

# **UNIVERSIDAD NACIONAL DE INGENIERÍA**

FACULTAD DE INGENIERÍA GEOLÓGICA MINERA Y METALÚRGICA



**REMOCIÓN DE ARSÉNICO EN CONCENTRADOS DE COBRE**

## **INFORME DE SUFICIENCIA**

**PARA OPTAR EL TÍTULO PROFESIONAL DE:**

**INGENIERO METALURGISTA**

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## **DEDICATORIA**

Este trabajo está dedicado a mi esposa, quien me acompaña de manera incondicional en cada etapa de mi vida.

## RESUMEN

En el presente informe se ha desarrollado considerando un conjunto de pruebas metalúrgicas a nivel exploratorio de lixiviación alcalina y flotación selectiva con la finalidad de remover el arsénico presente en los concentrados de cobres.

La muestra en estudio está constituida principalmente con un 78.5% de calcopirita ( $\text{CuFeS}_2$ ), y un 6 % de cobres grises (tetraedrita y tennantita), siendo la tennantita el principal portador de arsénico. Para el tratamiento de remoción de estos contaminantes se han realizado dos esquemas:

El primer esquema consiste en ejecutar pruebas de lixiviación alcalina, por lo que se ha utilizado Hidrosulfuro de Sodio ( $\text{NaSH}$ ) e hidróxido de sodio ( $\text{NaOH}$ ) en una pulpa a 30% en sólidos, manteniendo una misma temperatura de pulpa a  $90^\circ\text{C}$  para todas las pruebas. Se evaluó concentraciones de ambos reactivos y los tiempos necesarios para remover el arsénico de la muestra concentrado de cobre, logrando obtener extracciones de arsénico superiores a 95%.

El segundo esquema consiste en realizar una pre concentración mediante la flotación selectiva a la muestra en estudio, para ello se evaluó la flotación directa e inversa. Con esta flotación selectiva se logro obtener productos con concentraciones de arsénico inferiores a 0.6% (concentrado de calcopirita) y superiores a 9% (concentrado de cobres grises), este último se utilizó para realizar la lixiviación alcalina, logrando reducir el contenido de arsénico a valores inferior de 0.4%.

## ABSTRACT

In the present report has been developed considering a number of metallurgical tests on exploratory level of alkaline leaching and flotation selective with the purpose of remove the arsenic present in the concentrates of coppers

The under study sample is constituted by 78.5 % of chalcopyrite ( $\text{CuFeS}_2$ ) and 6% of gray coppers (tetrahedrite and tennantite), being the tennantite and the main carrier of arsenic. For the treatment of removal of these contaminants have been made two schemes:

The first one consist on run alkaline leaching tests, so it has been used sodium Hydrosulfide ( $\text{NaSH}$ ) and sodium hydroxide ( $\text{NaOH}$ ) in a pulp at 30% solids, at the same pulp temperature ( $90^\circ\text{C}$ ) for all test. We evaluated concentrations of both reagents and the time needed to remove arsenic from the sample of copper, obtaining extraction of arsenic above 95%.

The second one consists on made a pre concentration through the selective flotation to the sample under study, for this the direct and reverse flotation were evaluated . With this selective flotation we achieved obtain products of arsenic concentrations below 0.6% (chalcopyrite concentrate) and more than 9% (gray copper concentrate), the latter was used for alkaline leaching, thus reducing the arsenic content to values below 0.4%.

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## NOMENCLATURA

<b>UNIDAD</b>	<b>SÍMBOLO</b>
Antimonio	Sb
Arsénico	As
Bismutita	bmt
Bornita	bn
Calcopirita	cp
Carbón activado	C.A.
Cobres Grises	CGRs
Concentrado	Conc.
Covelita	cv
Esfalerita	ef
Galena	gn
Gangas	GGs
Horas	Hr
Luzonita	lz
Micrómetros	um
Millerita	mil
Minutos	min
Pirita	py
Porcentaje	%
Rutio	rt

## INTRODUCCIÓN

Algunos concentrados de cobre son afectados comercialmente por los contenidos altos de arsénico ( $> 0.5\%$ ), los cuales afectan su valor económico debido a los problemas ambientales asociados con el posterior tratamiento pirometalúrgico ya que se requieren instalaciones adicionales para extraer el arsénico. También el costo del tratamiento de tales materiales puede no ser económicamente viable, por lo que podríamos considerar como una alternativa realizar un proceso hidrometalúrgico previo al proceso pirometalúrgico para la eliminación de arsénico, el cual podría ser más rentable y de menor impacto para el medio ambiente.

Por tal propósito en el presente informe, se han ejecutado pruebas metalúrgicas exploratorias a nivel de laboratorio, para remover el arsénico mediante el proceso de lixiviación alcalina para el tratamiento de minerales de concentrados de cobre, que contienen cobres grises como portador de arsénico (tennantita), evaluando distintas concentraciones de hidrosulfuro de sodio (NaHS) como medio de lixiviación y concentración de hidróxido de sodio (NaOH) para obtener un pH alto y evitar la hidrólisis de los iones sulfuro, responsables de la sustitución de arsénico en la

tennantita. También se evaluó la alternativa de la pre-concentración de cobres grises mediante la flotación selectiva directa e inversa, obteniendo mejores resultados con una etapa de pre oxidación de los cobres grises para efectuar la flotación inversa, con el concentrado rico en cobres grises se continuó con el proceso de lixiviación de arsénico para la extracción de arsénico y antimonio con la finalidad de obtener un concentrado de cobre final bajo en estos elementos contaminantes.

**Objetivo General**

Remover el contenido de arsénico en los concentrados de cobre mediante los procesos de Lixiviación Alcalina y Flotación Selectiva – Lixiviación Alcalina, hasta obtener valores inferiores a 0.5% en arsénico.

**Justificación**

La mineralogía de las minas esta cambiado con el tiempo, obteniéndose minerales con mayor contenido de contaminantes, en este caso el arsénico. Los procesos habituales de las plantas metalúrgicas están obteniendo concentrados de cobre con un alto contenido de este contaminante, originando una reducción en el valor económico de este concentrado debido al alto costo por la penalidad de este elemento.

Se ha realizado un estudio mineralógico a la muestra, con la finalidad de visualizar las especies minerales presentes en dicho concentrado de cobre; se aprecia que la muestra (concentrado de cobre) contiene un 6% de cobres grises (tennantita y tetraedrita), siendo la tennantita el portador de arsénico.

# **CAPITULO I**

## **ASPECTOS GENERALES**

### **1.1 Fundamentos de Lixiviación de Minerales**

#### **1.1.1 Concepto**

La lixiviación es un proceso en el cual se extrae uno o varios solutos de un sólido, mediante la utilización de un disolvente líquido. Ambas fases entran en contacto íntimo y el soluto o los solutos pueden difundirse desde el sólido a la fase líquida, lo que produce una separación de los componentes originales del sólido. Tiene una gran importancia en el ámbito de la metalurgia ya que se utiliza mayormente en la extracción de algunos minerales como oro, plata, cobre y otros metales.

#### **1.1.2 Sistemas de Lixiviación**

En general, la práctica industrial de la lixiviación, presenta diferentes sistemas de operación que se seleccionan de acuerdo a factores técnicos y económicos en el análisis de un proyecto, algunos de los cuales son:

- Ley de la especie de interés a recuperar
- Reservas de mineral
- Caracterización mineralógica y geológica

- Comportamiento metalúrgico
- Capacidad de procesamiento
- Costos de operación y de capital
- Rentabilidad económica

En la Tabla 1.1 se presenta un cuadro resumen de las diferentes técnicas de lixiviación de minerales.

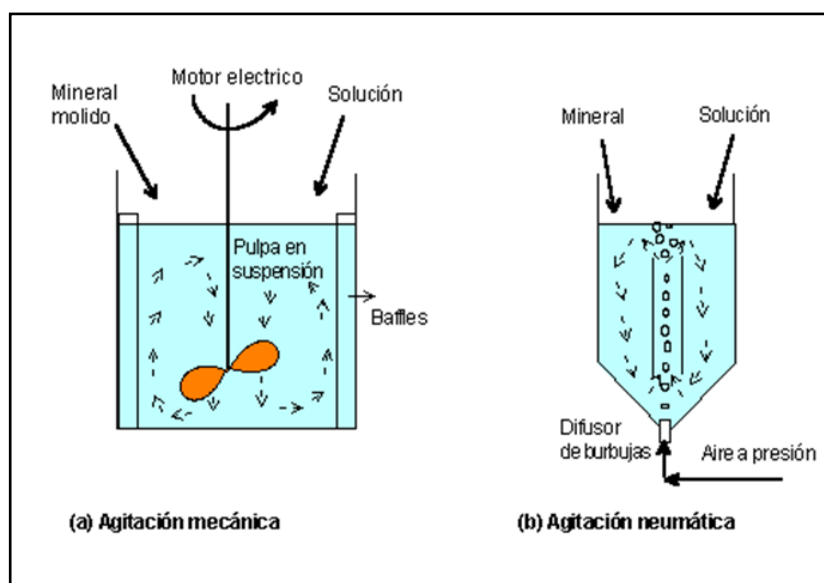
**Tabla 1.1:** Resumen de diferentes técnicas de lixiviación de minerales

Rangos de Aplicación	Métodos de Lixiviación			
	En Botaderos	En Pilas	Percolación	Agitación
Ley del mineral	Baja ley	Baja-media	Media-alta	Alta ley
Tonelaje	grande	Gran a mediano	Amplio rango	Amplio rango
Inversión	mínima	media	Media a alta	alta
Granulometría	Corrido de mina	Chancado grueso	Chancado medio	Molienda húmeda
Recuperaciones típicas	40 a 50 %	50 a 70%	70 a 80%	80 a 90 %
Tiempo de tratamiento	Varios años	Varias semanas	Varios días	horas
Calidad de soluciones	Diluidas (1-2 gpl Cu)	Diluidas (1-6 gpl Cu)	Concentradas(20-40 gpl Cu)	Medianas (5-15 gpl Cu)
Problemas principales en su aplicación	-recuperación incompleta, -reprecipitación de Fe y Cu, -canalizaciones, -evaporación - pérdidas de soluciones - soluciones muy diluidas.	-recuperación incompleta, -requiere de grandes áreas, canalizaciones, - reprecipita ciones, - evaporación.	- bloqueo por finos, - requiere de más inversión, - manejo de materiales, -necesidad de mayor control en la planta.	- molienda, - lavado en contracorriente, - tranque de relaves, - inversión muy alta, - control de la planta es más sofisticado.

