exóticos y oxidantes altamente agresivos, y juntos a ellos, la posibilidad de utilizar materiales de construcción de alta resistencia. Generalmente se requiere de una etapa posterior de lavado a contracorriente.

4.7. Lixiviación agitada

La lixiviación agitada necesita, tal como se ha señalado, que el mineral pase previamente por una reducción de tamaño (chancado – molienda) para ampliar lo más posible el área superficial, liberando las especies de interés, una vez realizada la reducción de tamaño, el mineral es lixiviado en estanques agitados, estos estanques pueden ser mecánicos, magnéticos o neumáticos.

El mineral se mantiene en suspensión en la solución lixivante, lo que se consigue regulando la velocidad de agitación, evitando problemas como que el mineral quede aposado en el fondo del estanque por falta de movimiento o que el mineral quede en permanente contacto con las paredes del estanque debido a la fuerza centrífuga [117].

La lixiviación agitada tiene como fin lograr una representación aproximada de la cinética de extracción de un mineral a escala laboratorio [63]. Para esto el mineral debe estar pulverizado, bajo malla 30 (0,595 mm) logrando de esta forma aumentar el área expuesta, la agitación disminuye el espesor de la capa límite y maximiza el área de la interfase gas-líquido [118].

Se usa para minerales que se lixivian fácilmente, como los óxidos, carbonatos y sulfuros secundarios (calcosina). La lixiviación se realiza en tanques agitados y la extracción de cobre puede acercarse al 100% en un corto tiempo debido a la alta cinética provocada por la velocidad de agitación y a la mayor área superficial del mineral [119].

5. Leaching Manganese Nodules in an Acid Medium and Room Temperature Comparing the Use of Different Fe Reducing Agents

Resumen: Los depósitos de Fe-Mn, en los fondos marinos, son una fuente alternativa de recursos minerales en algunos elementos de gran interés. Entre estos se encuentran los nódulos de manganeso, con un 24% de este metal, que constituyen una alternativa a la escasez de yacimientos ricos en el ámbito continental. En esta investigación se realiza un análisis ANOVA para buscar la relación entre el tiempo y la relación MnO_2 /agente reductor para la lixiviación de nódulos de manganeso con diferentes agentes reductores Fe (FeS_2 , Fe^{2+} , Fe^0 y Fe_2O_3). Se hicieron ensayos para cada uno de los agentes evaluando la relación MnO_2/Fe , en los que $Fe^0(FeC)$ del acero al carbono se mostró como el mejor de los reductores, alcanzando disoluciones del 97% en 20 min. Además, se demuestra que cuando el cociente MnO_2/Fe es bajo, la concentración de ácido no es relevante en el proceso y los niveles de potencial y de pH, entre -0.4 – 1.4 y -2 – 0.1 favorecen la disolución del Mn desde el óxido.

Article

Leaching Manganese Nodules in an Acid Medium and Room Temperature Comparing the Use of Different Fe Reducing Agents

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Abstract: The deposits of Fe-Mn, in the seabed of the planet, are a good alternative source for the extraction of elements of interest. Among these are marine nodules, which have approximately 24% manganese and may be a solution to the shortage of high-grade ores on the surface. In this investigation, an ANOVA analysis was performed to evaluate the time independent variables and MnO₂/reducing agent in the leaching of manganese nodules with the use of different Fe reducing agents (FeS₂, Fe²⁺, Fe⁰ and Fe₂O₃). Tests were also carried out for the different reducing agents evaluating the MnO₂/Fe ratio, in which the Fe⁰ (FeC) proved to be the best reducing agent for the dissolution of Mn from marine nodules, achieving solutions of 97% in 20 min. In addition, it was discovered that at low MnO₂/Fe ratios the acid concentration in the system is not very relevant and the potential and pH were in ranges of −0.4–1.4 V and −2–0.1 favoring the dissolution of Mn from MnO₂.

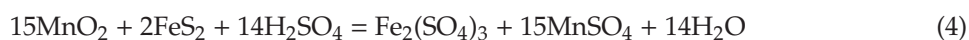
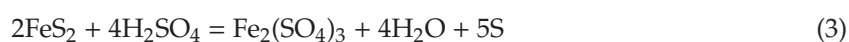
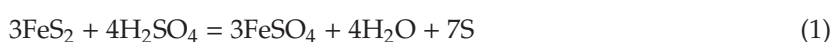
Keywords: MnO₂; acid media; ANOVA; dissolution

1. Introduction

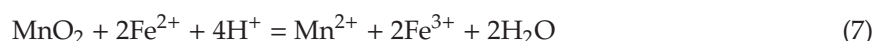
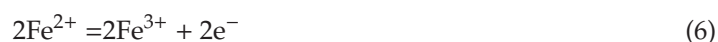
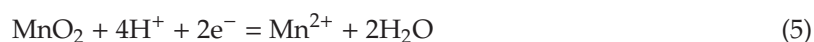
Deposits of ferromanganese (Fe-Mn) are found in the oceans around the world [1–4]. These deposits contain ferromanganese crusts, as well as cobalt-rich crusts and manganese nodules [5–7]. These marine resources are found mainly in the Pacific, Atlantic and Indian Ocean [8], and are formed by precipitation processes of Mn and Fe oxides around a nucleus, which is commonly composed of a fragment of an older nodule [9]. Manganese nodules also called polymetallic nodules because they are associated with large reserves of metals, such as Cu, Ni, Co, Fe and Mn, the latter being the most abundant, with an average content of around 24% [10]. In addition to the aforementioned elements, considerable quantities of Te, Ti, Pt and rare earths can also be found [11]. These nodules might be good source of manganese in the industry for high demand in steel production [12–14].

To extract Mn and other metals of interest from marine nodules, the use of a reducing agent is necessary [15,16]. Studies have used different reducing agents, such as, wastewater from the manufacture of alcohol from molasses [17], coal [18], H₂SO₃ [19,20], pyrite [21], sponge iron [22] and cast iron slag magnetite [23]. Iron has shown to be a good reducing agent for manganese extraction, from those, due to its low cost and abundance [23]. Several studies have been carried out to evaluate the effect of iron as a reducing agent in leaching in acid media of marine nodules [21,24]. For studies in acidic media and iron, it has been reported that the best results for extracting manganese are obtained by increasing the amounts of Fe in the Mn/Fe ratio and working at low acid concentrations [22,23].

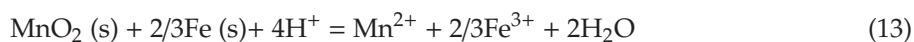
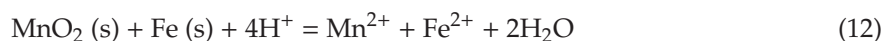
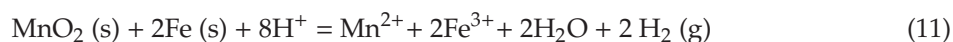
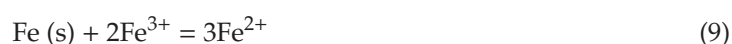
In the studies by Kanungo [21,25], an acid leaching (HCl) was conducted at different temperatures with the addition of pyrite as a reducing agent achieving 50% manganese extractions. The author concluded that, in a moderately acidic medium, pH of 1.5, the Fe (II) and Fe (III) ratio in the system remains essentially constant up to 50 min above, which the ratio tends to increase exponentially. From this, it is suggested that the reduction of MnO₂ by ferrous ions occurs at a faster rate than the oxidation of pyrite generating ferric ions. For the dissolution of Mn with the use of pyrite in acidic media, the following series of reactions is proposed [21]:



For the use of ferrous ions, Zakeri et al. [24] indicated that when working in a molar ratio of Fe²⁺/MnO₂ of 3/1, a molar ratio of H₂SO₄/MnO₂ of 2/1 and a mineral particle size of -60 + 100 Tyler mesh, 90% extractions of Mn can be obtained in less than 20 min at a temperature of 20 °C. In their work they proposed the following series of reactions:

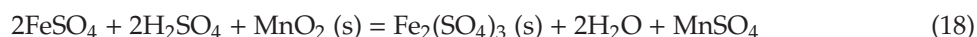
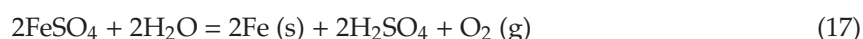
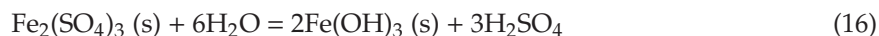
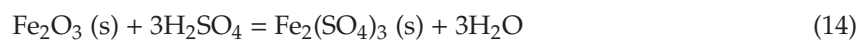


Subsequently, Bafghi et al. [22] conducted a similar experiment but with the use of Fe sponge, where he compared the results reported by Zakeri et al. [24] and indicated that under the same operating conditions, sponge Fe delivers better results than the addition of ferrous ions, because the metal of Fe allows us to have a high activity ratio through the regeneration of ferrous ions. For the dissolution of Mn with the use of Fe (s), the following reactions are presented [22]:



In the studies carried out by Toro et al. [23,26] smelting slag was used, taking advantage of the Fe₂O₃ presented in these to reduce MnO₂ in an acid medium. It was concluded that the ratios of MnO₂/Fe = 1/2 and 1 M H₂SO₄ significantly shorten the dissolution time of manganese (from 30 to

5 min). In addition, the authors indicated that the particle size is not as significant in Mn solutions as in the concentration of H₂SO₄. For the dissolution of Mn with the use of Fe₂O₃ in acid media, the following series of reactions is presented:



It is imperative to create innovative methods for the treatment of minerals that involve industrial waste reusing. Big mining companies are promoting recycling to generate a more sustainable sector. An example is the iron industry in China, where it is sought to reduce pollution by adding scrap in steelmaking [27]. Another example is mining in Chile, where companies like Collahuasi have recycling programs, in which they annually recover 3000 tons of scrap metal, 4 thousand kilos of electronic waste, 182 thousand units of plastic bottles and 680 kg of paper and cardboard [28]. Regarding steel scrap, the copper mining industry generates large amounts of this waste in the milling processes, but the steel balls or bars are discarded [29].

In this research, the leaching of MnO₂ to recover manganese with the use of different types of Fe reducing agents (pyrite, ferric ions, steel and magnetite) working under the same operating conditions was studied. The objective of this work is to find the most suitable iron reducing agent to extract manganese when working in an acidic environment and room temperature, with the novelty of testing the use of steel. A statistical analysis was conducted performed to evaluate the performance of the different selected reducers. Finally, the obtained results were compared in leaching tests over time, indicating which allow obtaining the best results.

2. Methodology

2.1. Manganese Nodule

The marine nodules used in this research were collected in the 1970s from the Blake Plateau in the Atlantic Ocean. The sample was reduced in size using a porcelain mortar and classified by mesh sieves until reaching a range between −140 + 100 μm. Later, it was analyzed chemically by atomic emission spectrometry via induction-coupled plasma (ICP-AES), developed in the Applied Geochemistry Laboratory of the Department of Geological Sciences of the Catholic University of the North, and its chemical composition was 0.12% of Cu, 0.29% Co and 15.96% Mn. Its mineralogical composition is presented in Table 1. Micro X-ray fluorescence spectrometry (Micro-XRF) is a method for elementary analysis of non-homogeneous or irregularly shaped samples, as well as small samples or even inclusions. The sample material was analyzed in a Bruker® M4-Tornado μ-FRX table (Fremont, CA, USA). This spectrometer consists of an X-ray tube (Rh-anode), and the system features a polycapillary X-ray optic, which concentrates the radiation of the tube in minimal areas, allowing a point size of 20 μm for Mo-K. The elementary maps created with the built-in software of the M4 Tornado™ (Fremont, CA, USA), ESPRIT, indicate that the nodules were composed of fragments of pre-existing nodules that formed its nucleus, with concentric layers that precipitated around the core in later stages.

Table 1. Mineralogical analysis of the manganese nodule.

Component	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	MnO ₂	Fe ₂ O ₃
Mass (%)	3.54	3.69	2.97	7.20	1.17	0.33	22.48	1.07	25.24	26.02

2.2. FeS₂

For this study, a cubic pyrite crystal obtained from the Navajún Mine (La Rioja, Spain) was used. This sample was reduced in size with the use of a cone crusher at laboratory level and later a sprayer. It was then classified through meshes sieves until reaching a size range of $-75 + 53 \mu\text{m}$. It was then analyzed chemically by atomic emission spectrometry via induction-coupled plasma (ICP-AES), developed in the Applied Geochemistry Laboratory of the Department of Geological Sciences of the Catholic University of the North. Table 2 shows the chemical composition of the samples.

Table 2. Chemical composition.

Component	Fe	S ₂
Mass (%)	46.63	53.37

X-ray diffraction analyses (XRD) of the pyrite were performed on a Bruker D8 ADVANCE diffractometer (Billerica, MA, US) with Cu $\lambda = 1.5406 \text{ \AA}$ radiation generated at 40 kV and 30 mA. The analysis and identification of the crystalline phases were obtained using the DIFFRAC.EVA V4.2.1 program, with the Powder Diffraction File of ICDD database (PDF-2 (2004)) (Billerica, MA, US). According to the initial qualitative analysis of XRD, the primary mineral phase in the samples was pyrite, whose main peaks are at 33.153° , 37.121° and 40.797° . These peaks correspond to those given in the reference pattern PDF 01-1295 (ICDD, 2004). As seen in Figure 1, the analysis showed the sample has a purity of 99.40%.

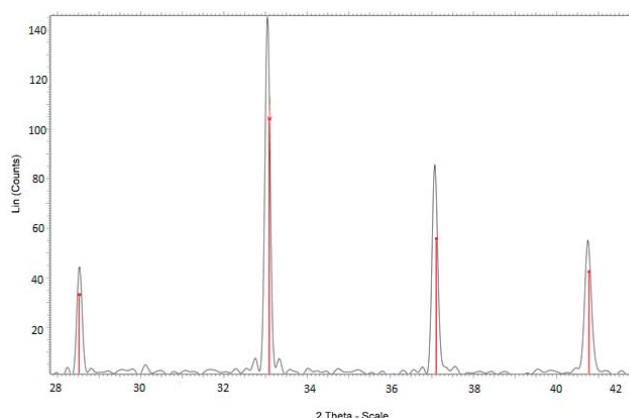


Figure 1. X-ray diffractogram for the pyrite mineral.

2.3. Fe₂O₃

The Fe₂O₃ used is found in tailings from the Altonorte Smelting Plant. Its size is in a range of $-75 + 53 \mu\text{m}$. The methods used to determine its chemical and mineralogical composition are the same as those used in marine nodules. Figure 2 and Table 3 shows the chemical species that use QEMSCAN (QEMSCAN has a database, which has the elemental composition, and density of the minerals that are detected). With this information, it is possible to obtain the elementary contribution of the measured sample), and several iron-containing phases are presented, while the Fe content is estimated at 41.9%.

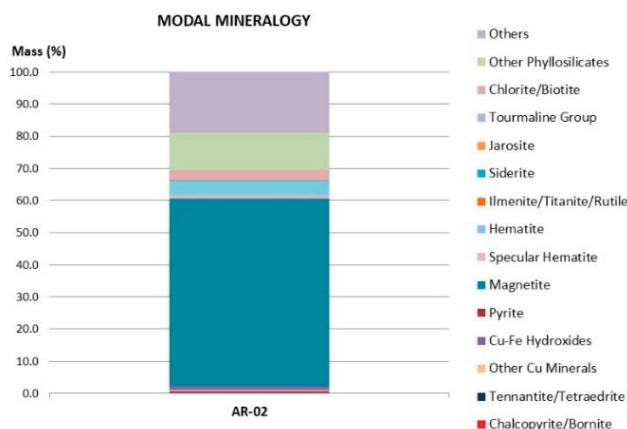


Figure 2. Detailed modal mineralogy.

Table 3. Shows the mineralogical composition of the tailings. The Fe in it was mainly in the form of magnetite.