### 1.1.3 Lixiviación por agitación

La lixiviación por agitación se utiliza en los minerales de leyes más altas, cuando los minerales generan un alto contenido de finos en la etapa de chancado, o cuando el mineral deseado está tan bien diseminado que es necesario molerlo para liberar sus valores y exponerlos a la solución lixivante. Es también el tipo de técnica que se emplea para lixiviar calcinas de tostación y concentrados.

Se recurre a la agitación mediante burbujeo o bien a la agitación mecánica para mantener la pulpa en suspensión hasta que se logra la disolución completa, siendo el tiempo de contacto de los sólidos con la solución del orden de horas comparado con el proceso de lixiviación en pilas que requiere meses. Los agitadores mecánicos son simplemente impulsores colocados en el interior del tanque (Figura 1.1 - a), mientras que los tanques agitados con aire son a menudo tanques de tipo "Pachuca" (Figura 1.1 - b).



**Figura 1.1:** Tipos de Agitadores mecánicos



Sus ventajas comparativas con otros métodos de lixiviación son:

- Alta extracción del elemento a recuperar
- Tiempos cortos de procesamiento (horas)
- Proceso continuo que permite una gran automatización
- Facilidad para tratar menas alteradas o generadoras de finos

Sus desventajas son:

- Un mayor costo de inversión y operación
- Necesita una etapa de molienda y una etapa de separación sólido-líquido (espesamiento y filtración)

## **1.2 Fundamentos de Flotación de Minerales**

### **1.2.1 Flotación de Sulfuros**

La importancia que ha adquirido el proceso de flotación se debe a que por medio de este método, pueden enriquecerse partículas cuyas dimensiones oscilan entre 0 y 0.5 mm. La constitución mineralógica de la mayoría de las menas requiere, generalmente una molienda precisamente en ese tamaño para permitir la liberación de las especies útiles.

Para muchas menas la flotación es el principal método de enriquecimiento universal empleado (por Ej. las menas de cobre, zinc, plomo y muchas otras).

### 1.2.2 Teorías de Flotación

Una teoría de flotación debe explicar el mecanismo mediante el cual actúan los colectores y modificadores, las condiciones para que un compuesto químico sea colector de un determinado mineral, y debe establecer las condiciones físico-químicas que producirán un mejor rendimiento del proceso.

El desarrollo de la teoría de la flotación de minerales sulfurados con xantatos ha estado sujeto a constante controversia. Especialmente interesante es la polémica que se planteó a partir de 1930 entre la escuela americana de A.F. TAGGART y la escuela australiana de I. W. WARK.

TAGGART postulaba la llamada Teoría Química, indicando que el colector reaccionaba químicamente y en forma estequiométrica con el mineral. Un reactivo heteropolar funcionaría como colector de un cierto mineral, siempre que el compuesto químico formado como producto de la reacción tuviera una solubilidad menor que la de la especie mineralógica del mineral. El desarrollo posterior de técnicas precisas para determinar los productos de solubilidad de los xantatos de metales pesados puso de manifiesto la concepción errónea de este postulado.

Por su parte WARK y SUTHERLAND desarrollan en la misma época su Teoría de Adsorción que supone que los aniones xantatos ocupan el lugar de iones sulfurosos sobre las caras libres de la red cristalina de la galena, puesto que el xantato en el sistema no puede eliminarse mediante lavado con agua, pero sí desplazarse con sulfuros solubles.

Por primera vez se aplica el método científico a la investigación en flotación y se desarrolla una técnica depurada para medir ángulos de contacto, se demuestra que el ángulo de contacto máximo depende solo del largo y configuración de la cadena hidrocarbonada y no de la naturaleza del sulfuro mineral.

Esta importante conclusión originó la idea, actualmente aceptada, que los iones de colector están anclados por medio de sus grupos polares a un catión metálico de la superficie del mineral.

Fue solo en el año 1957 cuando I.N. PLAKSIN y colaboradores dan a conocer sus trabajos en que empleando el método radiométrico con xantato marcado con un isotopo radioactivo muestra los cambios en la flotación de la calcopirita y la adsorción de xantato en relación a la concentración inicial de oxígeno en el agua.

Al mismo tiempo el avance de la ciencia y consecuentemente la aplicación a este campo de nuevas técnicas de Investigación Científica, tales como las técnicas electroquímicas de potenciometria y voltametria cíclica. etc., permitieron un mejor conocimiento de la superficie mineral en medio acuoso y de la naturaleza química de los productos superficiales.

## **CAPITULO II**

### **CARACTERIZACIÓN DE LA MUESTRA**

#### **2.1 Preparación de la Muestra (concentrado de cobre)**

Para el estudio de la remoción de arsénico en concentrados de cobre, se utilizó una muestra de 50 kg, proveniente de una planta concentradora (muestra representativa muestreada en una semana de operación).

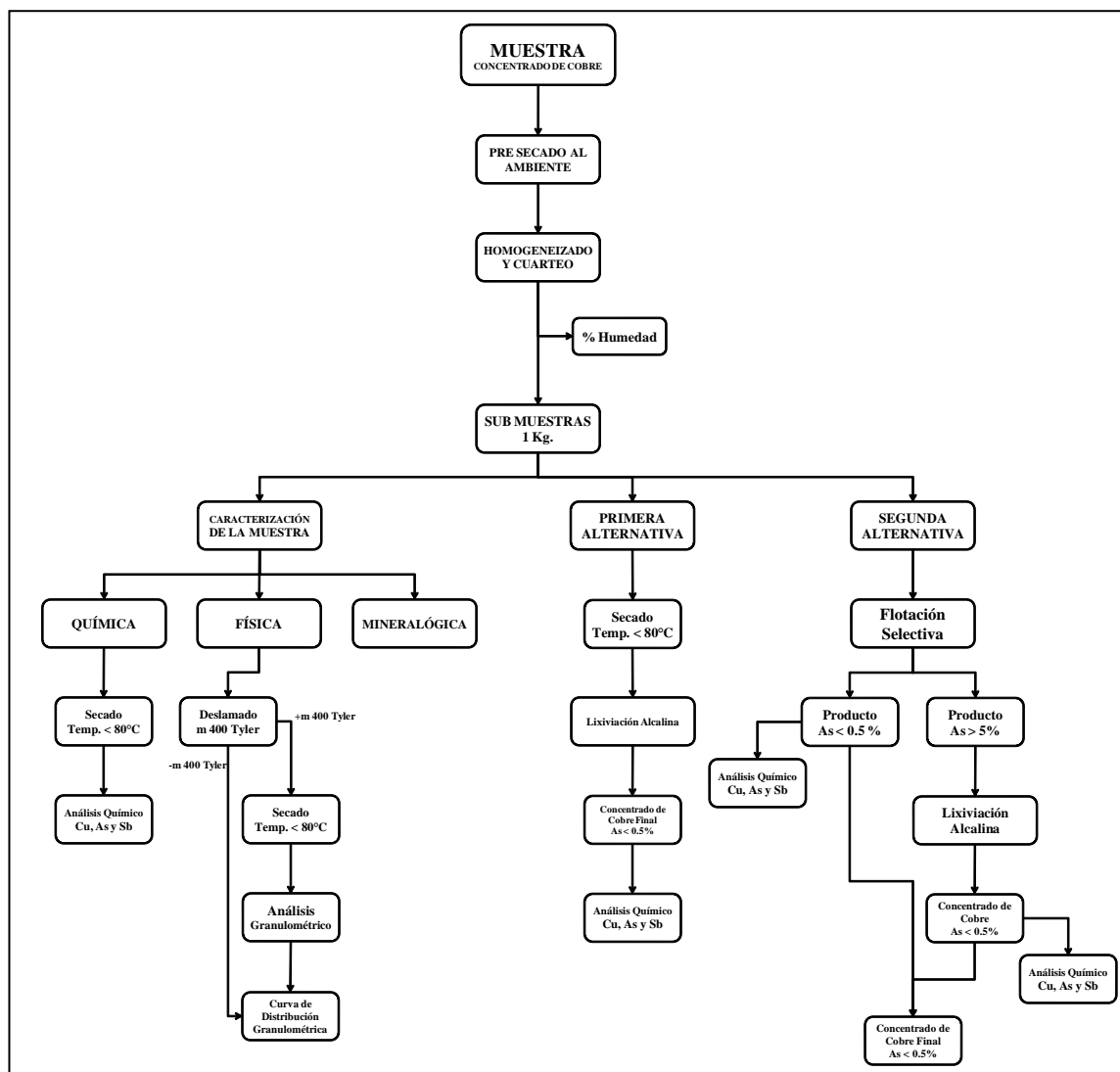
Para la eliminación del exceso de humedad de la muestra, se secó parcialmente al ambiente por dos días, para ello se utilizó una manta para evitar la contaminación y se dejó en un ambiente libre de polvos. Se cuarteó la muestra en fracciones repetitivas para las diversas pruebas metalúrgicas (Ver Esquema General en la Figura 2.1), sellando las muestras para que mantenga su humedad.

La humedad fue determinada tomando 3 muestras aleatoriamente para asegurar la representatividad del muestreo. Los resultados de la humedad se presentan en la Tabla 2.1.

**Tabla 2.1:** Humedad de la muestra

MUESTRA	PESO HUMEDO (g)	PESO SECO (g)	% HUMEDAD
Muestra 1	1134.2	1046.3	7.75
Muestra 2	1201.1	1109.3	7.64
Muestra 3	1101.0	1016.3	7.69
<b>PROMEDIO</b>			<b>7.70</b>

Luego de procedió a aforar cada bolsa a 1083.4 gramos (Peso seco 1000 gramos) para las diversas pruebas metalúrgicas.

**Figura 2.1:** Esquema General

## 2.2 Caracterización Química

A la muestra en estudio (concentrado de cobre) se le realizó el análisis químico por Cu, As y Sb, las leyes obtenidas se presenta en la Tabla 2.2.

**Tabla 2.2:** Leyes de muestra de cabeza (concentrado de cobre)

Muestra	Leyes (%)		
	As	Cu	Sb
Concentrado de cobre (Cabeza)	3.103	29.83	0.782
Concentrado de cobre (Cabeza) DUP	3.092	29.9	0.782
<b>Promedio</b>	<b>3.098</b>	<b>29.87</b>	<b>0.782</b>
<b>% RSD</b>	<b>0.25</b>	<b>0.17</b>	<b>0.00</b>

El análisis de la muestra fue realizado a dos muestras representativas tomadas aleatoriamente para verificar la representatividad de las muestras cuarteadas; el %RSD (desviación estándar relativa) indica que la variación entre las leyes son bajas por lo que se concluye que las leyes analizadas son representativas.

## 2.3 Caracterización Física

Se realiza el análisis granulométrico de la muestra inicial, determinando su distribución granulométrica y su  $d_{80}$ .

**Tabla 2.3:** Análisis Granulométrico de la muestra

ANÁLISIS GRANULOMÉTRICO					
Malla		% Peso			d <sub>80</sub>
Tyler	Abertura (µm)	Ret.	Ac. (+)	Ac. (-)	
65	212	0.11	0.11	99.89	
100	150	0.93	1.04	98.96	
150	106	4.14	5.18	94.82	
200	75	12.42	17.60	82.40	71
270	53	14.09	31.69	68.31	
325	44	7.09	38.78	61.22	
400	38	6.01	44.79	55.21	
-400		55.21	100.00	0.00	
TOTAL		100.00		D80	71 µm

El porcentaje de la malla -200 Ty se encuentra en 82.40 %, mientras el porcentaje bajo la malla 400 se encuentra a 55.21 %, su gráfico de distribución se presenta en la Figura 2.2.

**Figura 2.2:** Distribución Granulométrica de la muestra

## 2.4 Caracterización Mineralógica

Se realizó el Estudio por Microscopia Óptica y Fotomicrografías. En las siguientes tablas se presentan los minerales metálicos y no metálicos, tanto libres como asociados (o mixtos).

**Tabla 2.4:** Estudio por Microscopia Óptica – Minerales Libres

Minerales Libres	Porcentajes (%)
Calcopirita I	78.5
Cobres Grises	6
Gangas	<2
Pirita	<2
Esfalerita II	<2
Calcopirita II	<1
Esfalerita I	Trazas
Galena	Trazas
Enargita	Trazas

**Tabla 2.5:** Estudio por Microscopia Óptica – Minerales Mixtos (1)

Minerales Mixtos	Porcentajes (%)	Intercrecimientos
ef I - cp I	1.5	1b(IV)
gn - CGRs	<1.5	1b(IV)
GGs - cp I	<1	1b(II)
ef I - gn	<1	1b(IV)
py - CGRs	Trazas	1a(I)
py - mc - cp I - bn	Trazas	3d(I)
cp I - gn	Trazas	1b(II)
CGRs - cp I	Trazas	1e(III)
ef I - CGRs cp	Trazas	1a(I)



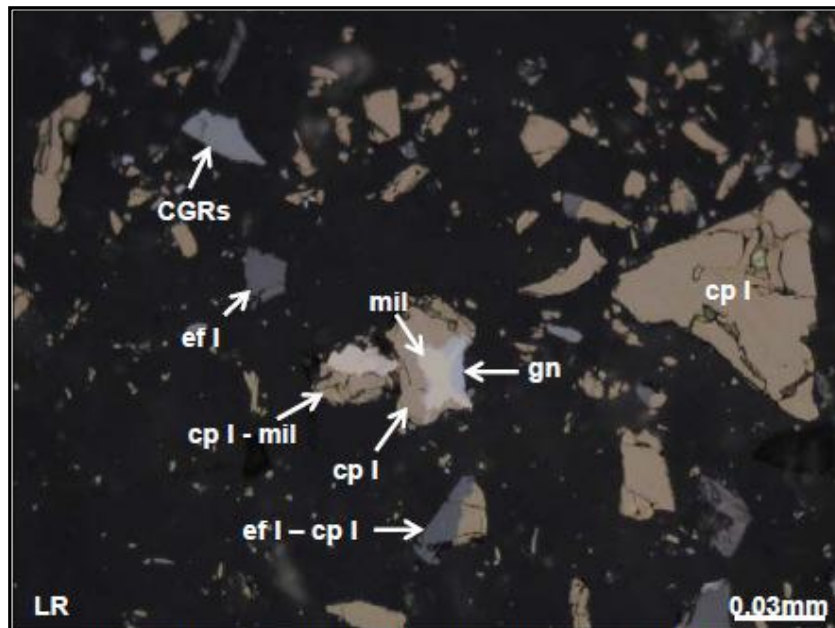
**Tabla 2.6:** Estudio por Microscopía Óptica – Minerales Mixtos (2)

Minerales Mixtos	Porcentajes (%)	Intercrecimientos
I - mil - gn py	Trazas	2b(IV); 1b(II)
ef I - cp I	Trazas	1b(IV)
py - cp I - gn - SFSs_Pb	Trazas	1b(IV); 1e(I)
py - gn	Trazas	1b(II)
cp I - CGRs - cv	Trazas	2b(III)
CGRs - ef I - gn	Trazas	1b(IV); 1e(IV)
GGs - py - CGRs	Trazas	1b(IV)
ef I - gn - CGRs	Trazas	1b(IV); 1e(IV)
ef II - cp I	Trazas	1a(II)
cp I - mil	Trazas	1b(II)

De los minerales libres, el más abundante corresponde a la calcopirita I con un porcentaje del 78.5 %, seguida de los cobres grises (6 %), gangas (<2%), pirita (<2%), esfalerita II (<2%), calcopirita I (<1%); la esfalerita I, galena, y enargita se encuentran a nivel de trazas.

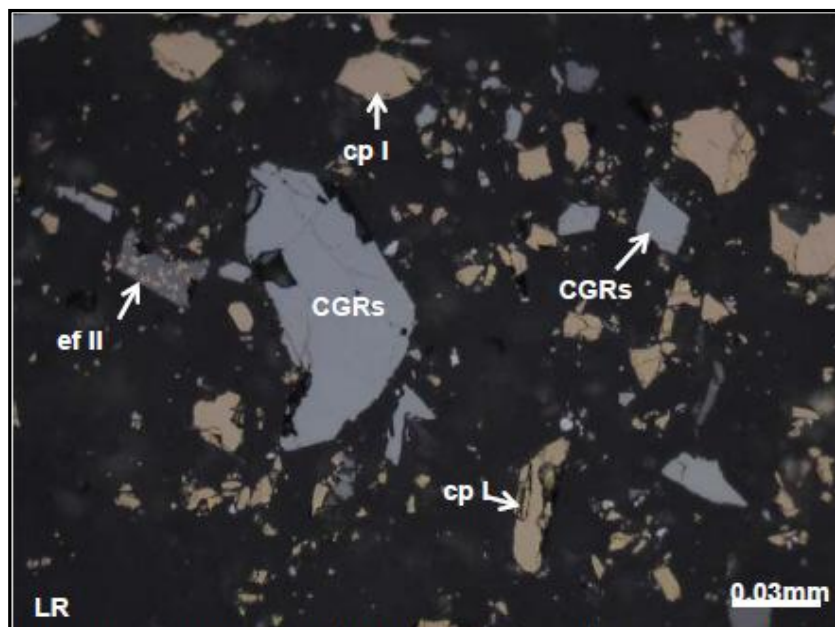
Entre los minerales asociados, se tiene ef I – cp I (1.5%), gn – CGRs (<1.5%), GGs – cp I (<1%); ef I – gn (<1%).

Las siguientes asociaciones se encuentran a manera de trazas: py – CGRs, py – mc – cp I – bn, cp I – gn, CGRs – cp I, ef I – CGRs, cp I – mil – gn, py – ef I – cp I, py – cp I – gn – SFSs\_Pb, py – gn, cp I – CGRs – cv, CGRs – ef I – gn, GGs – py – CGRs, ef I – gn – CGRs, ef II – cp I y cp – mil.