Mineral	Amount % (w/w)
Chalcopyrite/Bornite $\text{CuFeS}_2/\text{Cu}_5\text{FeS}_4$	0.47
Tennantite/Tetrahedrite $(\text{Cu}_{12}\text{As}_4\text{S}_{13}/\text{Cu}_{12}\text{Sb}_4\text{S}_{13})$	0.03
Other Cu Minerals	0.63
Cu–Fe Hydroxides	0.94
Pyrite (FeS_2)	0.12
Magnetite (Fe_3O_4)	58.52
Specular Hematite (Fe_2O_3)	0.89
Hematite (Fe_2O_3)	4.47
Ilmenite/Titanite/Rutile $(\text{FeTiO}_3/\text{CaTiSiO}_3/\text{TiO}_2)$	0.04
Siderite (FeCO_3)	0.22
Chlorite/Biotite $(\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2(\text{Mg})_3(\text{OH})_6/\text{K}(\text{Mg})_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2)$	3.13
Other Phyllosilicates	11.61
Fayalite (Fe_2SiO_4)	4.59
Dicalcium Silicate (Ca_2SiO_4)	8.3
Kirschsteinite (CaFeSiO_4)	3.4
Forsterite (Mg_2SiO_4)	2.3
Baritine (BaSO_4)	0.08
Zinc Oxide (ZnO)	0.02
Lead Oxide (PbO)	0.01
Sulfate (SO_4)	0.2
Others	0.03
Total	100

2.4. Steel (FeC)

A low carbon steel sheet (FeC; 0.25% C) from the steel supplier company Salomon Sack was used. This sample was reduced in size with the use of a cone crusher at laboratory level and later a pulverizer until reaching a size range between $-75 + 53 \mu\text{m}$.

2.5. Ferrous Ions

The ferrous ions used for this investigation ($\text{FeSO}_4 \times 7\text{H}_2\text{O}$) were the WINKLER brand (Santiago, Chile), with a molecular weight of 278.01 g/mol.

2.6. Reactor and Leaching Tests

The sulfuric acid used for the leaching tests was grade P.A., with 95–97% purity, a density of 1.84 kg/L and a molecular weight of 98.8 g/mol. The leaching tests were carried out in a 50 mL glass reactor with a 0.01 solid/liquid ratio in leaching solution. A total of 200 mg of Mn nodules were maintained

in agitation and suspension with the use of a 5 position magnetic stirrer (IKA ROS, CEP 13087-534, Campinas, Brazil) at a speed of 600 rpm. The tests were conducted at a room temperature of 25 °C, with variations in additives, particle size and leaching time. The tests performed in duplicate, measurements (or analyses) carried on 5 mL undiluted samples using atomic absorption spectrometry with a coefficient of variation $\leq 5\%$ and a relative error between 5% and 10%. Measurements of pH and oxidation-reduction potential (ORP) of leach solutions were made using a pH-ORP meter (HANNA HI-4222, St. Louis, MO, USA). The solution ORP was measured in a combination ORP electrode cell composed of a platinum working electrode and a saturated Ag/AgCl reference electrode.

2.7. Estimation of Linear and Interaction Coefficients for Factorial Designs of Experiments of 2^3

Two independent variables were chosen for the factorial design of 36 experiments, where: time and ratio MnO_2 /reducing agent represent the independent variables that explain the extraction of Mn for a certain type of reducing agent. The analysis through a factorial design allowed us to study the effect of the factors and their levels in a response variable, helping to understand which factors are the most relevant [30,31]. Four factorial designs were carried out that involved two factors with three levels each, with a total of 36 experimental tests (Table 4). The Minitab 18 software (version 18, Pennsylvania State University, State College, PA, USA) was used for modeling, experimental design and adjustment of a multiple regression [32].

Table 4. Experimental conditions.

Parameters/Values	Low	Medium	High
Time (min)	10	20	30
MnO_2 /Reducing agent	2/1	1/1	1/2
Codifications	-1	0	1

The expression of the response variable according to the linear effect of the variables of interest and considering the effects of interaction and curvature, is shown in Equation (19).

$$\text{Cu Recovery}(\%) = \alpha + \sum_{i=1}^n \beta_i \times x_i + \sum_{i=1}^n \beta_i^2 \times x_i^2 + \beta_{1,2} \times x_1 \times x_2, \quad (19)$$

where α is the overall constant, x_i is the value of the level “i” of the factor, β_i is the coefficient of the linear factor x_i , β_i^2 is the coefficient of the quadratic factors, $\beta_{1,2}$ is the coefficient of the interaction, n are the levels of the factors and Mn recovery is the dependent variable.

Table 4 shows the values of the levels for each factor, while Table 5 shows the recovery obtained for each configuration.

Table 5. Experimental configuration and Mn extraction data.

Exp. No.	Time (min)	MnO_2 /Reducing Agent Ratio	Mn Recovery (%; Reducing Agent)			
			FeS_2	Fe^{2+}	FeC	Fe_2O_3
1	10	2/1	4.12	20.52	22.31	33.33
2	10	1/1	8.51	40.69	44.00	50.23
3	10	1/2	10.66	80.27	87.13	71.00
4	20	2/1	8.34	27.80	30.22	39.22
5	20	1/1	12.69	63.11	67.43	57.32
6	20	1/2	19.21	90.18	97.00	73.21
7	30	2/1	15.84	40.32	41.99	42.55
8	30	1/1	19.11	70.00	74.33	72.96
9	30	1/2	26.32	93.50	97.34	75.14

3. Results

3.1. Statistical Analysis

From the analysis of the main components, the time and ratio factors MnO_2 /Reducing agent showed a main effect, since the variation between the different levels affected the response in a different way, as shown in Figure 3.

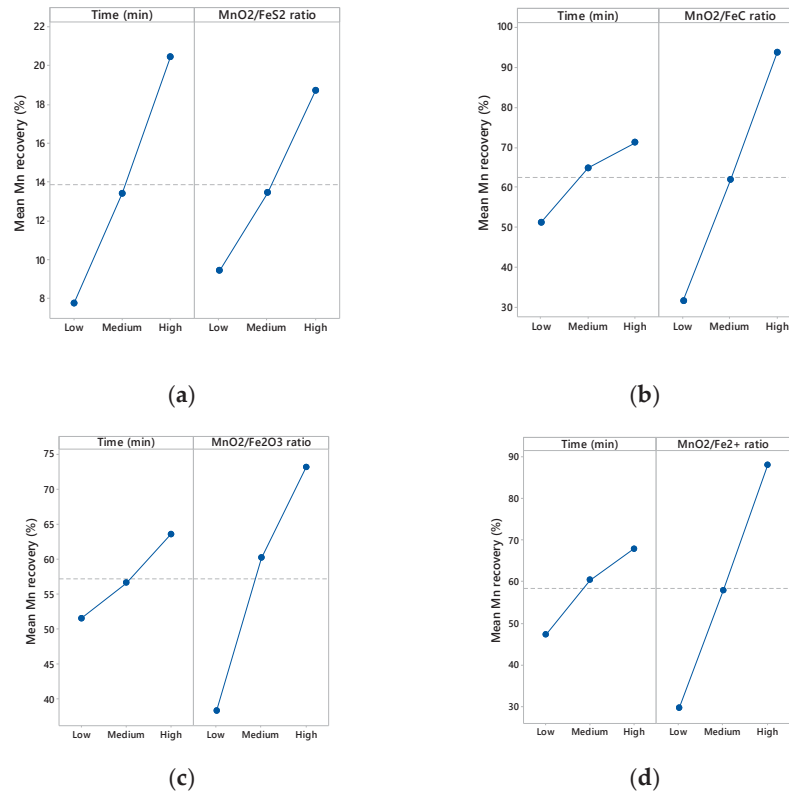


Figure 3. Main effect plots of Mn extraction in function of Time (min) and MnO_2 /Reductant agent ratio for (a) FeS_2 , (b) FeC , (c) Fe_2O_3 and (d) Fe^{2+} agents.

By developing the ANOVA test and the multiple linear regression adjustment for each of the configurations, it is necessary to recover the Mn as a function of the time predictor variables, and MnO_2 /reducing agent, which is given by:

$$\text{Mn Extraction (\%)} [\text{FeS}_2] = 13.867 + 6.330 \times \text{Time} + 4.648 \text{MnO}_2/\text{FeS}_2 \times \text{ratio}. \quad (20)$$

$$\text{Mn Extraction (\%)} [\text{Fe}^{2+}] = 58.49 + 10.39 \times \text{Time} + 29.22 \text{MnO}_2/\text{Fe}^{2+} \times \text{ratio}. \quad (21)$$

$$\text{Mn Extraction (\%)} [\text{FeC}] = 62.42 + 10.04 \times \text{Time} + 31.16 \text{MnO}_2/\text{FeC} \times \text{ratio}. \quad (22)$$

$$\text{Mn Extraction (\%)} [\text{Fe}_2\text{O}_3] = 57.22 + 6.01 \times \text{Time} + 17.37 \text{MnO}_2/\text{Fe}_2\text{O}_3 \times \text{ratio}. \quad (23)$$

The time and ratio MnO_2 /reducing agents were coded according to low and medium high levels. From the adjustment of multiple regression models, the interactions of the factors together with the curvature of the time factor and MnO_2 /reducing agent did not contribute to explain the variability in any of the adjusted models.

From Equations (20)–(23) and from the main effect graphs in Figure 3, the factor that had showed a higher marginal contribution in Mn recovery was the MnO_2 /Reducing agent ratio for the experimental design whose reducing agent was Fe^{2+} , FeC and Fe_2O_3 , while in case of using FeS_2 as a reducing agent, the factor that has a greater impact on recovery is time.

The ANOVA test indicates that the models adequately represent Mn extraction for the set of sampled values. The model does not require additional adjustments and is validated by the goodness-of-fit statistics shown in Table 6. The p value ($p < 0.05$) and the significance tests F ($F_{\text{Regression}} \gg (F_{\text{Table}} = F_{2,6}(5.1432))$) for a level of significance of $\alpha = 0.05$ (95% confidence level) indicate that all models generated for the representation of the experimental tests were statistically significant. The normality tests indicate that the assumption of normality of the residuals was met. The low values of the S statistic indicate that there were no large deviations between the experimental data and the values of the adjusted model.

Table 6. Goodness of fit statistics.

Response	F-Value	p -Value	S	R ²	R ² (Pred)
Mn Extraction (%) [FeS ₂]	102.13	0.000	1.34602	97.15%	92.65%
Mn Extraction (%) [Fe ²⁺]	145.76	0.000	4.44890	97.98%	95.63%
Mn Extraction (%) [FeC]	116.48	0.000	5.25341	97.49%	94.35%
Mn Extraction (%) [Fe ₂ O ₃]	42.02	0.000	4.91305	93.34%	84.37%

The value of the R^2 statistics was greater than 90%, which indicates that a large part of the total variability was explained by the models, while the similarity between the R^2 and R^2 predictive statistics indicates that the model could adequately predict the response to new observations.

3.2. Effect on MnO₂/Reducing Agent Ratio

In Figure 4, results are presented for the dissolution of Mn with the use of different Fe reducing agents at different ratios of Mn/Fe. For all the cases presented (Figure 4a–d), when working at low Mn/Fe ratios the highest recoveries of Mn were obtained. Ratios of 1/2 proved to be an optimum in Figure 4b–d. While for the Figure 4a in ratios of 1/3, the increase in the dissolution of Mn continued. The best results were obtained in Figure 4c when working with FeC because it allowed a high activity ratio through the regeneration of ferrous ions, favoring the dissolution of Mn and allowing better results to the use of Fe²⁺ in a direct way that is presented in Figure 4b. Using Fe₂O₃ shows good results when working with MnO₂/Fe₂O₃ ratios of 1/2, although it is lower than those presented when using Fe²⁺ and FeC. However, this may be an attractive proposal due to the reuse of tailings that are an environmental responsibility. For the use of pyrite, the lowest Mn solutions could be observed in this study. In previous studies [2,22,23,33], it has been indicated that it is not necessary to work at high concentrations of H₂SO₄ in the system to obtain high Mn solutions from marine nodules, but that if it is important to have low Mn/Fe ratios. The results presented in Figure 4a show a progressive increase in the Mn dissolution when increasing the amounts of FeS₂ in the system, however, it may be necessary to increase the acid concentration or temperature because of the kinetics of dissolution of ferrous ions from the pyrite ore.

For the performed tests, the values of potential and pH for the different reducing agents used for Mn/Fe ratios of 1/2 are presented in Figure 5. Senanayake [13] indicated that dissolving Mn from marine nodules requires to work in potential ranges between -0.4 and 1.4 V and pH between -2 and 0.1 . With this, it is possible to avoid the precipitation of the Mn through the oxidation-reduction reaction, due to the presence of ferrous and ferric ions [34]. The outcomes met the operational condition mentioned above, which is due to the high concentrations of reducing agent. The lowest potential values were obtained with Fe²⁺ and FeC, wherein the iron (FeC) favored the regeneration of ferrous ions, which allows maintaining low potential ranges [22].

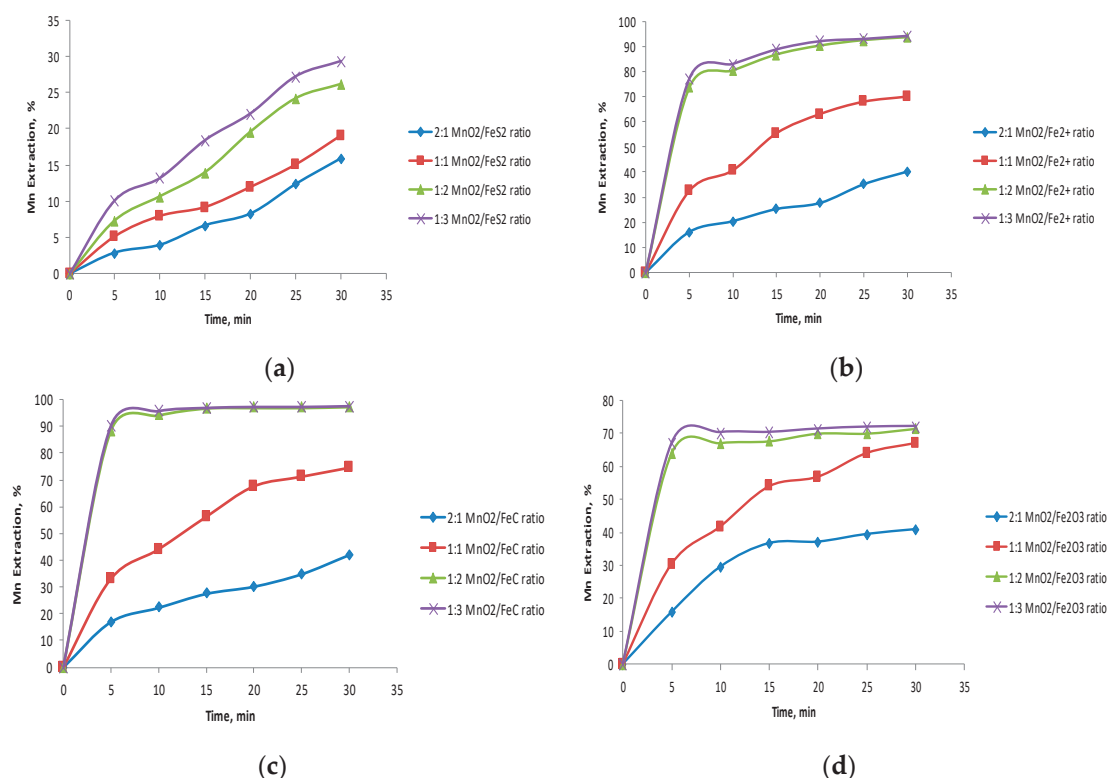


Figure 4. Effect on the ratio of MnO₂/reducing agent at room temperature (25 °C), 0.1 mol/L H₂SO₄, 600 rpm and particle size of $-75 + 53 \mu\text{m}$ (reducing agent: (a) FeS₂, (b) Fe²⁺, (c) FeC and (d) Fe₂O₃).