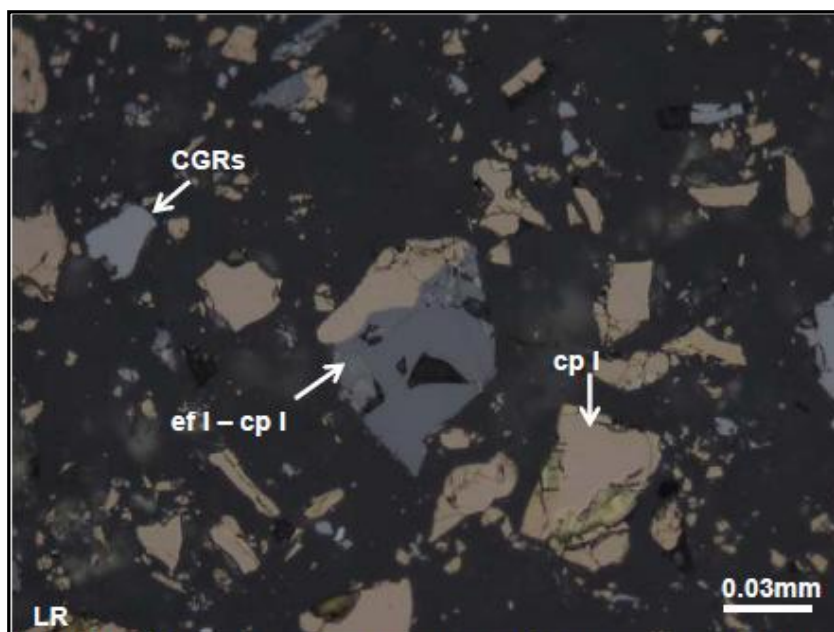
**Figura 2.3:** Fotomicrografía N° 01

Partículas libres de cobres grises (CGRs), calcopirita I (cp I) y esfalerita I (ef I). Granos mixtos conformados por calcopirita I – millerita (cpI . mil), calcopirita I (cp), galena (gn) y millerita (mil), y esfalerita I – calcopirita I (ef I – cp I). (LR; Obj. 50X).



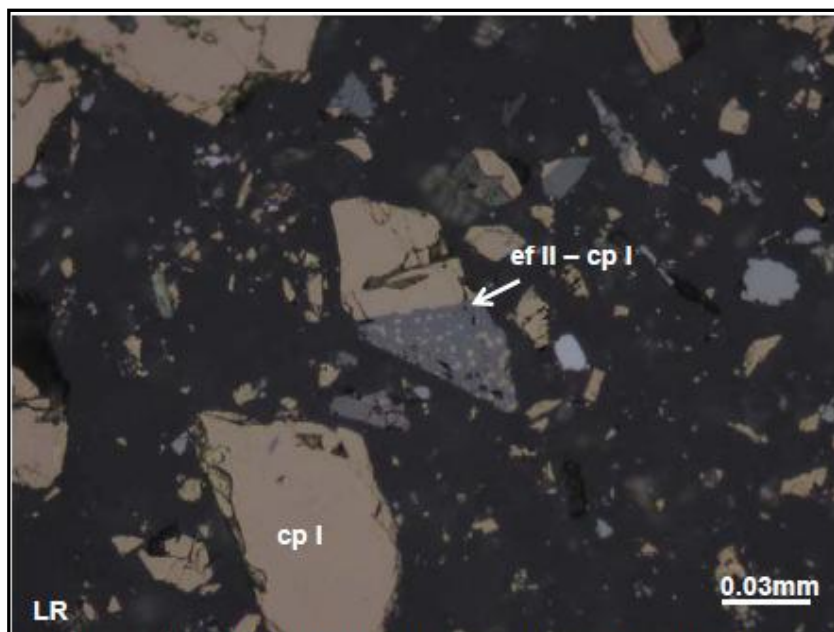
**Figura 2.4:** Fotomicrografía N° 02

Partículas libres de cobres grises (CGRs), calcopirita I (cp I) y esfalerita II (ef II). (LR; Obj. 50X).



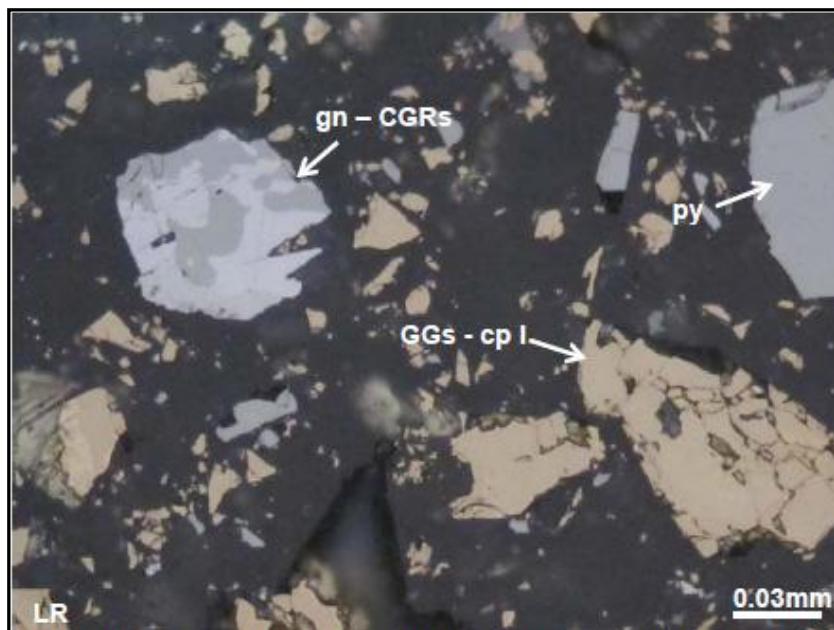
**Figura 2.5:** Fotomicrografía N°03

Partículas libres de cobres grises (CGRs) y calcopirita I (cp I). Grano mixto conformados por esfalerita I – calcopirita I (ef I – cp I). (LR; Obj. 50X).



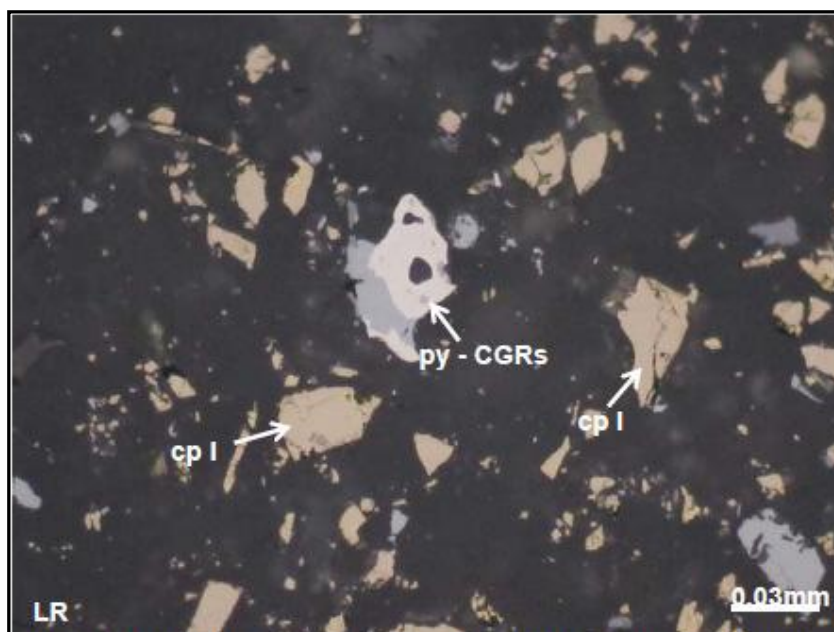
**Figura 2.6:** Fotomicrografía N° 04

Partículas libres de calcopirita I (cp I). Grano mixto conformados por esfalerita II – calcopirita I (ef II – cp I). (LR; Obj. 50X).



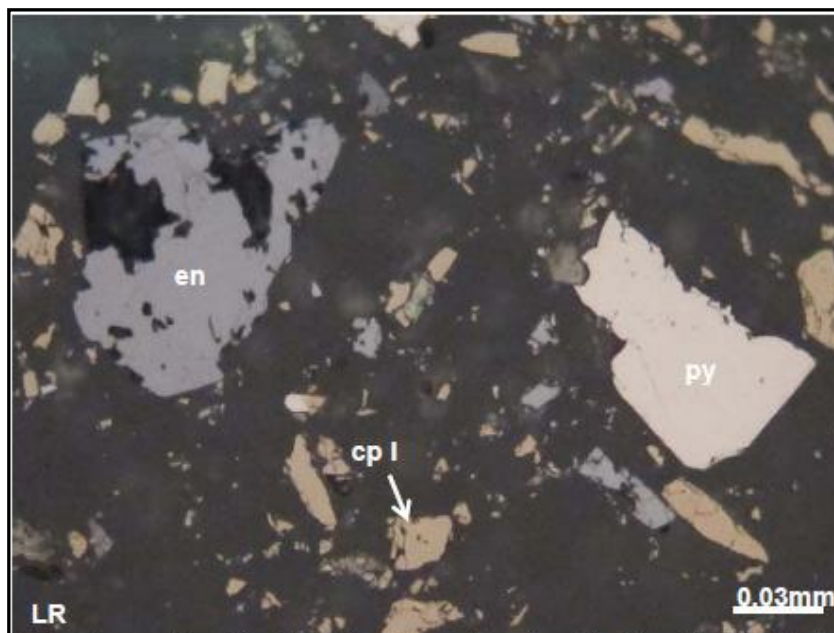
**Figura 2.7:** Fotomicrografía N° 05

Partículas libres de pirita (py). Grano mixto conformados por gangas – calcopirita I (GGs – cp I) y galena – cobres grises. (LR; Obj. 50X).



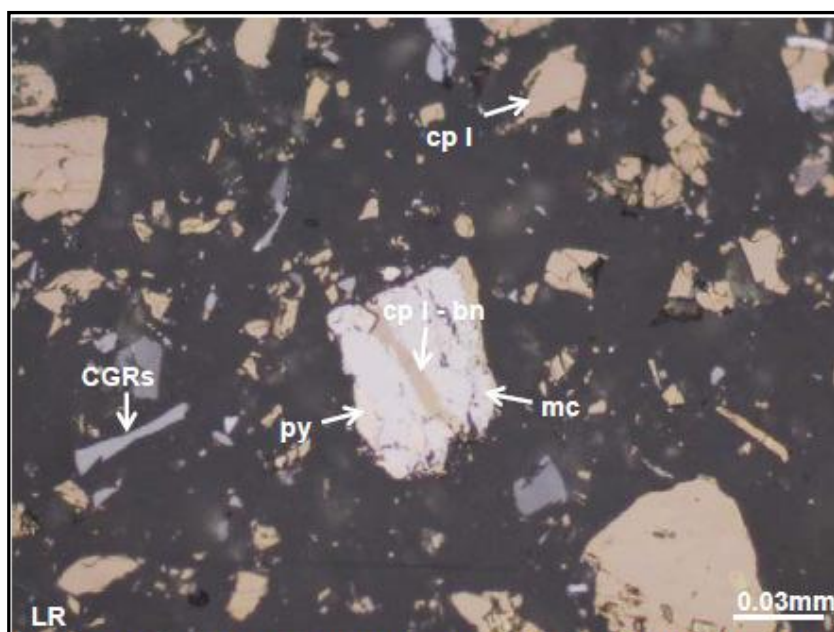
**Figura 2.8:** Fotomicrografía N° 06

Partículas libres de calcopirita I (cp I). Grano mixto conformados por pirita – cobres grises (py - CGs). (LR; Obj. 50X).



**Figura 2.9:** Fotomicrografía N° 07

Partículas libres de calcopirita I (cp I), pirita (py) y enargita (en). (LR; Obj. 50X).



**Figura 2.10:** Fotomicrografía N° 08

Partículas libres de calcopirita I (cp I) y cobres grises (CGRs). Grano mixto compuesto por pirita (py), marcasita (mc) y calcopirita I – bornita (cp I – bn). (LR; Obj. 50X).

## **CAPITULO III**

### **PRIMER ESQUEMA – LIXIVIACIÓN ALCALINA**

#### **3.1 Equipos y Materiales**

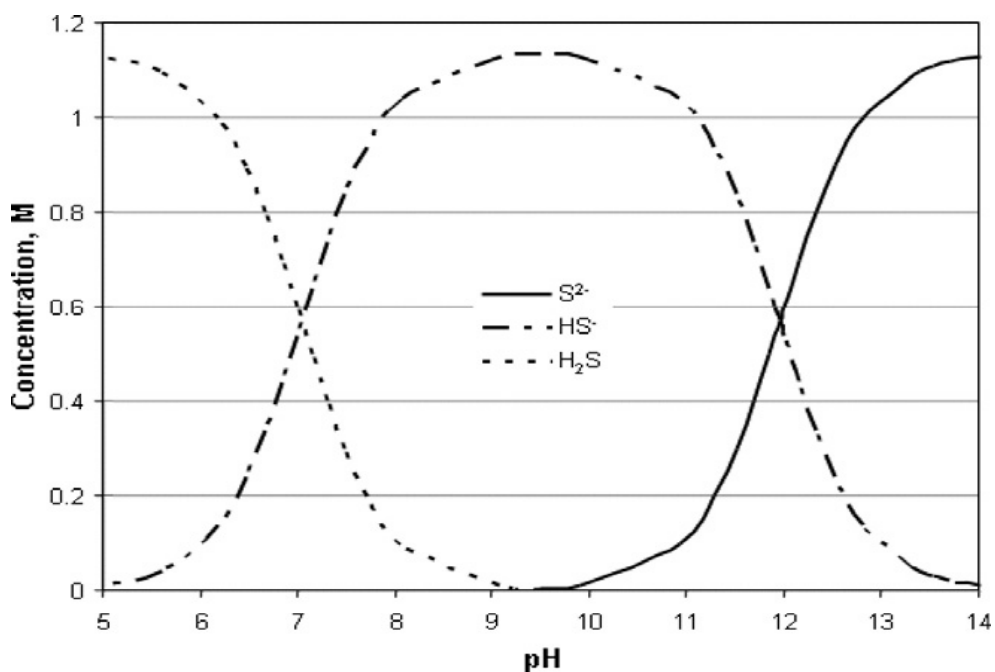
Para el estudio a nivel exploratorio se llevaron a cabo en instalaciones equipadas con campanas extractoras de gases, utilizando los siguientes equipos y materiales:

- Agitadores magnéticos
- Vasos de precipitado de 500 ml
- Kitasatos de 500 ml
- Termómetro digital
- Bombas peristálticas
- Baqueta de vidrio
- Papel de filtro
- Bomba de vacío
- Bandejas de acero inoxidable
- Estufa de secado
- Mini cuarteador Jones
- Molino de Bolas con capacidad de 1 Kg de muestra seca

### 3.2 Evaluación Previa del Primer Esquema

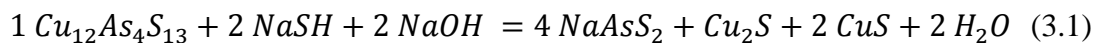
La muestra de concentrado en estudio contiene un 6% de cobres grises (principal portador de arsénico y antimonio) según la caracterización mineralógica. En el análisis químico nos indica que la muestra presenta 3.098 % de arsénico total y 0.782 % de antimonio total.

Para la lixiviación de estos contaminantes se utilizó hidrosulfuro de sodio (NaSH) como medio lixivante, el cual presentaba una pureza del 70%. También se utilizó el hidróxido de sodio (NaOH) con una pureza del 99%, el cual se utilizó para mantener un pH altamente alcalino ( $> 12.5$ ) y evitar la hidrólisis del azufre ( $\text{HS}^-$ ). En la Figura 3.1 se muestra el diagrama de equilibrio de las especies de sulfuro, donde podemos ver que a un pH altamente alcalino se evita la hidrólisis del sulfuro.



**Figura 3.1:** Diagrama de equilibrio de las especies de sulfuro

En la ecuación (3.1) se expresa de manera ideal la lixiviación del arsénico, donde tenemos que 4 moléculas de arsénico reaccionan con 2 moléculas de azufre:



Las pruebas ejecutadas han sido desarrolladas considerando un exceso de NaSH, debido a que este también logra lixiviar al antimonio y a otras especies de arsénico como enargita.

### 3.3 Pruebas de Lixiviación Alcalina – Recipiente Abierto

Inicialmente las pruebas de lixiviación alcalina se realizaron con 150 gramos de muestra, en recipientes de vidrio abiertos (vaso de precipitado 500ml), a una temperatura de pulpa constante de 90 °C. Para contrarrestar la evaporación de las soluciones y mantener el % sólidos se diseñó un sistema de reposición de solución mediante bombas dosificadoras.



**Figura 3.2:** Fotografía del Sistema de Lixiviación Alcalina





**Figura 3.3:** Control de Temperatura de Pulpa

### 3.3.1 Cinética Exploratoria N° I-01

Para esta prueba se tomaron 3 muestras las cuales fueron remolidas hasta 100% -m 200 Tyler, para posteriormente lixiviarlas en tres tiempos (2, 4 y 6 horas), considerando los parámetros de la Tabla 3.1. El propósito de esta prueba era de explorar si la viabilidad de lixiviar el arsénico de la muestra.

**Tabla 3.1:** Parámetros de Exploratoria N° I-01

Tipo de Muestra	: Cabeza (Concentrado de Cobre)
Granulometría	: 100% -m 200 Tyler
Peso de Muestra	: 150 g.
% Sólidos	: 30
Tiempo Lixiviación	: 2, 4 y 6 horas
Temperatura de Pulpa	: 90 °C
Agitación de Pulpa	: 300 rpm

Las adiciones de reactivos se presentan en la Tabla 3.2

**Tabla 3.2:** Adición de reactivos – Exploratoria N° I-01

Tiempo (horas)	Adición de NaOH (99%) g.			Adición de NaSH (70%) g.		
	Inicio	Reposición	Total (g)	Inicio	Reposición	Total (g)
2	8.6	7.4	<b>16.1</b>	20.2	17.3	<b>37.5</b>
4	8.6	14.8	<b>23.5</b>	20.2	34.6	<b>54.8</b>
6	8.6	19.8	<b>28.4</b>	20.2	46.2	<b>66.4</b>

Debido a la temperatura de 90°C, la solución se evaporaba, por lo que se reponía solución lixivante a las condiciones iniciales cada 10 minutos, obteniendo una adición total de NaOH y NaSH tal como se muestra en la Tabla 3.2.

Los ripios obtenidos de cada prueba fueron filtrados, lavados y secados a temperatura controlada de 100 °C, para su posterior análisis químico por As, Sb y Cu. Con estos resultados se realizó un balance metalúrgico, el cual se presenta en la Tabla 3.3.