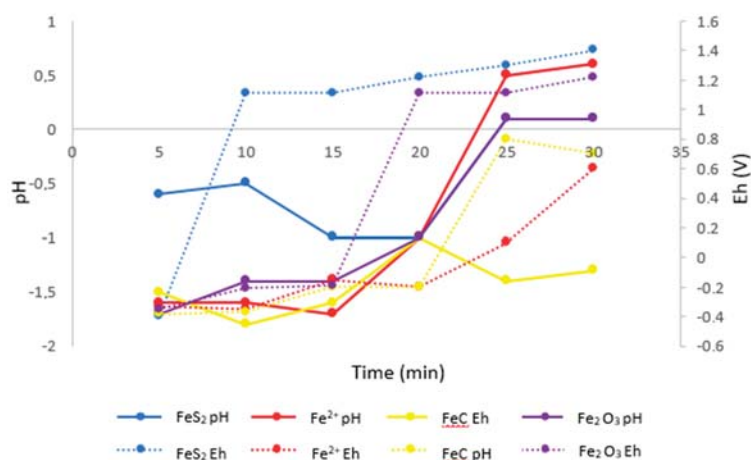


Figure 5. Effect of the potential and pH in the solution of Mn with different reducing agents (MnO₂/Fe₂O₃ ratio of 1/2, 25 °C, 600 rpm, $-75 + 53 \mu\text{m}$, acid concentration to 0.1 mol/L).

3.3. Effect on the Concentration of H₂SO₄

Figure 6 shows the effect of sulfuric acid concentration when working at Mn/Fe ratios of 1/2 with the use of different Fe reducing agents. Figure 6b,c shows that the concentration of H₂SO₄ was irrelevant in the extraction of Mn when working at low ratios of Mn/Fe with the use of Fe²⁺ and FeC. This is compatible with previous studies conducted by Zakeri et al. [24] and Bafghi et al. [22]. The researchers indicated that working at high concentrations of ferrous ions, variables like acid concentration and particle size were irrelevant. For the case shown in Figure 6d, it was observed that when working with the use of Fe₂O₃ there was a slight increase in Mn solutions when working above 0.1 mol/L, although it was observed that there were no differences between 0.5 and 1 mol/L, which reaffirms what was raised by Saldaña et al. [2], where they indicated that when working on

acid-reducing leaching of MnO_2 using tailings, the acid concentration only influenced the extractions of Mn when it was not operated in high levels of Fe or no temperature increase. Finally, it can be seen in Figure 6a that when working with pyrite, the concentration of acid in the system was important. This was consistent with the results obtained by Kanungo et al. [21], which states that in an acid solution of marine nodules with the use of pyrite as the acidity of the medium decreases, the rate of reduction of MnO_2 decreases.

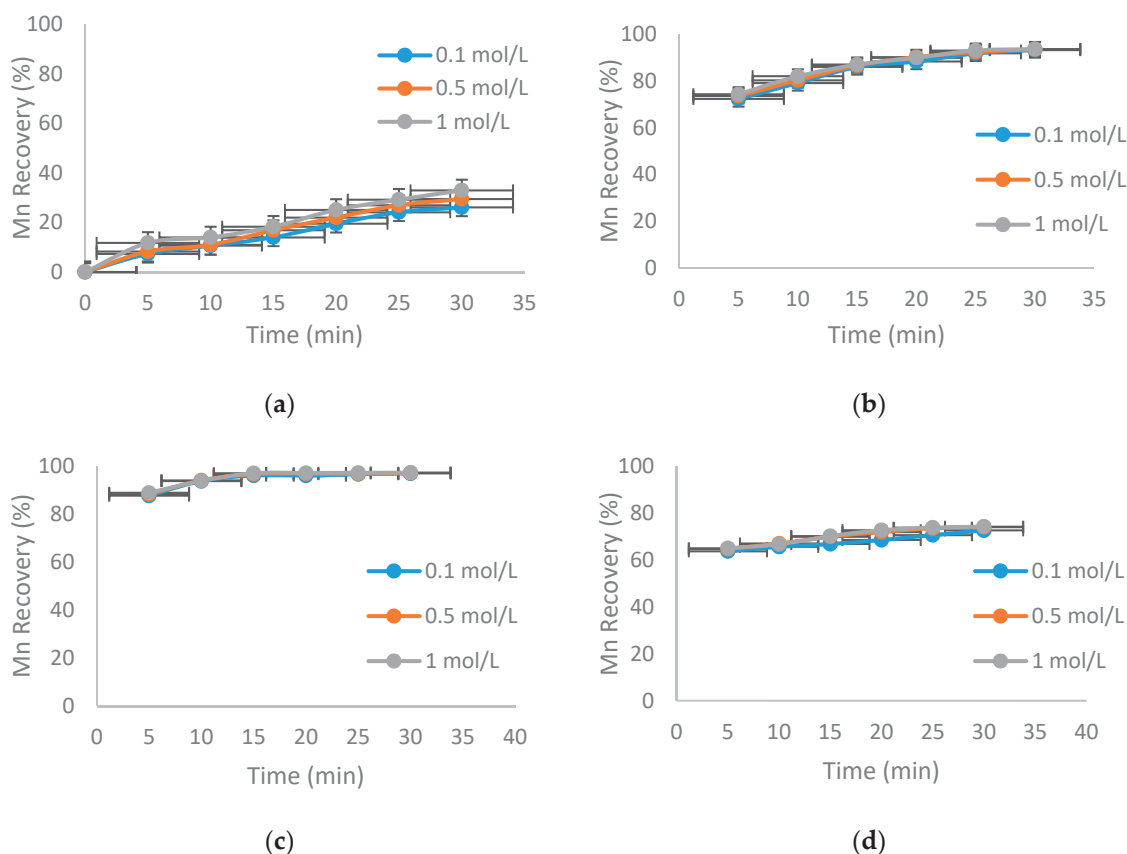


Figure 6. Effect on the concentration of H_2SO_4 at room temperature of ($25\text{ }^\circ\text{C}$), ratio of MnO_2 /reducing agent of 1/2, 600 rpm and particle size of $-75 + 53\ \mu\text{m}$ (reducing agent: (a) FeS_2 , (b) Fe^{2+} , (c) FeC and (d) Fe_2O_3).

4. Conclusions

The Fe presented in the different additives proved to be a good reducing agent, increasing the dissolution of MnO_2 . The main findings of this study were the following:

(1) Fe^0 (FeC) proved to be the best reducing agent for the dissolution of Mn from marine nodules since the direct contact of Fe in the liquid solution kept the regeneration of ferrous ions, due to high levels of ferrous and ferric ions.

(2) When working with Fe^{2+} , FeC and Fe_2O_3 , and having high concentrations of reducing agent (MnO_2 ratios/reducing agent 1/2 or lower), low potential values were maintained, which allowed working at low acid concentrations (0.1 mol/L). However, for FeS_2 , better results were achieved at higher ratios of $\text{MnO}_2/\text{FeS}_2$ (1/3) and acid levels of 1 mol/L, which was possibly due to the refractoriness of pyrite.

(3) For the tests carried out in this study with the different Fe reducing agents, the potential and pH ranges were from -0.4 to $1.4\ \text{V}$ and -2 to 0.1 , favoring the dissolution of Mn from marine nodules, and avoiding the formation of precipitates of the Fe.

(4) The best results of this research (97% of Mn) were obtained at MnO_2/FeC ratios of 1/2, 0.1 mol/L of H_2SO_4 , in a time of 20 min.

In future work, other industrial iron wastes, generated in large industries, should be evaluated to create novel acid-reducing processes of MnO_2 . Subsequently, to recover the manganese present in the solution, zero-valent iron (ZVI) is a good alternative. Zero valence iron can be reused, from scraps of the metal finishing industry.

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6. Leaching Chalcopyrite with High MnO₂ and Chloride Concentrations

Resumen: La mayor parte de los minerales de cobre son sulfuros, siendo la calcopirita el más abundante. Este mineral es refractario a los procesos de extracción hidrometalúrgicos habituales, por lo que ha sido históricamente tratado mediante flotación y fundición. Como resultado, su extracción provoca contaminación, depósitos de lodos estériles (relaves) y emisión de grandes volúmenes de SO₂ a la atmósfera. Dadas las mayores restricciones ambientales, es necesario establecer nuevas tecnologías de proceso, compatibles con el entorno y, en la medida de lo posible, consumidoras de otros residuos industriales. En esta investigación se estudia la lixiviación de Calcopirita empleando MnO₂ y aguas residuales de alto contenido en cloruros. Se produce un incremento de la extracción de cobre empleando partículas muy finas (-20 μm). Además, trabajando con altas temperaturas (80° C) no resultan relevantes las altas concentraciones de MnO₂. Las mayores recuperaciones de cobre (71%) se alcanzaron con temperaturas de (80° C); tamaños de partícula entre -47 y 38 μm; relaciones MnO₂/CuFeS₂ de 5/1 y concentraciones de H₂SO₄ de 1 mol/L.

Article

Leaching Chalcopyrite with High MnO_2 and Chloride Concentrations

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Abstract: Most copper minerals are found as sulfides, with chalcopyrite being the most abundant. However; this ore is refractory to conventional hydrometallurgical methods, so it has been historically exploited through froth flotation, followed by smelting operations. This implies that the processing involves polluting activities, either by the formation of tailings dams and the emission of large amounts of SO_2 into the atmosphere. Given the increasing environmental restrictions, it is necessary to consider new processing strategies, which are compatible with the environment, and, if feasible, combine the reuse of industrial waste. In the present research, the dissolution of pure chalcopyrite was studied considering the use of MnO_2 and wastewater with a high chloride content. Fine particles ($-20 \mu\text{m}$) generated an increase in extraction of copper from the mineral. Besides, it was discovered that working at high temperatures ($80 \text{ }^\circ\text{C}$); the large concentrations of MnO_2 become irrelevant. The biggest copper extractions of this work (71%) were achieved when operating at $80 \text{ }^\circ\text{C}$; particle size of $-47 + 38 \mu\text{m}$, $\text{MnO}_2/\text{CuFeS}_2$ ratio of 5/1, and 1 mol/L of H_2SO_4 .

Keywords: dissolution; CuFeS_2 ; chloride media; manganese nodules

1. Introduction

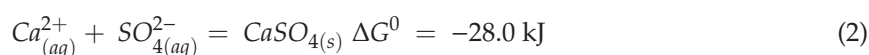
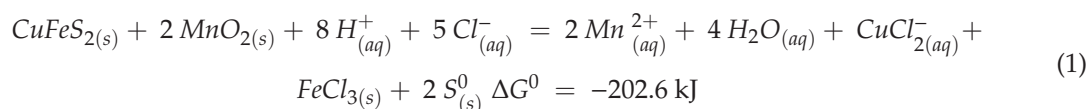
The most abundant type of copper mineral is chalcopyrite [1–5]. Chalcopyrite has traditionally been treated by conventional pyrometallurgical techniques [6], which consist of flotation, smelting and refining, and electrorefining [7]. These techniques yield approximately 19 million tonnes per annum [8]. Despite the high level of copper production, there is concern about the environmental contamination resulting from the application of these techniques owing to SO_2 atmospheric emissions [9,10]. Because of this, it is necessary to study more environmentally friendly hydrometallurgical alternatives [11]. The slow copper extraction rate of conventional leaching from chalcopyrite in sulfur media makes commercial scale leaching economically unfeasible [12]. This may be due to the formation of a passive layer that forms on the surface of the mineral [13–15]. There have been numerous studies on dissolving

copper from chalcopyrite [16–18]. However, none of these studies have obtained positive results working at ambient temperature and atmospheric pressure [19].

The polymetallic nodules are rock concretions formed by concentric layers of hydroxides [20]. Their high content of base, critical and rare metals makes them commercially interesting [21–23]. Their metal content includes high concentrations of Co, Ni, Te, Ti, and Pt, as well rare earth elements [24, 25].

There have been few studies on acid leaching of chalcopyrite using marine nodules (MnO_2) as an oxidizing agent [26–29]. These studies showed that good copper dissolution rates of chalcopyrite can be obtained at room temperature, provided that the $MnO_2/CuFeS_2$ rate is high. Devi et al. [26,27] indicated that this is due to the galvanic interaction between chalcopyrite and MnO_2 , the action of Fe^{3+}/Fe^{2+} ratio, and the formation of chlorine gas through the reaction between MnO_2 and HCl. Havlik et al. [28] showed that 4 mol/L of HCl and a 4/1 de $MnO_2/CuFeS_2$ ratio is optimal conditions to obtain good results at ambient temperature (54% of copper in 90 min).

The proposed reaction for chalcopyrite leaching with magnesium nodules is expressed as follows [29]:



Equation (1) represents dissolving copper in a sulfur-chloride medium, owing to the use of sulfuric acid and the high presence of chloride (wastewater) in the system. Among the advantages of leaching in a chlorinated rather than sulphated environment is increased leaching kinetics, the generation of elemental sulfur and cupric and/or cuprous ions are stable in the form of chloride complexes. The Gibbs free energy of Equation (1), which negative, is spontaneous under normal conditions and forms a stable copper product and a non-polluting elemental sulfur residue. While the calcium in wastewater and the manganese nodules reacts with the sulfate in the system, forming Equation (2) which is spontaneous and more likely to occur under normal conditions with the elements present (higher affinity of sulfate for calcium than magnesium and manganese in solution), the calcium sulfate formed is insoluble because calcium precipitates when it comes in contact with sulfate, nitrates and other elements. Equation (1) shows a 2/1 $MnO_2/CuFeS_2$ ratio for leaching copper using manganese nodules as an oxidizing agent, which was initially proposed by Toro et al. [29], but the best conditions to leach copper is at a 4/1 $MnO_2/CuFeS_2$ ratio. The values of the Gibbs free energy were calculated using the software HSC 5.1.

Other investigations have reported the positive effect of the chloride concentration on chalcopyrite leaching [18,30–32]. Velasquez et al. [33] indicated that chloride ions play an important role in oxidizing copper and iron. The copper dissolution is improved with high chloride concentrations.

The level of energy consumed in industrial scale operations related to comminution processes, reactor design, and leaching residence time largely depend on the particle size of the working material [19]. Studies have found a positive effect of smaller particle size on chalcopyrite leaching owing to the large area of contact for leaching [34,35]. Skrobian et al. [36] conducted chalcopyrite leaching tests in agitating reactors, with the addition of 300 g/L of NaCl to all the reactors, but with different particle sizes (–40 μm , –80 + 60 μm and –200 + 100 μm) and a temperature of 100 °C. Their results indicate that particle size has a negligible effect on the copper dissolution rate from chalcopyrite.

Different researchers agree on the positive effects of higher temperature on copper dissolution from chalcopyrite in terms of substantially increasing dissolution velocity [37]. Ruiz et al. [17] used sulfate–chloride media for dissolve chalcopyrite of a particle size 12.3 μm , 20 g/L of acid, 35.5 g/L of chloride, a stirring rate of 1000 rpm and 0.3 L/min O_2 and obtained a copper dissolution rate of 90% in 180 min, with. Other studies of chalcopyrite leaching in chloride media and using oxidizing

agents like cupric ions [30] and nitrates [38] have also reported good results in copper extraction at higher temperatures.

The scarcity of fresh water in arid zones is an economic, environmental and social problem [39,40]. The availability of water resources and the quality of potable water have decreased significantly owing to human activity, whose effects at the small-scale are significant for the entire basin [41]. Because of this situation the mining industry is driven to conserve the water it uses and minimize water discharges [41,42]. As well, conventional water resources that mining companies and communities compete for are limited [43]. Seawater has been shown to be a good alternative for mining, not only because of its positive effects on leaching owing to its chloride content, but also as a strategic and indispensable resource [40]. Another attractive alternative is using wastewater from desalination plants, not only because of the economic benefits, but also to avoid contaminating ocean waters [44].