**Figura 3.4:** Fotografía – Etapa de filtrado de ripios

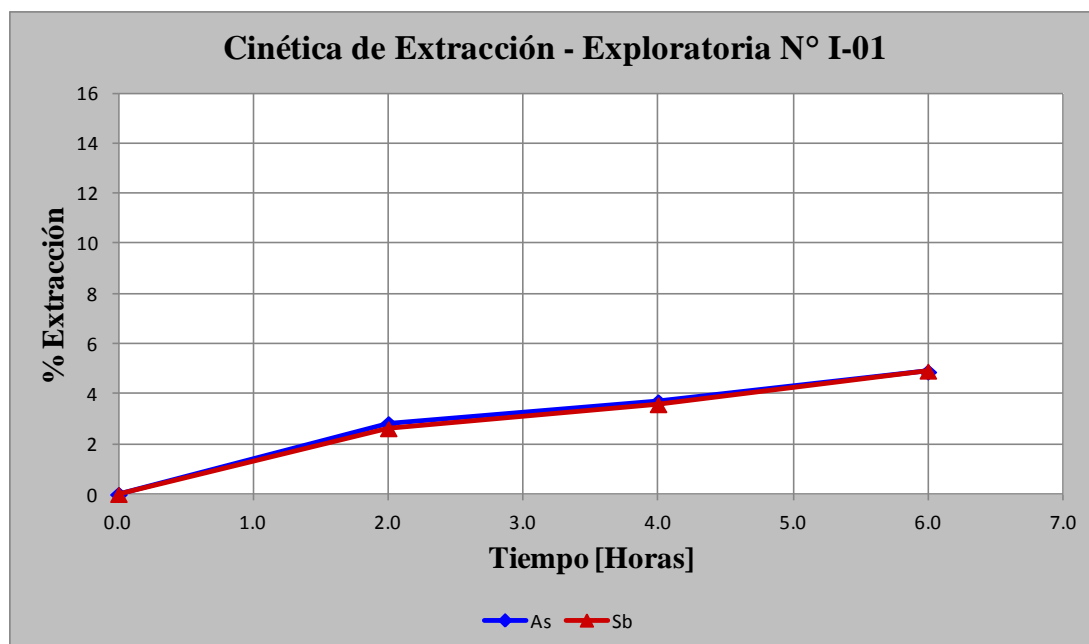


**Figura 3.5:** Fotografía de muestras filtradas

**Tabla 3.3:** Balance Metalúrgico – Exploratoria N° I-01

MUESTRA	Relación Mol.S/As	Tiempo (horas)	LEYES [%]						% EXTRACCIÓN	
			CABEZA			RIPIO			As	Sb
			As	Cu	Sb	As	Cu	Sb		
Muestra 1 - 2H	15	2.0	3.098	29.87	0.782	3.012	29.86	0.762	2.82	2.62
Muestra 2 - 4H	22	4.0	3.098	29.87	0.782	2.987	29.89	0.755	3.70	3.58
Muestra 3 - 6H	27	6.0	3.098	29.87	0.782	2.952	29.82	0.745	4.89	4.92

En estas primeras 3 pruebas denominadas Exploratoria N° I-01, no se obtuvieron resultados positivos, las extracciones de As y Sb están por debajo de 5%. En la Figura 3.6 se muestra la Curva de Cinética de Extracción, donde se aprecia las bajas extracciones obtenidas en esta primera etapa.



**Figura 3.6:** Curva de Cinética de Extracción – Exploratoria N° I-01

### 3.3.2 Lixiviación Alcalina - Exploratoria N° I-02

Para esta prueba se tomaron 3 muestras las cuales fueron remolidas hasta 100% -m 400 Tyler, para posteriormente lixiviarlas considerando los parámetros de la Tabla 3.4. El propósito de esta prueba era de continuar explorando por lo que se optó por aumentar las concentraciones, el grado de molienda y mantener un tiempo de lixiviación constante de 6 horas y el hidróxido de sodio como factor variable.

**Tabla 3.4:** Parámetros de Exploratoria N° I-02

Tipo de Muestra	: Cabeza (Concentrado de Cobre)
Granulometría	: 100% -m 400 Tyler
Peso de Muestra	: 150 g.
% Sólidos	: 30
Tiempo Lixiviación	: 6 horas
Temperatura de Pulpa	: 90 °C
Agitación de Pulpa	: 300 rpm

Las adiciones de reactivos se presentan en la Tabla 3.5

**Tabla 3.5:** Adición de reactivos – Exploratoria N° I-02

Muestra	Adición de NaOH (99%) g.			Adición de NaSH (70%) g.		
	Inicio	Reposición	Total (g)	Inicio	Reposición	Total (g)
1	10.0	24.2	<b>34.2</b>	40.0	96.6	<b>136.6</b>
2	25.0	60.2	<b>85.2</b>	40.0	96.3	<b>136.3</b>
3	40.0	95.9	<b>135.9</b>	40.0	95.9	<b>135.9</b>

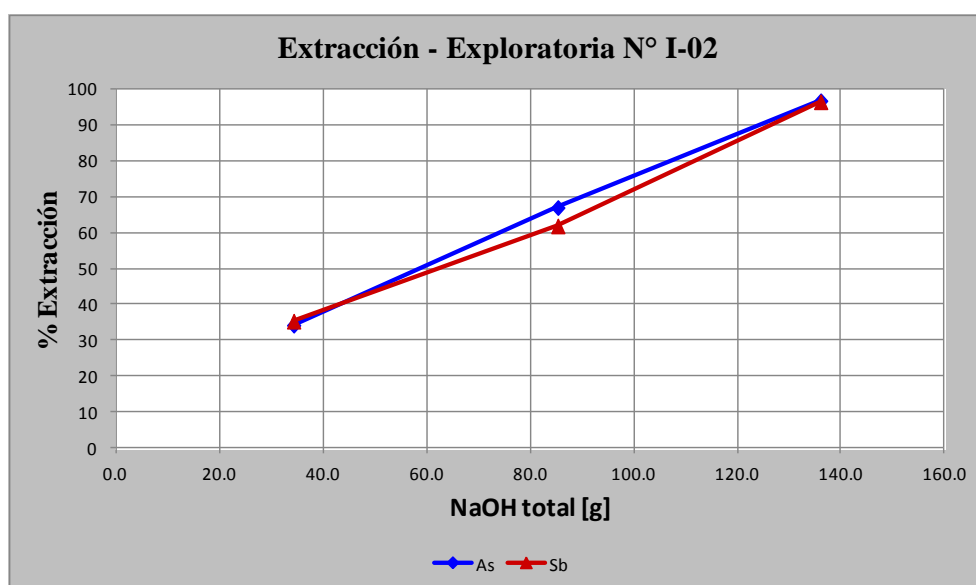
En esta Exploratoria N° 02 aún se continuó con el sistema de reposición debido a las evaporaciones de las soluciones; las adiciones totales son las mostradas en la Tabla 3.5.

Los rípios obtenidos de cada prueba fueron filtrados, lavados y secados a temperatura controlada de 100 °C, para su posterior análisis químico por As, Sb y Cu. Con estos resultados se realizó un balance metalúrgico, el cual se presenta en la Tabla 3.6.

**Tabla 3.6:** Balance Metalúrgico – Exploratoria N° I-02

MUESTRA	Relación Mol.S/As	LEYES [%]						% EXTRACCIÓN	
		CABEZA			RIPIO			As	Sb
		As	Cu	Sb	As	Cu	Sb		
Muestra 1 (10 NaOH)	55	3.098	29.87	0.782	2.063	29.92	0.512	34.11	35.23
Muestra 2 (25 NaOH)	55	3.098	29.87	0.782	1.046	29.91	0.305	66.91	61.78
Muestra 3 (40 NaOH)	55	3.098	29.87	0.782	0.106	30.08	0.029	96.68	96.40

Con este grupo de pruebas denominadas Exploratoria N° I-02, se han obtenido resultados positivos. En la Figura 3.7 se muestra gráficamente las extracciones obtenidas, apreciando claramente la significancia de mantener un pH altamente alcalino, donde a mayor adición de hidróxido de sodio existe una mejor extracción de arsénico y antimonio.



**Figura 3.7:** Gráfica de Extracción – Exploratoria N° I-02

### 3.3.3 Lixiviación Alcalina - Exploratoria N° I-03

Para esta prueba se tomaron 4 muestras las cuales fueron remolidas a diferentes granulometrías, para posteriormente lixiviarlas con los mejores parámetros obtenidos en la Exploratoria N° I-02 de la muestra 3. El propósito de esta prueba era de continuar explorando por lo que se optó analizar las extracciones de arsénico y antimonio a diferentes granulometrías, manteniendo las adiciones de reactivos, tiempo de lixiviación y otros parámetros constantes.