There are few studies for the dissolution of chalcopyrite incorporating MnO_2 and chloride in the system [26–29], achieving positive results in the extraction of Cu at room temperature, mainly evaluating the concentration of MnO_2 in the system. Previously, Toro et al. [29] conducted an investigation in which they evaluated the use of wastewater with high chloride, seawater and manganese nodules contents, for the dissolution of chalcopyrite in an acidic medium. In this investigation, the effect on the concentration of MnO_2 , chloride and agitation speed in the system was evaluated. The authors found that high levels of MnO_2 (4/1 and 5/1) allow potential values to be between 580 and 650 mV, favouring the dissolution of $CuFeS_2$, and preventing the formation of a passivating layer. However, no other fundamental variables have been evaluated to favor the dissolution of $CuFeS_2$. In the present research, we evaluated the use of wastewater with high chloride content, and MnO_2 present in manganese nodules as an oxidizing agent in leaching chalcopyrite. Also, wastewater with high chloride levels from a desalination plant was reused. The particle size and temperature were optimized.

2. Methodology

2.1. Chalcopyrite Sample

The chalcopyrite sample used in this study was the same as that used in the first part, published in Toro et al. [29]. The sample was taken selectively from a copper deposit (800 g) and then crushed in a porcelain mortar to avoid contamination. We removed the impurities by hand (with the help of a microscope). The homogenization of the material was done by sampling techniques, selecting a representative fraction of 40 g (20 g for chemical analysis and 20 g for mineralogical analysis). Through a mineralogical analysis using a Bruker brand X-ray diffractometer (Bruker, Billerica, MA, USA), automatic and computerized model of D8 determined that the sample has a purity of 99.9% as can be seen in Figure 1. Finally, a chemical analysis performed by means of an atomic emission spectrometry via induction-coupled plasma (ICP-AES) (AMETEK, SPECTRO, Boschstraße, Germany) determined 33.89% of Cu, 30.62% of Fe and 35.49% of S (See Table 1).

Table 1. Chemical analysis of chalcopyrite.

Component	Cu	Fe	S
Mass (%)	33.89	30.62	35.49

In addition, the sample was analyzed mineralogically using a Bruker brand X-ray diffractometer, automatic and computerized model of D8. In Figure 1, you can see the results of the analysis, from which it was obtained that the chalcopyrite mineral has a purity of 99.90%.

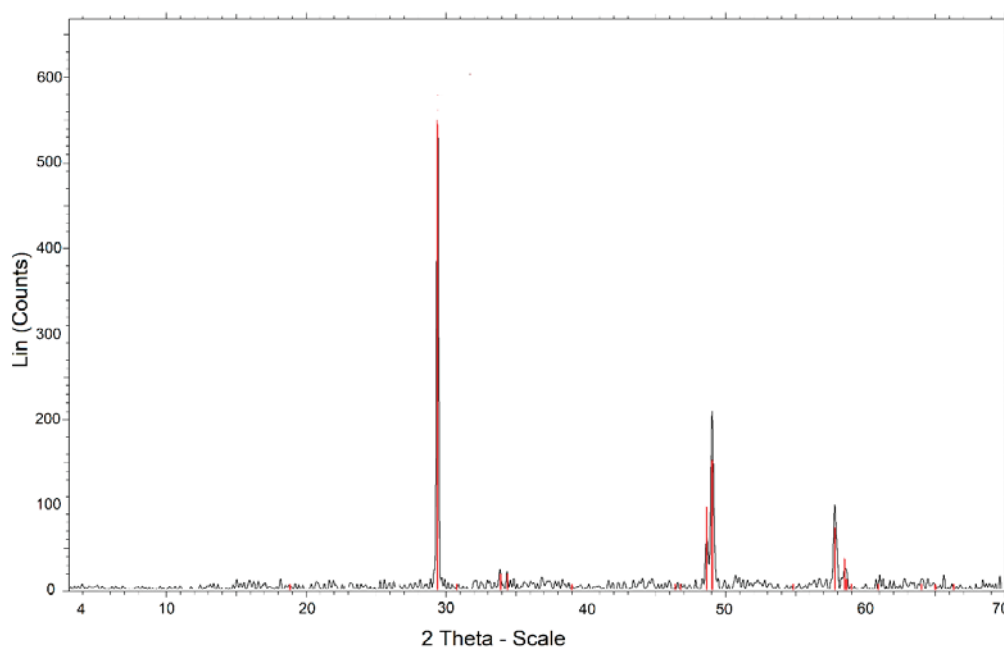


Figure 1. X-ray diffractogram for the chalcopyrite.

2.2. MnO_2 (Manganese Nodules)

The manganese nodules used in this study are the same as those used in the study by Toro et al. [29]. This sample was reduced in size with the use of a porcelain mortar until reaching a size range between $-75 + 53 \mu m$. This sample contains 15.96% of Mn. Table 2 shows the mineralogical composition. The sample was analyzed with a Bruker® tabletop M4-Tornado μ -FRX (Fremont, CA, USA). The interpretation of the μ -XRF data shows that the nodules were composed of fragments of preexisting nodules that formed their nucleus, with concentric layers that precipitated around the nucleus in later stages.

Table 2. Mineralogical Analysis of the Manganese Nodule.

Component	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	MnO ₂	Fe ₂ O ₃
Mass (%)	3.54	3.69	2.97	7.20	1.17	0.33	22.48	1.07	29.85	26.02

2.2.1. Reagent and Leaching Test

The sulfuric acid used for the leaching tests was P.A. grade (Merck, Darmstadt, Germany), purity 95–97%. We also work with the use of waste water from the Aguas Antofagasta Desalination Plant, which has a concentration of 39.16 g/L of chloride. Tables 3 and 4 shows the chemical composition of waste water and sea water.

Table 3. Chemical composition of waste water.

Compound	Concentration (g/L)
Fluoride (F ⁻)	0.002
Calcium (Ca ²⁺)	0.8
Magnesium (Mg ²⁺)	2.65
Bicarbonate (HCO ₃ ⁻)	1.1
Chloride (Cl ⁻)	39.16
Calcium carbonate (CaCO ₃)	13

Table 4. Reference composition of seawater, with principal ions (Modified from Cisternas and Gálvez, [45]).

Solute	g/kg of solution
Na ⁺	10.781
Mg ²⁺	1.283
Ca ²⁺	0.412
K ⁺	0.399
Cl ⁻	19.353
SO ₄ ²⁻	2.712
HCO ₃ ⁻	0.105
Br ⁻	0.067
CO ₃ ²⁻	0.014
Total	35.146

Leaching tests were carried out in a 50 mL glass reactor with a 0.01 S/L ratio. A total of 200 mg of chalcopyrite ore, with the addition of different concentrations of MnO₂ (manganese nodules), was maintained in agitation and suspension with a 5 position magnetic stirrer (IKA ROS, CEP 13087-534, Campinas, Brazil) at a speed of 800 rpm. Temperature was controlled using an oil-heated circulator (Julabo). The temperature range tested in the experiments was 25 to 80 °C. The tests were performed in triplicate, and measurements (or analyzes) were carried out on 5 mL undiluted samples using atomic absorption spectrometry with a coefficient of variation $\leq 5\%$ and a relative error between 5 to 10%. The pH levels and oxidation-reduction potential (ORP) of leaching solutions were measured with a pH-ORP meter (HANNA HI-4222 (HANNA instruments, Woonsocket, RI, USA)). The ORP solution was measured in a combination ORP electrode cell of a platinum working electrode and a saturated Ag/AgCl reference electrode.

In the previous study (Toro et al. [29]) the ratio of MnO₂/CuFeS₂, agitation rate, H₂SO₄ concentration, and chloride concentration were evaluated. Besides, the obtained residues were analyzed, but the formation of contaminating elements was not observed. However, no other fundamental variables were evaluated, and the performance in the extraction of Fe and Mn was not mentioned. For the reasons discussed above, the leaching of CuFeS₂ with MnO₂ and wastewater in the present investigation continues, evaluating the particle size and temperature.

2.2.2. Effect of Particle Size

In previous studies conducted by Devi et al. [27] and Havlik et al. [28], it was shown that high MnO₂ concentrations favour the kinetics of chalcopyrite dissolution. Recently, Toro et al. [29] indicated that when working on MnO₂/CuFeS₂ ratios of 5/1, attractive results were obtained for short periods. Based on previous background, the effect of the chalcopyrite particle size was evaluated by adding MnO₂ at different sulfuric acid concentrations over time under the conditions shown in Table 5.

Table 5. Experimental conditions for the study of the effect of chalcopyrite particle size.

Parameters	Values
Particle size (μm)	-75 + 53, -47 + 38, -20
Time (min)	5, 20, 40, 60, 80
H ₂ SO ₄ (mol/L)	1, 2, 3
MnO ₂ /CuFeS ₂ ratio	5/1

2.2.3. Effect of Temperature

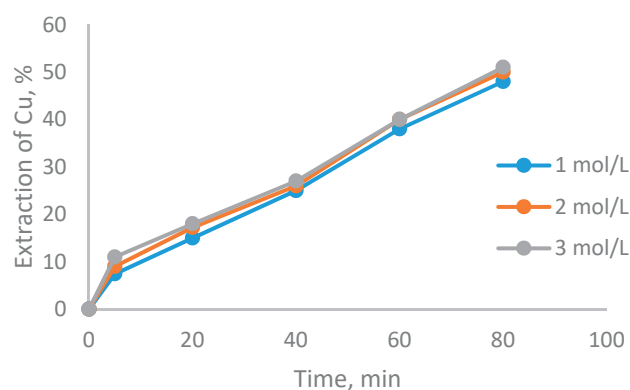
In the study conducted by Toro et al. [29], positive results were obtained when working at high ratios of MnO₂/CuFeS₂ (5/1). However, the effect of temperature was not evaluated to shorten leaching times or decrease MnO₂ concentrations.

This study investigated the effect of temperature (in which interval 25–80 °C) on the copper dissolution rate from chalcopyrite with the addition of MnO_2 , working with a particle size of $-47 + 38 \mu\text{m}$, $\text{MnO}_2/\text{CuFeS}_2$ ratios of 2/1 and 5/1, 1 mol/L of sulfuric acid, 39.16 g/L of chloride (wastewater) and at a stirring speed of 800 rpm.

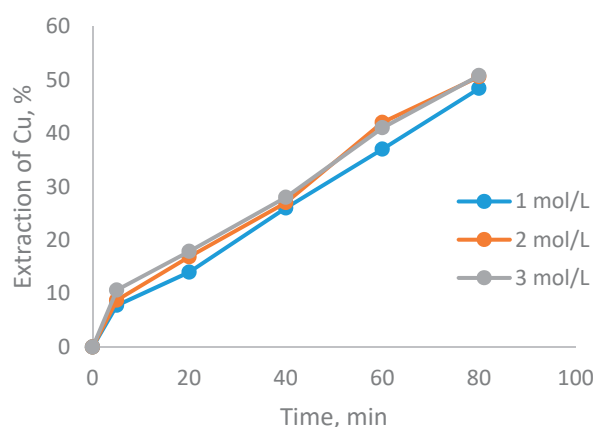
3. Results

3.1. The Effect of Particle Size on CuFeS_2 Dissolution

Figure 2 shows the effect on CuFeS_2 dissolution of particle size with the addition of MnO_2 (5/1 $\text{MnO}_2/\text{CuFeS}_2$ ratio, at different concentrations of H_2SO_4 and wastewater. It can be observed that no differences in copper dissolution rates can be obtained at particle size of $-75 + 53$ to $-47 + 38 \mu\text{m}$ (Figure 2a,b). At small increases in the dissolution rate can be obtained by increasing the sulfuric acid concentration, with the best results obtained at 3 mol/L. This concurs with Skrobjan et al. [36], who stated that particle size is irrelevant in chalcopyrite leaching in stirring reactors. However, the copper extraction rate increases with smaller particles ($-20 \mu\text{m}$), which could be due to the mechanical-chemical activation of the mineral resulting from extended milling [19], which Juhász and Opoczky [46] termed electrochemical activation. At this size, the concentration of H_2SO_4 is irrelevant.

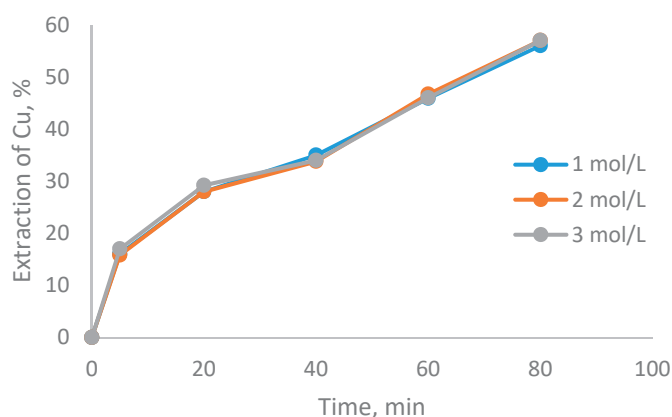


(a)



(b)

Figure 2. Cont.

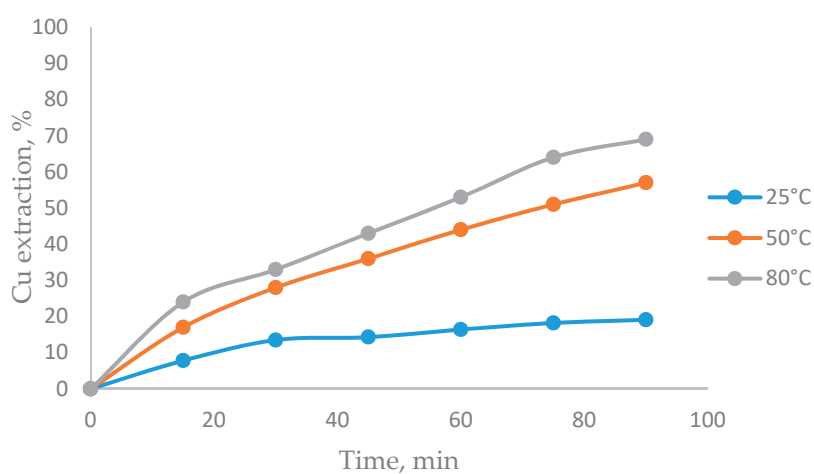


(c)

Figure 2. Effect of particle size and sulfuric acid concentration on copper dissolution. Particle size of: (a) $-75 + 53 \mu\text{m}$; (b) $-47 + 38 \mu\text{m}$; (c) $-20 \mu\text{m}$ (acid concentration of 1, 2 and 3 mol/L and 25°C).

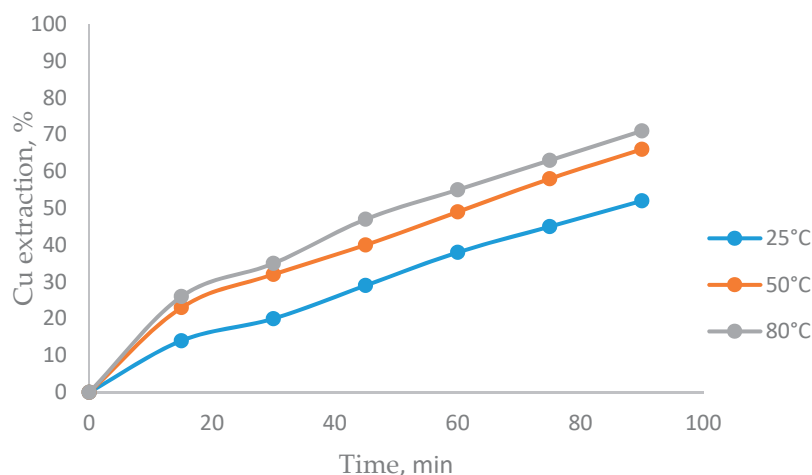
3.2. The Effect of Temperature on CuFeS_2 Dissolution

Figure 3 shows the effect of temperature and $\text{MnO}_2/\text{CuFeS}_2$ ratios on CuFeS_2 dissolution. Dutrizac [35] stated that it is difficult to precisely determine the effect of temperature on copper dissolution from chalcopyrite in chloride media, owing to the presence of small amounts of secondary copper mineralization that can affect data interpretation. However, this problem was avoided in this study by using pure chalcopyrite. It can be seen from Figure 3 that at high temperatures (80°C), the extraction of copper in the system is greater, with similar results obtained with $\text{MnO}_2/\text{CuFeS}_2$ ratios of 2/1 and 5/1. It can also be seen that at ambient temperature there is a significant difference in Cu extraction (About 30%) at ambient temperature between $\text{MnO}_2/\text{CuFeS}_2$ ratios of 2/1 and 5/1. The potential values for the tests at room temperature were between 540 and 590 mV, which is within the potential range where the dissolution rate of the chalcopyrite is linear (550 and 620 mV), as Velásquez-Yévenes et al. [37] noted. The potential values in the tests at temperatures of 50 and 80°C were between 610 and 660 mV, and yielded higher copper dissolution rates. This is because high concentrations of chloride can raise the range of potential values [34]. The pH levels ranged between -0.5 and 1.4 in all the tests.



(a)

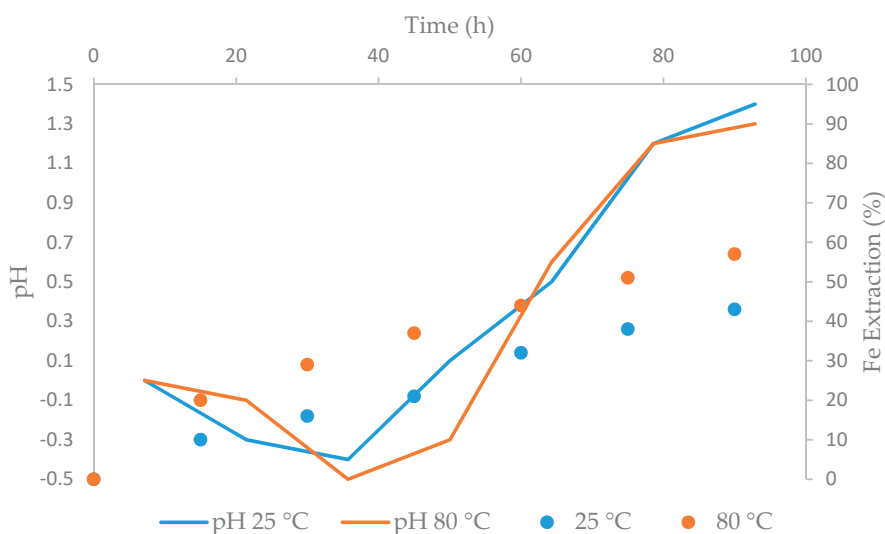
Figure 3. Cont.



(b)

Figure 3. Effect of the temperature on the dissolution of Cu from chalcopyrite at different ratios of $\text{MnO}_2/\text{CuFeS}_2$ (particle size of $-47 + 38 \mu\text{m}$, ratio $\text{MnO}_2/\text{CuFeS}_2$ of 2/1 (a) and 5/1 (b), H_2SO_4 concentration to 1 mol/L and 39.19 g/L of chloride).

Manganese nodules are composed of 29.85% MnO_2 and 26.02% Fe_2O_3 , which are dissolved in the acidic environment. Figure 4a shows how the MnO_2 used as an oxidising agent for the dissolution of copper, where the Mn (IV) is reduced to Mn (II). Manganese has a high extraction at a temperature of 80 °C. The manganese dissolved in the PLS can be present in two forms, such as MnSO_4 or as MnCl_2 , due to the effect of sulfuric acid and/or chloride, respectively. In Figure 4b, the iron (II) present in the chalcopyrite oxidises and slowly dissolves in an environment of high concentration of sulfuric acid and high level of chloride forming ferric chloride, which is positive since it is a compound that helps the copper solution from the chalcopyrite, and the kinetics of the iron solution increases with temperature. Regarding the pH, it can be seen that lowering the acidity in the Mn solution it does not decrease the dissolution of this element. While in iron, more positive results are presented in a more acidic environment.



(a)

Figure 4. Cont.

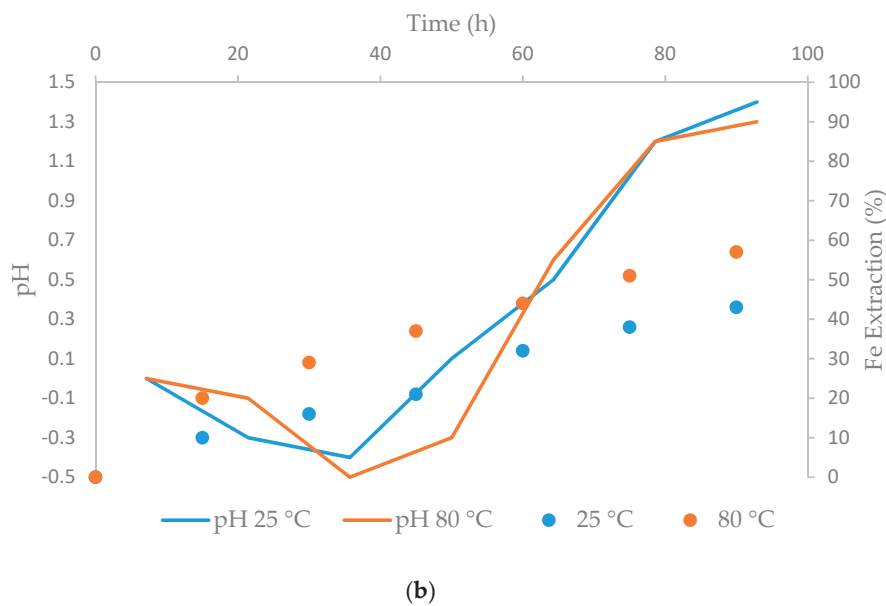


Figure 4. Dissolution of Fe and Mn over time from CuFeS_2 at room temperature (25 °C) and high temperature (80 °C) (a): Dissolution of Fe and its behavior at changes in pH; (b): Dissolution of Mn and its behavior at changes in pH).

In the big copper mining in Chile, the Fe and Mn present in the pregnant leaching solution (PLS) are considered as impurities, this because in the electro-obtaining process, the Fe reduces the efficiency of current. At the same time, the Mn generates corrosion in lead anodes. However, both impurities are controlled in metallurgical plants minimizing the problems that they could produce. Manganese and iron can be transferred to the electro-obtaining stage through physical drag generated by solvent extraction. To reduce the physical transfer of impurities, the plants must optimize the equipment to retain water trawlers in organic (A/O), in addition to adopting some operational practices like maintaining good organic quality through the treatment of organic with clay; avoid over agitation in the mixers; surfactant addition control; and maintain design parameters within the recommended range (linear speed, specific decantation flow, etc.). For the reasons stated, it is possible to apply this process at the industrial level through the conventional hydrometallurgical route (leaching, solvent extraction and electro-obtaining), since solvent extraction processes in Chile have solved this problem. Also, it works in several miners with the use of seawater or adding high concentrations of chloride in synthetic form.

4. Conclusions

This research presents the results of dissolving copper from chalcopyrite by adding MnO_2 as an oxidizing agent (manganese nodules) in a chloride medium (wastewater). As previously concluded by Devi et al. [26]; Devi et al. [27]; Havlik et al. [28] and Toro et al. [29], the addition of MnO_2 and chloride in high concentrations generate a positive effect on the chalcopyrite solution. The main findings of this study are:

- There were no differences in copper dissolution rates at particle sizes between $-75 + 53$ and $-47 + 38 \mu\text{m}$. at different H_2SO_4 concentrations.
- Small particle size ($-20 \mu\text{m}$) increases CuFeS_2 dissolution kinetics, due to the mechanical-chemical activation of the mineral.
- Temperatures of 80 °C positively affect CuFeS_2 dissolution, while the MnO_2 concentration did not have a significant effect in the system.
- The biggest copper extractions in this research (71%) was obtained working at 80 °C, a particle size of $-47 + 38 \mu\text{m}$, a 5/1 $\text{MnO}_2/\text{CuFeS}_2$ ratio, and 1 mol/L of H_2SO_4 .

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Conflicts of Interest: The authors declare no conflict of interest.

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7. Reducing-Effect of Chloride for the Dissolution of Black Copper

Resumen: Los óxidos negros de cobre son minerales difícilmente solubles, lo que impide recuperar sus elementos de interés por medios lo habituales. Esto está provocado porque su estructura es amorfa, no cristalizada. De entre estos minerales, los denominados “copper pitch” y “copper wad” presentan gran interés por su contenido en cobre y manganeso. Es habitual rechazar estos minerales o eliminarlos de los circuitos de tratamiento, almacenándolos, tratándolos en pilas de lixiviación o desechándolos en vertederos. Para recuperar los elementos principales (Cu y Mn) es necesario emplear agentes reductores que disuelvan el Mn y permitan recuperar el Cu. En esta investigación, se muestran los resultados del proceso de disolución de Cu y Mn de un óxido negro, evaluando el efecto reductor del NaCl sobre el MnO₂ en una fase de pretratamiento y curado con una fase posterior de lixiviación con el (Fe²⁺) como agente reductor. Las elevadas concentraciones de cloruro en la fase de aglomeración y el aumento del tiempo de curado previo favorecen la reducción de MnO₂ disolviendo el Mn, pero la adición de NaCl no beneficia la extracción de Cu. En condiciones normales, se obtienen bajos niveles de extracción de Mn, mientras que con agente reductor en medio ácido sí se disuelve el MnO₂ de manera significativa, lo que facilita la recuperación de Cu.

Article

Reducing-Effect of Chloride for the Dissolution of Black Copper

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Abstract: Oxidized black copper ores are known for their difficulty in dissolving their components of interest through conventional methods. This is due to its non-crystalline and amorphous structure. Among these minerals, copper pitch and copper wad are of great interest because of their considerable concentrations of copper and manganese. Currently, these minerals are not incorporated into the extraction circuits or left untreated, whether in stock, leach pads, or waste. For the recovery of its main elements of interest (Cu and Mn), it is necessary to use reducing agents that dissolve the present MnO₂, while allowing the recovery of Cu. In this research, the results for the dissolution of Mn and Cu from a black copper mineral are exposed, evaluating the reducing effect of NaCl for MnO₂ through pre-treatment of agglomerate and curing, and subsequently leaching in standard condition with the use of a reducing agent (Fe²⁺). High concentrations of chloride in the agglomerate process and prolonged curing times would favor the reduction of MnO₂, increasing the dissolution of Mn, while the addition of NaCl did not benefit Cu extractions. Under standard conditions, low Mn extractions were obtained, while in an acid-reducing medium, a significant dissolution of MnO₂ was achieved, which supports the removal of Cu.

Keywords: agglomerate; copper pitch; copper wad; curing; pre-treatment

1. Introduction

The interactions that occur in mineral deposits through geological agents help the formation of new mineral species [1]. An example is the oxidation of pyrite, which when reacted with water produces sulfuric acid, favouring the mobility of metals like copper, which under particular conditions of potential and pH can be transported, precipitating downstream, forming deposits called “exotic” [2]. The principal copper minerals being in this type of deposit are chrysocolla-atacamite, copper-pitch, and copper-wad [3].

The “copper wad” and “copper pitch” are hydrated silicates of manganese and iron, rich in copper, which appear as brotoidal masses, compact or earthy. When it is alone and shows earthy

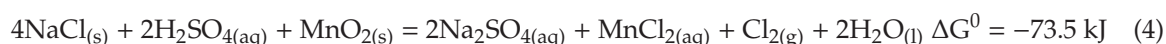
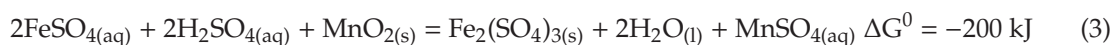
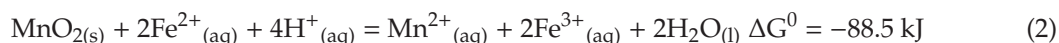
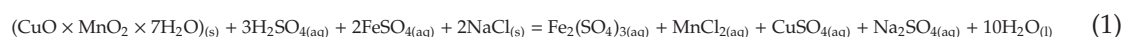
habit, it is called wad; if it is associated with chrysocolla, it is called pitch or “black chrysocolla” [4]. Pincheira et al. [5] proposed the name of black copper silicate to designate both mineraloids, without crystalline structure. They have a similar composition and in greater quantity are elements such as Cu, Mn, Fe, Al, and Si, accompanied by traces of Ca, Na, K, Mg, S, P, Cl, Mo, Co, Ni, As, Zn, Pb, U, V.

Black copper ores are a resource that is generally not incorporated into the extraction circuits or left untreated, whether in stock, leach pads, or waste [6,7]. This is due to the difficulty of recovering elements of interest like Cu or Mn by conventional hydrometallurgical processes since the complex structure is non-crystalline or amorphous [8]. However, several studies have been carried out to extract these elements from marine nodules and other manganese minerals, which generates alternatives for processing by similar leaching systems.

Several studies have been carried out in recent years for the extraction of Mn from marine nodules in acidic media, testing diverse reducing agents such as oxalic acid [9], glucose [10], FeO [11], cane molasses [12], corn cob [13], biomass from residual tea [14], etc. Toro et al. [15,16] obtained promising results when employing FeSO₄, formed from the reaction between tailings and H₂SO₄. Benavente et al. [7] conducted a study for the dissolution of Cu and Mn from black copper under oxidizing and reducing conditions. The authors indicated that at oxidizing conditions, better results are not obtained than in a standard state (without oxidizing agents or reducing agents), concluding that the addition of an oxidizing agent does not improve the dissolution rate of black copper. Otherwise, in a reducing condition, the decrease in redox potential favors the dissolution of manganese, increasing the extraction of Cu.

Wang and Zhou [17] investigated the recovery of cobalt from residues of zinc plants by a hydrometallurgical process, using ammonium peroxydisulfate ((NH₄)₂S₂O₈) for the precipitation of manganese as MnO₂. The researchers noted that the chloride ion negatively affected manganese precipitation, which was attributed to the reduction of manganese oxide. The standard redox potentials are: Mn₃O₄/Mn²⁺ = 1.76 V and Cl₂/Cl⁻ = 1.39 V. Then, it was concluded that manganese oxide could be thermodynamically reduced to Mn²⁺ through chloride. Fuerstenau and Han [18] indicated that by working at 100 °C in the leaching of marine nodules, good extractions of copper, nickel, and cobalt could be obtained after a long period of residence, either with sulfuric acid or hydrochloric acid. Senanayake [19] compared the leaching of marine nodules in H₂SO₄ and HCl, in temperature ranges of 30–90 °C, with absence and presence of SO₂, Na₂SO₃, NaCl, and CaCl₂, concluding that at a higher temperature (90 °C) the HCl gives better results.

For the dissolution of manganese from black copper with the use of sulfuric acid and chloride, the following series of reactions is proposed:



On the other hand, pre-treatment processes that involve agglomeration and curing stages have shown positive results to improve mineral reaction rates [20,21]. In the study conducted by Bahamonde et al. [22], pre-treatment with sodium chloride and sulfuric acid was carried out to enhance copper extractions in a concentrate formed mainly by bornite and chalcopyrite. Different concentrations of sodium chloride (15, 30 and 60 kg/t) and cure time (15 and 30 d) were studied, where finally, a significant increase in Cu extractions was obtained. In a more recent study by Cerda et al. [21], pre-treatment experiments were carried out for a copper sulphide mineral (chalcopyrite), where sulfuric acid (20 kg/t) and sodium chloride were added at different concentrations (20, 50, and 90 kg/t). The authors concluded that the cure time is more important than the level of chloride in the agglomerate process.