**Tabla 3.7:** Parámetros de Exploratoria N° I-03

Tipo de Muestra	: Cabeza (Concentrado de Cobre)
Granulometría	: Natural, 100% -m 200, 270 y 400 Tyler
Peso de Muestra	: 150 g.
% Sólidos	: 30
Tiempo Lixiviación	: 6 horas
Temperatura	: 90 °C
Agitación	: 300 rpm

Las adiciones de reactivos se presentan en la Tabla 3.8

**Tabla 3.8:** Adición de reactivos – Exploratoria N° I-03

Muestra	Adición de NaOH (99%) g.			Adición de NaSH (70%) g.		
	Inicio	Reposición	Total (g)	Inicio	Reposición	Total (g)
1	40.0	83.4	<b>123.4</b>	40.0	83.4	<b>123.4</b>
2	40.0	82.5	<b>122.5</b>	40.0	82.5	<b>122.5</b>
3	40.0	82.6	<b>122.6</b>	40.0	82.6	<b>122.6</b>
4	40.0	82.8	<b>122.8</b>	40.0	82.8	<b>122.8</b>

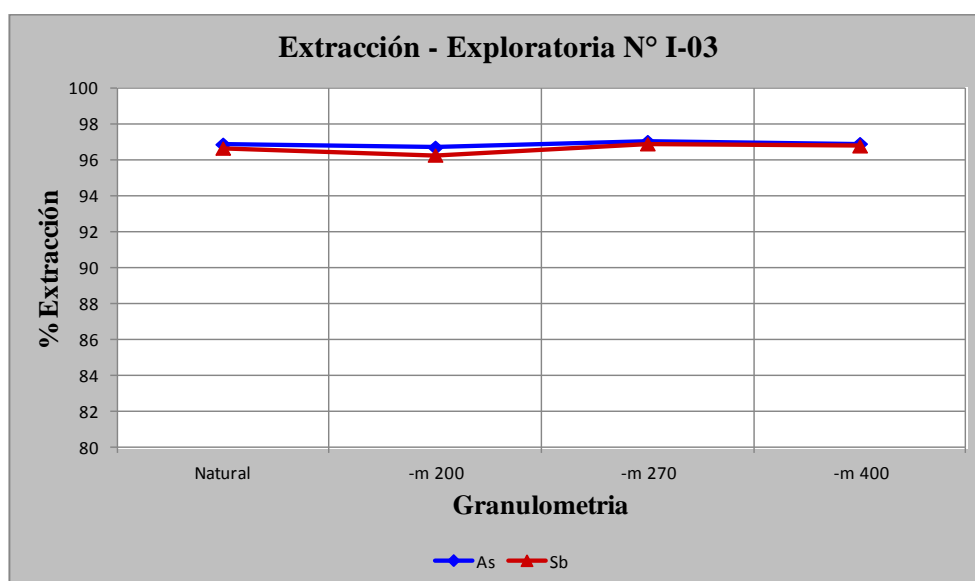
En esta Exploratoria N° I-03 aún se continuó con el sistema de reposición debido a las evaporaciones de las soluciones; las adiciones totales son las mostradas en la Tabla 3.8.

Los ripsos obtenidos de cada prueba fueron filtrados, lavados y secados a temperatura controlada de 100 °C, para su posterior análisis químico por As, Sb y Cu. Con estos resultados se realizó un balance metalúrgico, el cual se presenta en la Tabla 3.9.

**Tabla 3.9:** Balance Metalúrgico – Exploratoria N° I-03

MUESTRA	Relación Mol.S/As	LEYES [%]						% EXTRACCIÓN	
		CABEZA			RIPIO			As	Sb
		As	Cu	Sb	As	Cu	Sb		
Muestra 1	49	3.098	29.87	0.782	0.100	30.02	0.027	96.87	96.66
Muestra 2	49	3.098	29.87	0.782	0.105	29.96	0.030	96.71	96.27
Muestra 3	49	3.098	29.87	0.782	0.095	29.98	0.025	97.03	96.90
Muestra 4	49	3.098	29.87	0.782	0.099	30.09	0.026	96.91	96.78

Con este grupo de pruebas denominadas Exploratoria N° I-03, se han obtenido resultados positivos con extracciones de As y Sb mayores a 96% para todas las granulometrías, por lo que estaríamos demostrando que para el comportamiento de la extracción para una granulometría menor a la que presenta la muestra (natural = 82.40 % –m200 Tyler) no influye significativamente, obteniendo extracciones muy similares en estas 4 pruebas pertenecientes a la Exploratoria N° I-3. En la Figura 3.8 se muestra gráficamente las extracciones obtenidas.

**Figura 3.8:** Gráfica de Extracción – Exploratoria N° I-03



### **3.4 Pruebas de Lixiviación Alcalina – Recipiente Cerrado**

Luego de realizar tres etapas de pruebas con el recipiente abierto, se han notado muchas deficiencias para cuantificar la cantidad de reactivos adicionados, ya que al no controlar la evaporación la adición constante de reactivos podría estar siendo acumulativa. A partir de ahora, las siguientes pruebas de Lixiviación Alcalina han sido ejecutadas con 100 gramos de muestra, en recipientes de vidrio cerrados (kitasato de 500ml con tapón y una manguera tipo chimenea para condensar los vapores), a una temperatura constante de pulpa de 90 °C, y con una sola adición de reactivos al inicio de cada prueba. En las pruebas denominadas Exploratoria N° I-03, se ha comprobado que la granulometría no está influyendo a este tipo de muestra, por lo que en adelante las siguientes pruebas se realizaron a su granulometría natural (82.40 % -m 200 Tyler).

#### **3.4.1 Cinética Exploratoria N° I-04**

Para este grupo de pruebas se consideró realizarlas con adición constante de NaOH de 50 gramos, y adiciones de NaSH variables de 50, 35 y 20 gramos. Los parámetros de trabajo de temperatura de pulpa, velocidad de agitación, granulometría de muestra y el tiempo se mantuvieron constantes, tal como se indican en la Tabla 3.10.

**Tabla 3.10:** Parámetros de Exploratoria N° I-04

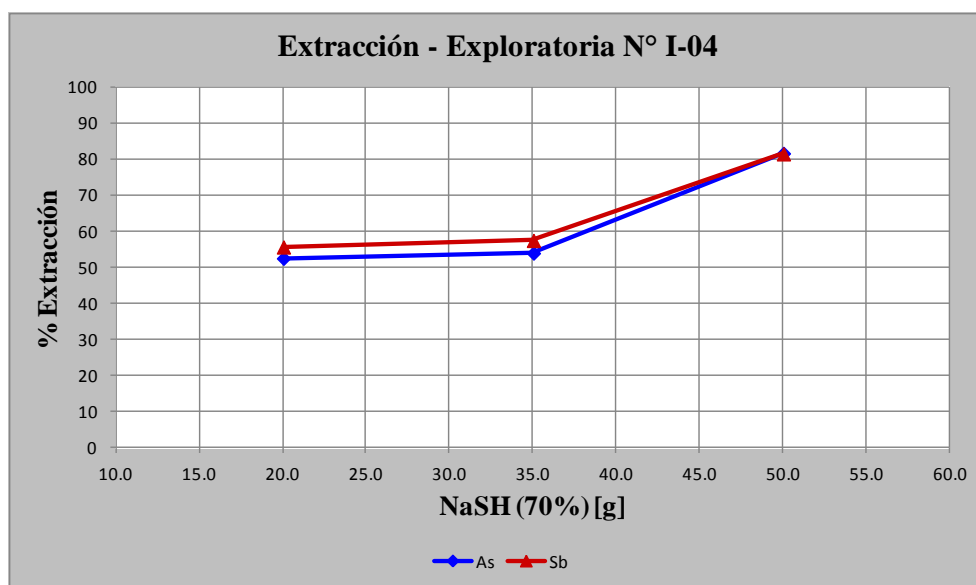
Tipo de Muestra	: Cabeza (Concentrado de Cobre)
Granulometría	: Natural (82.40 % -m 200 Ty)
Peso de Muestra	: 100 g.
% Sólidos	: 30
NaSH (70 %)	: 50, 35 y 20 g
NaOH (99 %)	: 50 g.
Tiempo Lixiviación	: 6.0 horas
Temperatura	: 90 °C
Agitación	: 300 rpm

Los rипios obtenidos de cada prueba fueron filtrados, lavados y secados a temperatura controlada de 100 °C para su posterior análisis químico por As, Sb y Cu. Con estos resultados se realizó un balance metalúrgico, el cual se presenta en la Tabla 3.11.

**Tabla 3.11:** Balance Metalúrgico – Exploratoria N° I-04

MUESTRA	Relación Mol.S/As	LEYES [%]						% EXTRACCIÓN	
		CABEZA			RIPIO			As	Sb
		As	Cu	Sb	As	Cu	Sb		
Muestra 1 - 50 NaOH	30	3.098	29.87	0.782	0.582	30.11	0.148	81.62	81.49
Muestra 2 - 50 NaOH	21	3.098	29.87	0.782	1.458	30.29	0.340	53.97	57.48
Muestra 3 - 50 NaOH	12	3.098	29.87	0.782	1.493	29.22	0.352	52.52	55.66

En estas primeras 3 pruebas realizadas con un recipiente cerrado, denominadas Exploratoria N° I-04, se han obtenido resultados con extracciones bajas. Esto nos conduce a realizar una prueba considerando aumentar el hidróxido, ya que este podría estar motivando a la formación de la hidrólisis del azufre. La Gráfica de Extracciones de As y Sb se presentan en la Figura 3.9.



**Figura 3.9:** Gráfica de Extracción – Exploratoria N° I-04

### 3.4.2 Cinética Exploratoria N° I-05

Para este grupo de pruebas se consideró realizarlas con adición constante de NaOH de 80 gramos y adiciones de NaSH variables de 50, 60 y 70 gramos. Los parámetros de trabajo de temperatura de pulpa, velocidad de agitación, granulometría de muestra y el tiempo se mantuvieron constantes, tal como se indican en la Tabla 3.12.