Currently, the mining industry must generate a new approach that helps overcome the stagnation in its growth. Despite its surplus-generating role, large-scale mining faces significant challenges such as the deterioration of the ore grade, increased operational costs, and input costs must be adjusted to the demand for sustainable development [23]. In recent years, in Chile the treatment of other commodities has been incorporated into the extraction processes, for example, the recovery of Mo together with the Cu in flotation processes has been encouraged [24]. This helps to diversify the business and boost the export of additional products [6]. It is necessary to incorporate the minerals of black copper in the leaching processes, because of their considerable amounts of Mn (29%) which, when dissolved, favor the extraction of Cu, and would allow giving a high commercial value of these “residues”.

In this research, the outcomes for the dissolution of Mn and Cu from a black copper ore are exposed. The reducing effect of NaCl for MnO₂ was evaluated by pre-treatment, adding this reagent in the agglomerate stage and then leaving it at rest. Subsequently, a leaching process was carried out under standard conditions and adding a reducing agent (Fe²⁺).

2. Experimental

2.1. Black Copper Simple

For the present study, a sample of black copper from a mining company in northern Chile was used. The sample was from a high-grade vein, with purity near to 100%. The ore was ground in a porcelain mortar to sizing between -173 and $+147$ μm . The chemical composition was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) (see Table 1). A QEMSCAN (Quantitative Evaluation of Minerals by SCANning) analysis was applied, which is a modified electronic scanning microscope, both in hardware and software. This performs the identification and automated quantification of ranges of elementary definitions that can be associated with inorganic solid phases (minerals, alloys, slags, etc.). The samples were mounted on briquettes and polished to determine the mineralogical composition. The identification, mapping of 2-D distribution, and quantification of inorganic phases were done by combining the emissions of retro-dispersed electrons (BSE), with a Zeiss EVO series, a Bruker AXS XFlash 4010 detector (Bruker, Billerica, MA, USA), and the iDiscover 5.3.2.501 software (FEI Company, Brisbane, Australia). The QEMSCAN analyses are based on the automated obtaining of EDS spectra (dispersed energy from X-rays), in hundreds of thousands or millions of collected analysis points, each in a time of milliseconds. The classification of mineralogical phases was done by classifying each EDS spectrum in a hierarchical and descending compositional list, known as the “SIP List”. The BSE image was used to discriminate between resin and graphite in the sample, to specify entries in the SIP list, and to establish thresholds for acceptance or rejection of particles. As a result, pixelated, 2-D and false color images of a specimen or a representative subsample of particles are obtained. Each pixel retains its elementary and BSE brightness information, which allows subsequent offline data processing. Through software, customized filters are generated that quantify the ore and gangue species, mineral release, associations between inorganic phases, classifying particles according to criteria of shape, size, texture, etc. Figure 1 shows the chemical species to black oxides using QEMSCAN.

Table 1. Chemical composition of black oxide samples.

Mn (%)	Cu (%)	Fe (%)
22.01	40.24	7.92

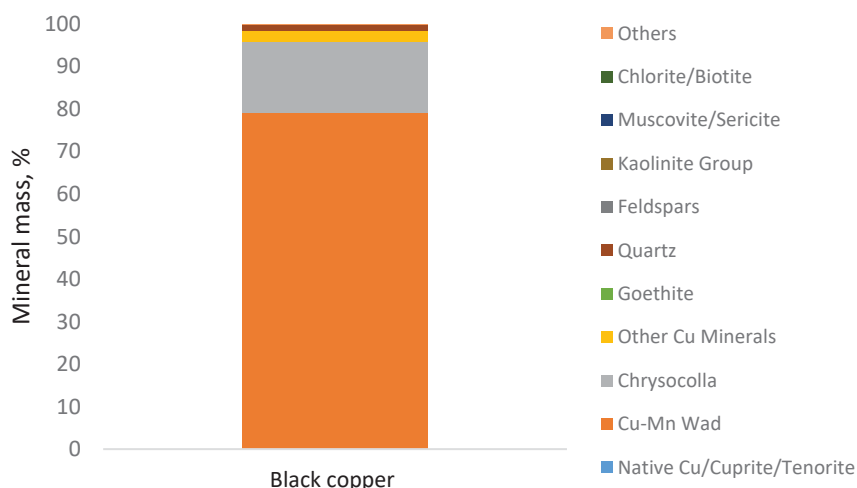


Figure 1. Detailed modal mineralogy.

Table 2 shows the mineralogical composition of the black copper samples. Copper wad refers to a subgroup of copper composed of manganese and copper hydroxides, as well as also traces of other elements such as Co, Ca, Fe, Al, Si, and Mg.

Table 2. The mineralogical composition of the black copper samples as determined by QEMSCAN.

Mineral (% Mass)	Black Copper
Native Cu/Cuprite/Tenorite	0.12
Cu-Mn Wad	78.90
Chrysocolla	16.72
Other Cu Minerals	2.69
Goethite	0.01
Quartz	1.41
Feldspars	0.02
Kaolinite Group	0.01
Muscovite/Sericite	0.01
Chlorite/Biotite	0.01
Others	0.09
Total	100

2.2. Ferrous Ions

The ferrous ions used for this investigation ($\text{FeSO}_4 \times 7\text{H}_2\text{O}$) were WINKLER brand, with a molecular weight of 278.01 g/mol. These were incorporated during the leaching process in stirred reactors, after the pretreatment process.

2.3. Pre-Treatment and Subsequent Leaching in reactors

For the pre-treatment, we worked with 10 g of ore, adding 20 kg of $\text{H}_2\text{SO}_4/\text{t}$ (according to the level to be studied) and different concentrations of NaCl (See Table 1). The sample and reagents were homogenized and subsequently placed on a Petri dish, which was covered with plastic to avoid evaporation. The temperature during the resting time was controlled at 25 °C with the use of an air conditioner. Subsequently, leaching tests were carried out in a 100-mL glass reactor with a 0.01 S/L ratio. A total of 10 g of black copper ore and MnO_2 (manganese nodules) at different concentrations were mixed and dispersed with a five-position magnetic stirrer (IKA ROS, CEP 13087-534, Campinas, Brazil) at a speed of 600 rpm. The temperature was controlled at 25 °C using an oil-heated circulator (Julabo) (Julabo, St. Louis, MO, USA). All the tests were duplicated, and the measurements (or analyses) were carried out on 5 mL undiluted samples using atomic absorption spectrometry with a coefficient of variation $\leq 5\%$ and a relative error between 5 to 10%. Measurements of pH and oxidation-reduction

potential (ORP) of leach solutions were made using a pH-ORP meter (HANNA HI-4222) (HANNA instruments, Woonsocket, RI, USA). The ORP solution was measured in a combination ORP electrode cell of a platinum working electrode and a saturated Ag/AgCl reference electrode.

2.4. Dissolution of Mn and Cu

In a previous research conducted by Wang and Zhou [17], it was discovered that after a long contact time, chloride could reduce MnO_2 . For this reason, it was resolved to assess this impact by agglomerate assays and subsequently a leaching process.

For the agglomerate tests, we worked by adding 20 kg of H_2SO_4 /t and 10 kg of NaCl/t, with a curing time of 48 h. While the following operational parameters were used for leaching: $\text{Fe}^{2+}/\text{MnO}_2$ ratio of 1/1, particle size of $-75 + 53 \mu\text{m}$, agitation rate of 600 rpm, 1 mol/L sulfuric acid, and room temperature (25 °C).

2.5. Effect of NaCl Concentration and Cure Time

For the agglomerate and curing tests, we worked under the parameters presented in Table 3:

Table 3. Variables studied in the pretreatment step.

Test	Curing Time (h)	NaCl Concentration (kg/t)
1	48	10
2	48	20
3	96	10
4	96	20

For the leaching tests, the following operational parameters were worked: $\text{Fe}^{2+}/\text{MnO}_2$ ratio of 1/1, particle size of $-75 + 53 \mu\text{m}$, agitation rate of 600 rpm, 1 mol/L sulfuric acid, and room temperature (25 °C).

3. Results

3.1. Effect of Agglomerate with NaCl to Dissolve Mn

Figure 2 shows the dissolution of Mn from a sample of black copper under four conditions: (1) without the use of reducing agent or prior agglomerate (standard state), (2) with the use of reducing agent (Fe^{2+}) without prior agglomerate, (3) without reducing agent, but with a previous agglomerate process (Standard condition + NaCl), (4) with previous agglomerate and use of reducing agent (Fe^{2+} + NaCl). It can be seen that without the use of a reducing agent, it is not possible to dissolve the Mn present in the black copper sample and, besides, a beneficial effect cannot be appreciated by adding chloride to the system. This is consistent with the results obtained by Benavente et al. [7], where Mn was not dissolved for a black copper ore under standard conditions. On the other hand, it can be seen that with the use of Fe^{2+} high solutions of Mn (over 50%) are obtained in short periods (20 min), a result very similar to that set forth by Pérez et al. [6] under similar conditions. When a previous agglomerate process is added by adding NaCl, a positive effect on the dissolution of Mn is generated. This allows confirming the statements made by Wang and Zhou [17], who indicate that the chloride being in contact with MnO_2 for a long time can generate a reducing effect on the mineral, favoring its subsequent leaching.

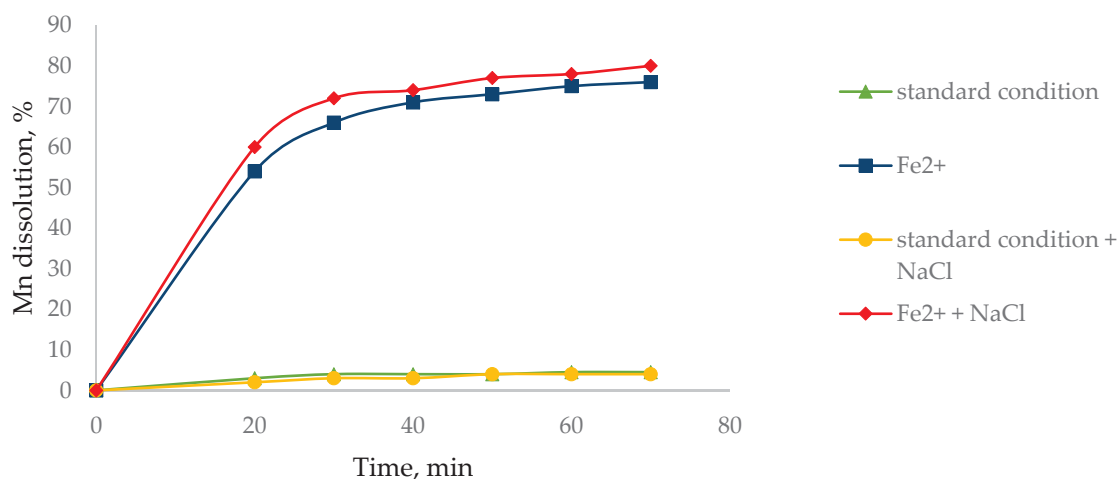


Figure 2. Dissolution of Mn from a black copper ore.

3.2. Effect of Agglomerate with NaCl to Dissolve Cu

Figure 3 shows the dissolution of Cu from a sample of black copper under the same conditions previously set out in Figure 2. There was no beneficial effect on the dissolution of copper when performing a previous agglomerate process by adding NaCl, but promising outcomes were achieved when adding a reducing agent. In the study conducted by Benavente et al. [7], it was indicated that no favorable results are obtained by adding O₂ for the dissolution of Cu from black copper ore. This situation was improved by working in a reducing condition, which favors the dissolution of MnO₂ by means of a reducing agent in an acid medium [11,25–27], allowing subsequent increase in Cu extractions.

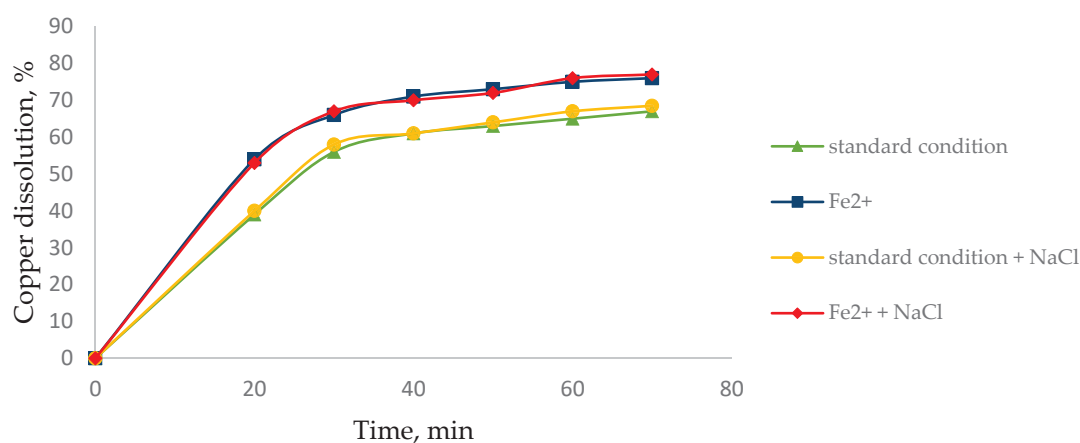


Figure 3. Dissolution of Cu from a black copper ore. Effect of NaCl concentration and cure time.

3.3. Effect of NaCl Concentration and Cure Time

Figure 4 shows the effect of carrying out a pre-treatment process by adding NaCl, giving a rest time and subsequently leaching the material. Sodium chloride did not generate any increase in the dissolution of Cu from black copper. However, a positive effect on manganese dissolution was seen, as the concentration of NaCl in the pre-treatment increased. In general, better results were obtained for both elements as the curing time increased, which is consistent with previous researches for the dissolution of Cu minerals [20,21]. A beneficial effect is also observed in the reductive leaching of MnO₂ over time, as the chloride concentration increased. The potential and pH values were in the range of -0.2 to 1.5 V and -0.5 to 0.4 , for all the tests performed. These results are consistent according to the statement by Senanayake et al. [19], where it is indicated that the ranges of pH and potential suitable for a leaching of MnO₂ reductive using Fe are from -2 to 0.1 and -0.4 to 1.4 [28].

In addition, when working in these ranges, Mn ions remain in solution, and do not precipitate through oxidation-reduction reactions [29].

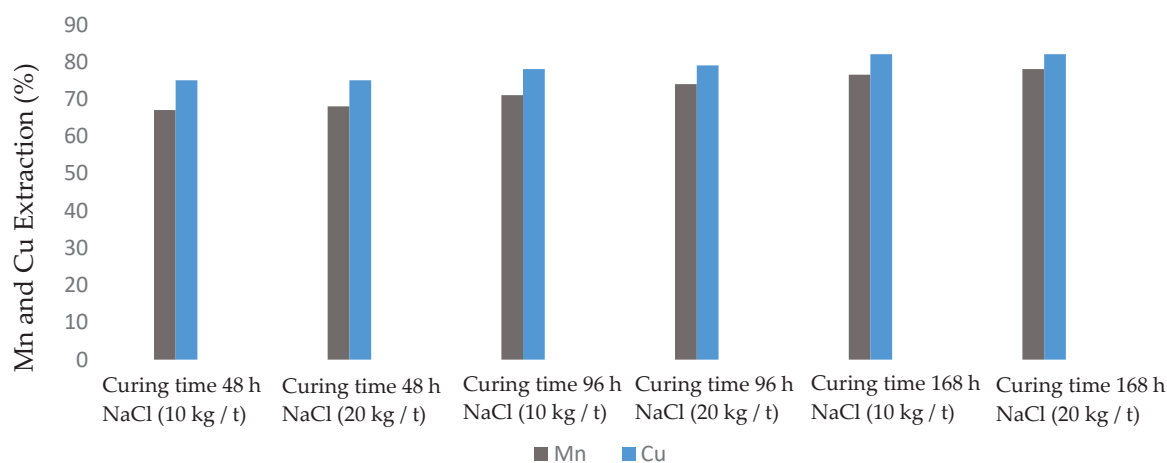


Figure 4. Effect of NaCl concentration and cure time on the dissolution of Mn and Cu.

Figure 5 shows that the main compound in the residues is copper oxide that has not yet dissolved, this oxide is from black copper, chrysocolla, and other copper oxides (tenorite, cuprite, among others) that were present in the initial mineral. The presence of copper-chloride complexes within the system stands out, this is mainly due to the curing with NaCl and the formation of solid species such as CuCl. The other species are oxides of manganese, iron and aluminum and silicon species, the latter elements originating from the chrysocolla and are present in small quantities in the mineral residue.

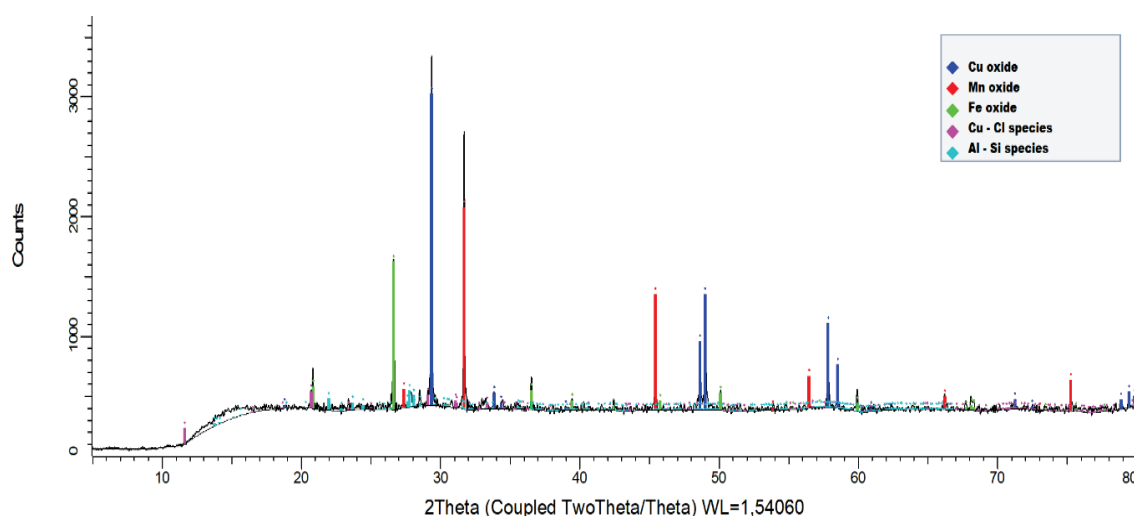


Figure 5. X-ray diffractogram for solid residue (black copper ore) after being leached at 25 °C with NaCl and FeSO₄ in a time of 70 min.

4. Conclusions

The present research displays outcomes where it is sought to dissolve Cu and Mn from black copper, with a pre-treatment of agglomerate incorporating NaCl, a cured time and subsequent acid-reducing leaching at room temperature (25 °C). The main findings are the following:

Under standard conditions, low Mn solutions were obtained, and pre-treatment with NaCl did not influence the solutions thereof.

When working in an acid-reducing medium, a more significant dissolution of MnO₂ was achieved, which favors the extraction of Cu.

High concentrations of chloride in the agglomerate process and prolonged curing times would favor the reduction of MnO_2 , increasing the dissolution of Mn.

An increase in curing time favors Cu solutions while the addition of NaCl in the agglomerate process is irrelevant for its dissolution.

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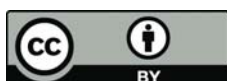
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8. Leaching of Pure Chalcocite with Reject Brine and MnO₂ from Manganese

Resumen: La Calcosina (Cu₂S) es el sulfuro de cobre mineral con mayor cinética de disolución de Cu en medios clorados. Este mineral presenta relevante interés económico por su abundancia, aunque, en muchas regiones, el agua que se necesita para tratarlo es escasa. En este trabajo, se analiza el remplazamiento del agua dulce por agua de mar o por salmuera de plantas desalinizadoras. También se estudia la adición de MnO₂ procedente de nódulos marinos, que existen en de forma abundante en los fondos marinos. Las salmueras reutilizadas ofrecen mejores resultados que el agua de mar y la adición de MnO₂ conduce a mejoras cinéticas en la disolución de Calcosina en el corto plazo. La concentración de H₂SO₄ no influye cuando se trabaja con altas concentraciones de cloruro y MnO₂. Los mejores resultados, con 71% de Cu recuperado en 48 h, se obtienen con salmuera, 100 mg MnO₂ por 200 g de mineral y concentraciones de H₂SO₄ de 0,5 mol/L. Estos resultados permiten mantener las expectativas en disponer de un proceso sostenible para la disolución de la Calcosina como el de utilizar salmueras de las plantas desalinizadoras.

Article

Leaching of Pure Chalcocite with Reject Brine and MnO_2 from Manganese Nodules

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Abstract: Chalcocite (Cu_2S) has the fastest kinetics of dissolution of Cu in chlorinated media of all copper sulfide minerals. Chalcocite has been identified as having economic interest due to its abundance, although the water necessary for its dissolution is scarce in many regions. In this work, the replacement of fresh water by sea water or by reject brine with high chloride content from desalination plants is analyzed. Additionally, the effect of adding MnO_2 from available manganese nodules in vast quantities at the bottom of the sea is studied. Reject brine shows better results than sea water, and the addition of MnO_2 to the brine significantly increases the kinetics of chalcocite dissolution in a short time. H_2SO_4 concentration is found to be irrelevant when working at high concentrations of chloride and MnO_2 . The best results, 71% Cu extractions in 48 h, are obtained for reject brine, 100 mg of MnO_2 per 200 g of mineral and H_2SO_4 0.5 mol/L. The results are expected to contribute to a sustainable process of dissolution of chalcocite by using the reject brine from desalination plants.

Keywords: sulfide leaching; chalcocite dissolution; desalination; reject brine; replace water; sustainability

1. Introduction

Currently, 19.7 million tons of copper are produced worldwide [1,2], mainly by pyrometallurgical processes (75%) and, to a lesser extent, by hydrometallurgy (25%) [3,4].

The vast majority of copper minerals in the world correspond to sulfide minerals and a smaller quantity to oxidized minerals [5–8]. Among the sulfurous minerals, the most abundant copper mineral is chalcopyrite [9–11], followed by chalcocite [12]. However, chalcopyrite is a very refractory mineral to be treated hydrometallurgically [13]. On the other hand, chalcocite has been shown to be relatively easy to treat using hydrometallurgical processes [14]. The literature reports an important number of works on the dissolution of chalcocite in acidic media, pressure leaching [15], bioleaching [15–17] and

leaching in chlorinated media [18–21]. This last process is very attractive because it is cost effective and leads to high copper extractions.

There is no record in the literature on the use of MnO_2 as an oxidizing agent in the leaching of chalcocite in chlorinated media. However, there are records in which this oxidant is added to improve the dissolution of chalcopyrite with good results [22–24]. Havlik et al. [24] use HCl and manganese nodules to extract Cu from chalcopyrite. This study finds that, when working at high concentrations of MnO_2 ($\text{MnO}_2/\text{CuFeS}_2$ ratio of 4/1) and HCl (4 mol/L), the best copper extractions are obtained, reaching values above 40% at room temperature and near 70% at 50 °C.

The dissolution of chalcocite in chlorinated media has been analyzed several times [14,20,21,25,26], obtaining high copper extraction in the presence of oxidants, such as ferric or cupric, at high temperature, which greatly improves the leaching kinetics of this mineral. To evaluate the effect of chloride, both the concentration and the source have been analyzed, that is, sea water, HCl, NaCl, FeCl_3 , etc. Cheng and Lawson [25] have proposed that chloride acts as a catalyst that forms long sulfur crystals that allow the diffusion of oxidizing agents within the mineral avoiding the formation of a passivating layer that retards the dissolution of the mineral. Several authors [27,28] have obtained similar results, and to demonstrate the mechanism they have measured the porosity at the mineral surface when copper sulfides are leached in the presence of NaCl, HCl, FeCl_3 or other sources of chloride. It is this porosity that allows the mineral to contact the leaching agent through these sulfur layers that form on the mineral surface.

Two reactions are proposed for the dissolution of chalcocite in chlorinated media and in the presence of manganese (IV) as an oxidizing agent.



In the first leaching stage (Equation (1)), chalcocite is converted to covellite; this reaction is thermodynamically possible according to the Gibbs free energy that is negative under the described conditions. The second reaction (Equation (2)) is slower. The energies were calculated using the HSC 5.1 software. Thus, Equation (1) is more likely to occur than Equation (2) as suggested by other authors [12,29].

The shortage of fresh water in various regions of the world is a major economic, environmental and social problem [30]. The use of sea water has become increasingly important for mining, for example, in northern Chile, not only for its positive effects on leaching processes due to its chloride content, but as a strategic and indispensable resource for the sustainability of the industry [4,31,32]. A very attractive alternative is the use of wastewater from desalination plants, which, following the example of Chile, are abundant in the north of the country. Desalination plants produce drinking water for the population, but the reject brine pollutes the sea, threatening the marine ecosystem, and therefore alternatives are required to recycle or reuse this concentrated brine.

In this study, the kinetics of chalcocite dissolution in acid solution and at room temperature in chlorinated media and in the presence of manganese nodules are determined. The kinetics of chalcocite dissolution in sea water and in reject brine from a desalination plant are compared, and the effect of MnO_2 and sulfuric acid on the percentage of copper extraction is evaluated, at short and long times.

2. Materials and Methods

2.1. Chalcocite

The chalcocite mineral sample was obtained from Mina Atómica, located in Antofagasta, Chile. The material was reduced to reach a size range between -150 and $+106 \mu\text{m}$. The grinding was done in a porcelain mortar to avoid contamination. The chemical composition was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, (FEI Company, Brisbane,

Australia)). Table 1 shows the results. In addition, the mineralogy of the sample was analyzed using a Bruker X-ray diffractometer (Bruker, Billerica, MA, USA), automatic and computerized model D8, Figure 1 shows the results. The sample was 99.90% chalcocite.

Table 1. Chemical analysis of the chalcocite ore sample.

Component	Cu	S
Mass (%)	79.83	20.17

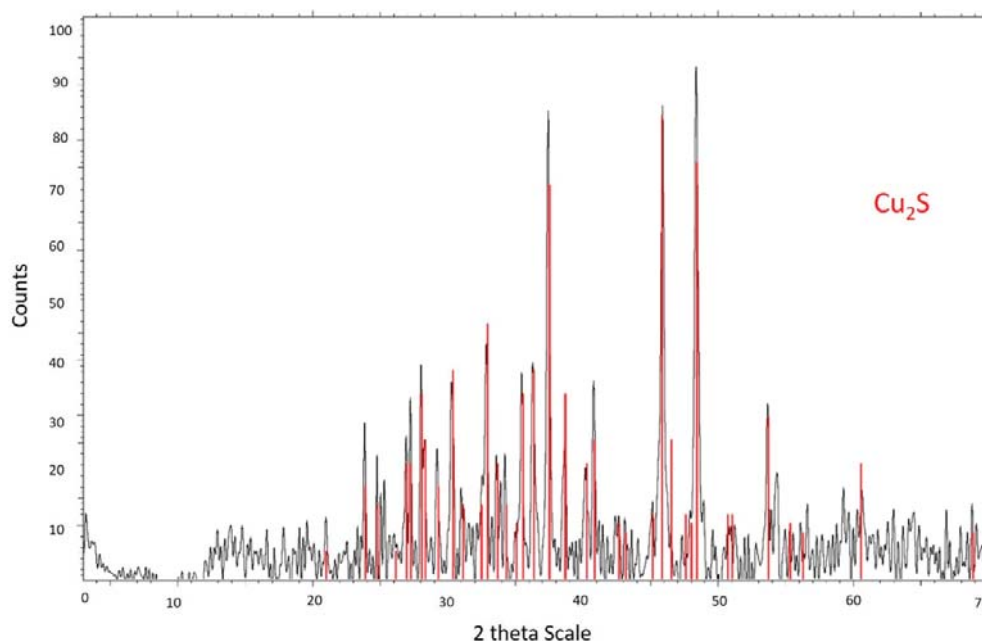


Figure 1. X-ray spectrum of the chalcocite mineral sample.

2.2. Manganese Nodules

The MnO_2 used came from manganese nodules collected during the 1970s from the Blake Plateau in the Atlantic Ocean. The sample was reduced in size in a porcelain mortar until reaching a size range between -140 and $+100$ μm . The chemical composition was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). Table 2 shows the results. The mineralogy of the sample was analyzed using Bruker[®] M4-Tornado μ -XRF table-top equipment (Fremont, CA, USA). μ -XRF data interpretation showed the sample is comprised of a pre-existent nodule fragment forming the core with concentric layers precipitated around it at later stages. The experiments showed pyrolusite (MnO_2) as the predominant phase (See Table 3).

Table 2. Chemical analysis of manganese ore.

Component	Mn	Fe	Cu	Co
Mass %	15.96	0.45	0.12	0.29

Table 3. Mineralogical analysis of manganese ore.

Component	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	MnO ₂	Fe ₂ O ₃
Mass (%)	3.54	3.69	2.97	7.20	1.17	0.33	22.48	1.07	29.85	26.02

2.3. Reagents and Leaching Tests

Sea water from Antofagasta (Chile) and reject brine from Aguas Antofagasta, Antofagasta (Chile), were used. The sulfuric acid used in the leaching tests is Merck, grade p.a., purity 95–97%, density 1.84 kg/L and molecular weight 98.08 g/mol. Leaching tests were carried out in a 50 mL glass reactor with a 0.01 solid to liquid (S/L) ratio of leaching solution. A total of 200 mg of chalcocite ore was kept suspended by agitation with the use of a 5-position magnetic stirrer (IKA ROS, CEP 13087-534, Campinas, Brazil) at a speed of 600 rpm. The tests were conducted at room temperature of 25 °C at different concentrations of sulfuric acid and chloride, and leaching times. The tests were performed in duplicate. Analyses were performed on 5 mL undiluted samples using atomic absorption spectrometry with a coefficient of variation $\leq 5\%$ and a relative error between 5% and 10%. Measurements of pH and oxidation-reduction potential (ORP) of the suspensions were made using a pH-ORP meter (HANNA HI-4222, St. Louis, MO, USA). An ORP electrode cell combination consisting of a platinum working electrode and a saturated Ag/AgCl reference electrode was used.

2.4. Experimental Design

Two sources of water that provide chloride, sea water (20 g/L Cl^-) and reject brine (39 g/L Cl^-), were evaluated. The copper extraction was determined every 4 h until reaching a total time of 48 h. The total mass of chalcocite in all tests was always 200 mg. The tests were repeated adding MnO_2 to the reactor with the chalcocite pulp and measuring every 4 h until completing 48 h. Two concentrations of MnO_2 were used, 0.25:1 and 0.5:1, with respect to the total mass of chalcocite. Finally, to evaluate the effect of H_2SO_4 on all the tests carried out, three concentrations were used, 0.1, 0.5 and 1 M.

3. Results

3.1. Effect of Chloride Concentration on Copper Extraction

The effect of chloride ions in leaching processes has proven beneficial for the treatment of sulphide minerals [14,25,26]. On the other hand, recent studies have shown the benefits of oxidizing primary sulphides incorporating MnO_2 into the system [22–24]. Figure 2 for chalcocite shows better results in chloride-concentrated water such as the brine reject from reverse osmosis plants (ca. 39 g/L of Cl^-) than in seawater (20 g/L of Cl^-) both in the presence of MnO_2 in a concentration 0.25:1 *w/w* with respect to the chalcocite mass. Using reject brine, extractions over 50% Cu are obtained in 8 h and 67.5% Cu in 48 h, apart from the fact that other ions present such as calcium, magnesium and carbonate do not adversely affect the Cu_2S dissolution. Figure 2 shows that 80% or more of the copper extraction occurs quickly within the first 8 h.

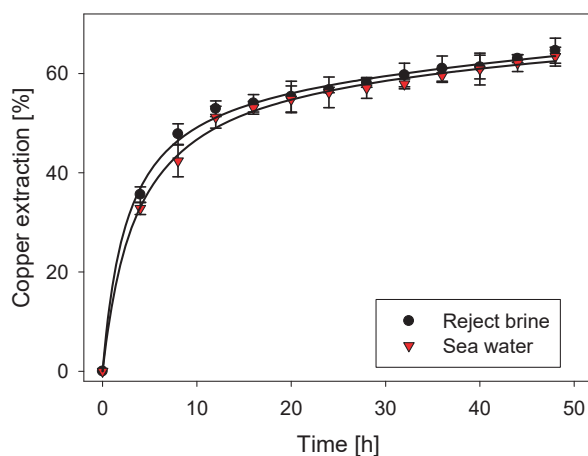


Figure 2. Cu extraction from chalcocite in two water sources and the addition of MnO_2 in a ratio 0.25:1 *w/w* with respect to the chalcocite mass.

3.2. Effect of MnO_2 Concentration on Copper Extraction

Figure 3 shows the effect of MnO_2 concentration on chalcocite dissolution in reject brine. As the MnO_2 concentration increases, the dissolution of chalcocite increases. This is consistent with the results presented by Devi et al. [22] and Havlik et al. [24], which show that MnO_2 increases the dissolution of even a more refractory sulfide such as chalcopyrite when working at very high concentrations of MnO_2 and HCl. Figure 3 shows that the kinetics of chalcocite dissolution is faster in the presence of MnO_2 but it is more so when the concentration of MnO_2 is higher (ratio 0.5:1 *w/w* or more with respect to the chalcocite mass). In the latter case, a greater dissolution is obtained at very short times (less than 10 h) which slowly stabilizes at higher dissolution values at longer times.

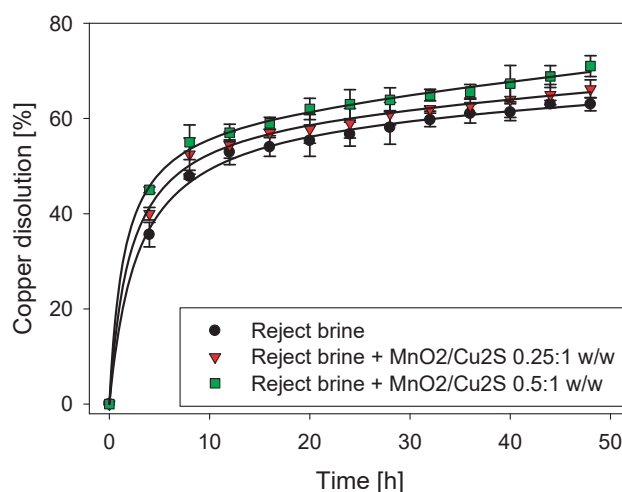


Figure 3. Kinetics of chalcocite dissolution in reject brine. Effect of MnO_2 concentration.

Table 4 compares the results of chalcocite dissolution in chlorinated media (sea water and reject brine) in two cases: Without the addition of an oxidizing agent and with the incorporation of a small amount of MnO_2 under the same operating conditions. The table shows that the higher the chloride concentration, the greater the leaching performance, and that the presence of MnO_2 increases the dissolution in all cases. Dissolution data without MnO_2 in Table 4 are from Toro et al. [14]. Note that for reject brine the data is very similar to that shown in Figure 3. MnO_2 increases chalcocite dissolution at short times of 4 h by 8% in sea water and by 10% in reject brine. At long times of 48 h the increase is more moderate, 2% in sea water and 2.5% in reject brine. More interesting are the short time data considering that in a field operation the leaching solution is continuously refreshed.

Table 4. Comparison of chalcocite dissolution in sea water and reject brine and the effect of MnO_2 .

Experimental Conditions and Results	Toro et al. [14]	This Work
Temperature ($^{\circ}C$)	25	25
Particle size of Cu_2S (μm)	$-147 + 104$	$-147 + 104$
H_2SO_4 concentration (mol/L)	0.5	0.5
MnO_2/Cu_2S ratio (<i>w/w</i>)	-	0.25:1
Dissolution in sea water after 4 h (%)	32.8	35.6
Dissolution in reject brine after 4 h (%)	36	40
Dissolution in sea water after 48 h (%)	63.4	64.7
Dissolution in reject brine after 48 h (%)	64.6	66.2

Figure 4 shows the potential for the tests performed in Figure 3. The potential varies between 550 and 630 mV in agreement with Senanayake [33], which indicates that for the dissolution of chalcocite in a chloride-iron solution at $25^{\circ}C$ it is necessary to reach potential values greater than 500 mV. Figure 4 shows higher potentials and copper extractions at short leaching times. Furthermore, Miki et al. [29] have

stated that upon dissolving 50% of chalcocite, the dissolution kinetics becomes slower because the mineral changes phase to covellite, which implies the need to reach potentials greater than 600 mV to dissolve it.

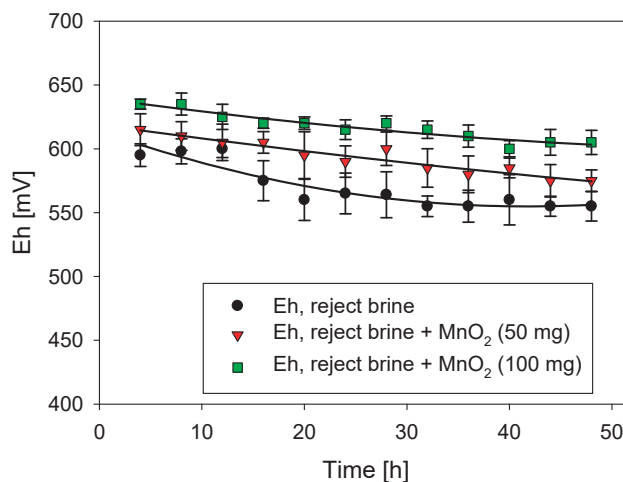


Figure 4. Effect of potential on the extraction of Cu from chalcocite in reject brine concentrate at different masses of MnO₂.

3.3. Effect of Sulfuric Acid Concentration on Copper Extraction

The effect of the sulfuric acid concentration on the chalcocite dissolution in reject brine from desalination is presented in Figure 5. In general, the H₂SO₄ concentration does not have a significant effect on the Cu₂S dissolution in a chlorinated medium; this is in agreement with Cheng and Lawson [25] who determined that only a minimal amount of sulfuric acid is needed. An increase in the concentration of sulfuric acid has no significant effect on the dissolution of chalcocite in the presence of MnO₂, whatever its concentration.

The results of this study confirm the findings of Toro et al. [14], Dutrizac [34], Cheng and Lawson [25] and Senanayake [26] regarding that high concentrations of chloride favor dissolution kinetics of chalcocite, and of other copper sulfides such as chalcopyrite and covellite [27–29], other variables or conditions are not as relevant. At the same time, the results of this study suggest that the addition of MnO₂ enhances the dissolution of chalcocite regardless of the concentration of chlorides.

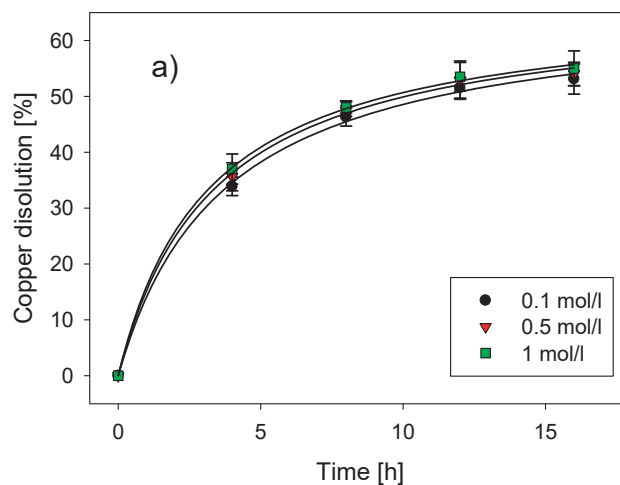


Figure 5. Cont.

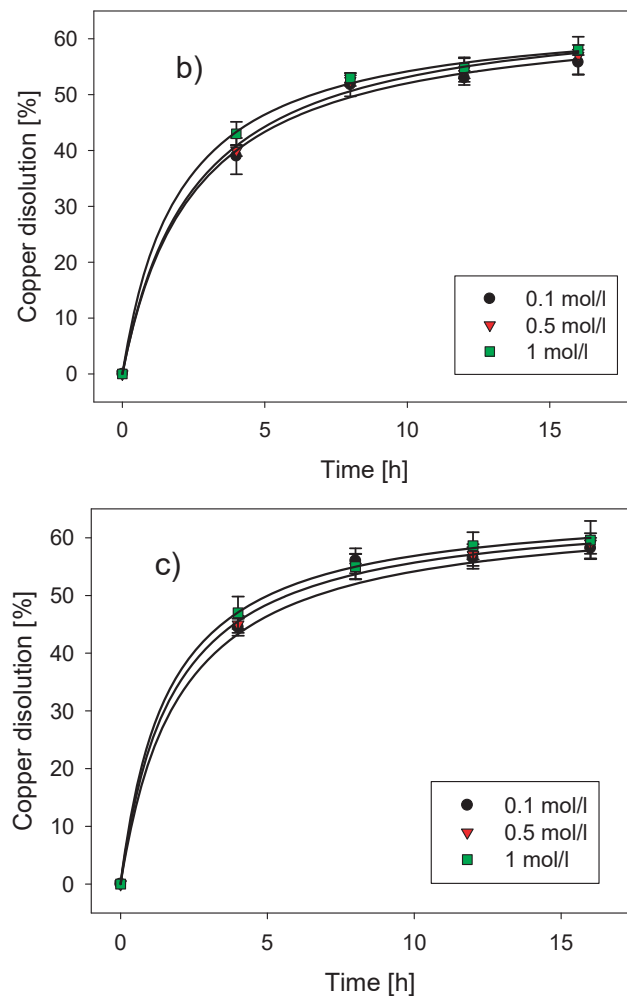


Figure 5. Effect of sulfuric acid concentration on copper extraction using reject brine, (a) without MnO_2 , (b) $\text{MnO}_2/\text{Cu}_2\text{S}$ 0.25:1 *w/w* and (c) $\text{MnO}_2/\text{Cu}_2\text{S}$ 0.5:1 *w/w*.

4. Conclusions

Reject brine from desalination plants and manganese nodules improve the dissolution kinetics of chalcocite, especially at short times. The main conclusions of this work are:

1. Reject brine shows higher Cu extracts from chalcocite compared to sea water due to its higher chloride concentrations.
2. Low concentrations of MnO_2 significantly improve the dissolution kinetics of chalcocite in a short time, which is important for continuous leaching operations.
3. High concentration of H_2SO_4 is not important when working at high concentrations of chloride and MnO_2 .
4. Best results are obtained in reject brine, with $\text{MnO}_2/\text{Cu}_2\text{S}$ 0.5:1 *w/w* and 0.5 mol/L H_2SO_4 , that is, 71% Cu extractions in 48 h.
5. Results are expected to contribute to a sustainable process of dissolution of chalcocite.

In future works, these expressions should be replicated but reusing black copper minerals, in order to reuse MnO_2 from waste, and thus justify the additional cost of adding an oxidizing agent. Finally, these new results should be compared with those presented in this study.

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9. Conclusiones. Líneas futuras

En esta Tesis se presentan los principales resultados obtenidos dentro del trabajo de investigación enfocado a conocer el comportamiento de determinados reactivos y condiciones del proceso de lixiviación para hacer viable el tratamiento de minerales no convencionales, optimizando la recuperación del cobre y otros elementos metálicos de valor asociados a este.

Se ha trabajado en la lixiviación agitada para la disolución de minerales con alto contenido de MnO₂ (nódulos de manganeso y cobres negros), y con minerales sulfurados de cobre (calcopirita y calcosina).

Los resultados de los trabajos, para cada grupo, son los siguientes:

Minerales con alto contenido de MnO₂:

Para los nódulos de manganeso, el Fe es un excelente agente reductor, siendo muy conveniente el uso de aceros al carbono FeC (Hierro de cero valencias, ZVI). Estos materiales, en contacto con la disolución, permiten la aparición de iones ferroso-férricos cuya concentración se mantiene en el proceso. Se recupera hasta el 97% de Mn en 20 min.

También en el caso de los nódulos, las altas concentraciones de agente reductor Fe²⁺ permiten emplear concentraciones de ácido bajas (0,1 mol/L). No pasa lo mismo si se emplea pirita FeS₂ requiriéndose en ese caso niveles de acidez mucho mayores (1 mol/L). Hay que mantener los rangos de potencial y pH para evitar la precipitación de las sales de hierro.

Se presentan extracciones similares de Mn tanto para nódulos de manganeso como para cobres negros bajo condiciones de temperatura ambiente (25 °C), alta razón de agente reductor (2/1 de Fe²⁺/MnO₂) y baja concentración de H₂SO₄ (0,1 mol/L). Esta similitud permite aventurar que será posible replicar procesos previos que tienen éxito para los nódulos de manganeso en el caso de óxidos negros de cobre que en ocasiones se desechan.

Para estos óxidos, se debe trabajar en medio ácido para mejorar la disolución de MnO_2 y de Cu y las elevadas concentraciones de NaCl permiten una mayor disolución de Mn pero no de Cu. En tiempos de curado prolongados (sobre 48 h), se vuelve irrelevante el trabajar a concentraciones de NaCl sobre 20 kg por tonelada de mineral, logrando incrementar de forma significativa la extracción de Cu a causa de la previa disolución de MnO_2 .

Minerales sulfurados de cobre:

El uso de salmueras y nódulos de Manganeso acelera de forma importante la disolución de la Calcosina a corto plazo, incluso con pequeñas dosis de MnO_2 . Las salmueras son mejores que el agua de mar en este proceso de recuperación de Cu.

Se alcanza un rendimiento del 71 % en 48 horas con concentraciones de MnO_2 equivalentes a la mitad de la de mineral, y acidez de 0,5 mol/L de H_2SO_4 .

Para la Calcopirita, mineral mucho más refractario, incorporando la reducción de partícula en molinos de bolas a tamaños reducidos ($-20 \mu\text{m}$) genera una activación mecano-química que incrementa en al menos un 10% la tasa de extracción. La temperatura tiene una gran importancia, debiendo recurrir a temperaturas de unos 80 °C para obtener un rendimiento adecuado.

La combinación de aditivos entre agua residual de plantas desalinizadoras y MnO_2 en el sistema, se presenta como la alternativa que más incrementa la disolución de Cu desde minerales sulfurados a temperatura ambiente en la literatura actual, esto debido a que permite trabajar a altos valores de potencial en el sistema.

Para procesos mixtos de extracción de Cu-Mn es necesario investigar alternativas de bajo costo para la recuperación final de manganeso, siendo el hierro de valencia cero una posible alternativa a evaluar en futuras investigaciones. Siendo la alta concentración de cloruro en el PLS una problemática que ya ha sido superada por la industria minera en Chile.

Líneas de investigación futuras

En futuros trabajos, es necesario incrementar la concentración de MnO_2 en el sistema, para la disolución de calcosina, con el fin de evaluar si existe un aumento significativo en la extracción de Cu, y posteriormente compararlo con el proceso diseñado previamente por [97] para calcopirita.

Se debe estudiar, también en el proceso de tratamiento de la Calcosina, la utilización de óxidos de cobre negros como fuente de MnO_2 y la recuperación de este óxido desde los residuos del proceso.

Además, se debe evaluar la utilización de los residuos de hierro de la siderurgia local de Chile, como un posible agente reductor para procesos de disolución de cobre negros, y posterior recuperación de Cu-Mn por separado.

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