**Tabla 3.12:** Parámetros de Exploratoria N° I-05

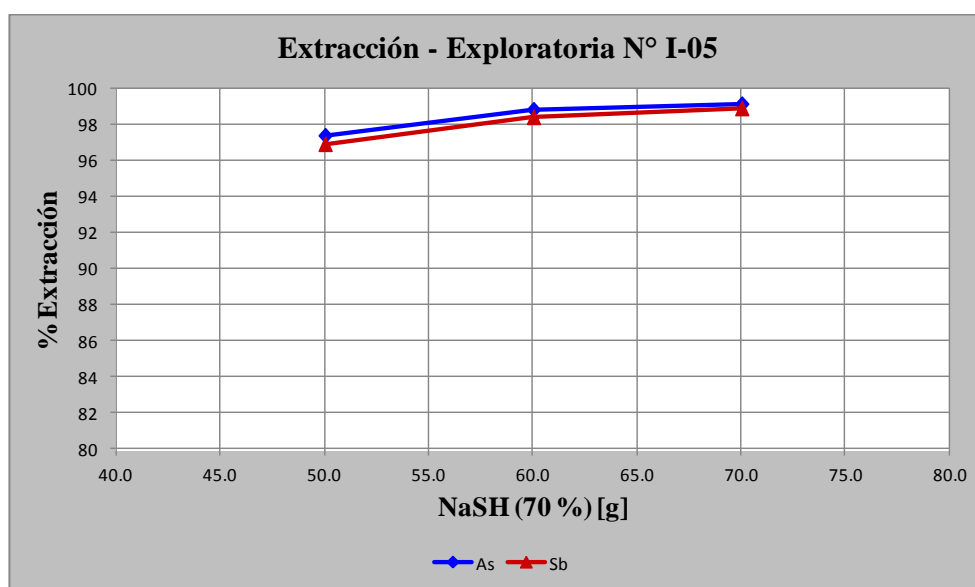
Tipo de Muestra	: Cabeza (Concentrado de Cobre)
Granulometría	: Natural (82.40 % -m 200 Ty)
Peso de Muestra	: 100 g.
% Sólidos	: 30
NaSH (70 %)	: 70, 60 y 50 g
NaOH (99 %)	: 80 g.
Tiempo Lixiviación	: 6.0 horas
Temperatura	: 90 °C
Agitación	: 300 rpm

Los rипios obtenidos de cada prueba fueron filtrados, lavados y secados a temperatura controlada de 100 °C para su posterior análisis químico por As, Sb y Cu. Con estos resultados se realizó un balance metalúrgico, el cual se presenta en la Tabla 3.13.

**Tabla 3.13:** Balance Metalúrgico – Exploratoria N° I-05

MUESTRA	Relación Mol.S/As	LEYES [%]						% EXTRACCIÓN	
		CABEZA			RIPIO			As	Sb
		As	Cu	Sb	As	Cu	Sb		
Muestra 1 - 80 NaOH	42	3.098	29.87	0.782	0.028	30.02	0.009	99.14	98.90
Muestra 2 - 80 NaOH	36	3.098	29.87	0.782	0.038	30.27	0.013	98.83	98.41
Muestra 3 - 80 NaOH	30	3.098	29.87	0.782	0.084	30.01	0.025	97.39	96.92

En este segundo grupo de pruebas de lixiviación alcalina con recipiente cerrado, denominadas Exploratoria N° I-05, se han obtenido resultados con extracciones de As y Sb superiores a 96%. Esto nos confirma que el hidróxido de sodio es fundamental para este tipo de lixiviación. La Gráfica de Extracciones de As y Sb se presentan en la Figura 3.10.



**Figura 3.10:** Gráfica de Extracción – Exploratoria N° I-05

### 3.4.3 Cinética Exploratoria N° I-06

Para este grupo de pruebas se consideró una adición de NaSH de 50 gramos con adición de NaOH de 80 gramos y a diferentes tiempos para observar la cinética de extracción para este tipo de Lixiviación de As y Sb. Los parámetros de trabajo de temperatura de pulpa, granulometría de muestra y velocidad de agitación se mantuvieron constantes, tal como se indican en la Tabla 3.14.

**Tabla 3.14:** Parámetros de Exploratoria N° I-06

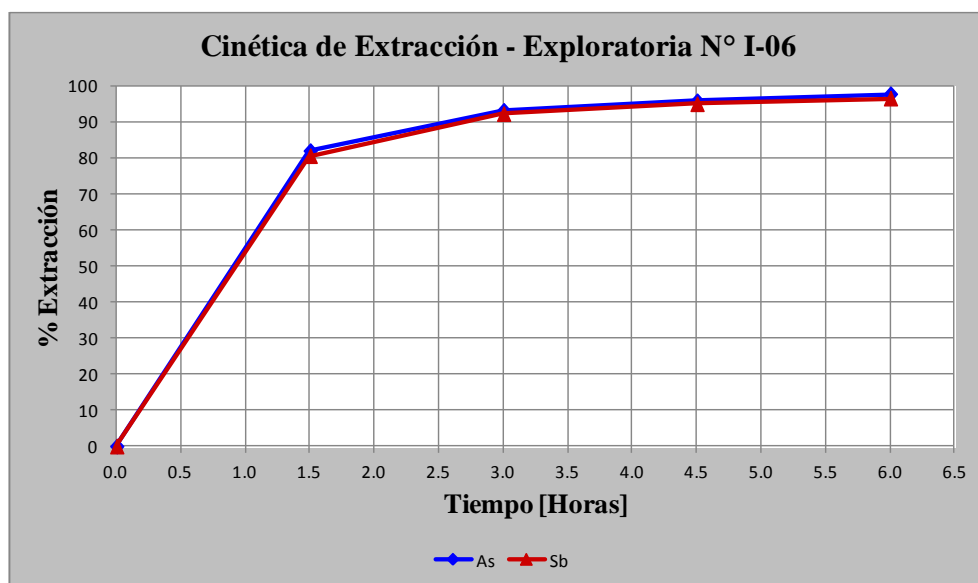
Tipo de Muestra	: Cabeza (Concentrado de Cobre)
Granulometría	: Natural (82.40 % -m 200 Ty)
Peso de Muestra	: 100 g.
% Sólidos	: 30
NaSH (70 %)	: 50 g
NaOH (99 %)	: 80 g
Tiempo Lixiviación	: 1.5, 3.0, 4.5 y 6.0 horas
Temperatura	: 90 °C
Agitación	: 300 rpm

Los rипios obtenidos de cada prueba fueron filtrados, lavados y secados a temperatura controlada de 100 °C para su posterior análisis químico por As, Sb y Cu. Con estos resultados se realizó un balance metalúrgico, el cual se presenta en la Tabla 3.15.

**Tabla 3.15:** Balance Metalúrgico – Exploratoria N° I-06

MUESTRA	Relación Mol.S/As	Tiempo (horas)	LEYES [%]						% EXTRACCIÓN	
			CABEZA			RIPIO			As	Sb
			As	Cu	Sb	As	Cu	Sb		
Muestra Cab (1.5)	30	1.5	3.098	29.87	0.782	0.577	29.94	0.157	82.04	80.65
Muestra Cab (3.0)	30	3.0	3.098	29.87	0.782	0.213	30.07	0.061	93.23	92.32
Muestra Cab (4.5)	30	4.5	3.098	29.87	0.782	0.132	30.13	0.040	95.88	95.06
Muestra Cab (6.0)	30	6.0	3.098	29.87	0.782	0.069	30.14	0.027	97.82	96.63

En este tercer grupo de pruebas de lixiviación alcalina con recipiente cerrado, denominadas Exploratoria N° 06, se han obtenido resultados con extracciones a diferentes tiempos de As y Sb. Las curvas de la Cinética de Extracciones de As y Sb se presentan en la Figura 3.11.



**Figura 3.11:** Curvas de Cinética de Extracción – Exploratoria N° I-06

## **CAPITULO IV**

### **SEGUNDO ESQUEMA – FLOTACIÓN / LIXIVIACIÓN**

#### **4.1 Equipos y Materiales**

Para el estudio del segundo esquema a nivel exploratorio, se ha utilizado lo siguiente:

Para Flotación Selectiva:

- Molino de Bolas con capacidad de 1 Kg de muestra seca
- Medidor de pH y ORP
- Maquina de Flotación con celdas para 1 Kg de muestra
- Bandejas de acero inoxidable

Para Lixiviación Alcalina de Concentrados

- Kitasatos de 500 ml
- Termómetro digital
- Agitadores magnéticos
- Bombas peristálticas
- Baqueta de vidrio
- Papel de filtro

- Bomba de vacío
- Bandejas de acero inoxidable
- Estufa de secado
- Mini cuarteador Jones
- Campanas Extractoras de Gases

#### **4.2 Evaluación Previa del Segundo Esquema**

La muestra de concentrado de cobre en estudio contiene un 6% de cobres grises según sus microscopía, por lo que el Segundo Esquema consiste en realizar una pre concentración para lograr separar una de menor masa con un alto contenido de arsénico ( $> 5\%$ ) para que este sea procesado por lixiviación alcalina, todo con el objetivo de obtener un concentrado final con bajos contenidos de arsénico ( $< 0.5\%$ ). Ver Esquema General en la Figura 2.1.

Se cuenta con muy poca bibliografía para realizar la flotación selectiva de cobres grises en concentrados de cobre, por lo que en este informe se realizaran pruebas de carácter exploratorio para analizar una posibilidad de optimización. En todas las pruebas se acondicionó la pulpa utilizando el carbón activado (C.A.) con la finalidad de reducir los efectos de los reactivos remanentes de la muestra proveniente de procesos de flotación polimetálica.

#### **4.3 Flotación Selectiva - Evaluando Pre Oxidación**

Considerando lo mencionado en el artículo de la revista Minerals Engineering “**A review of copper–arsenic mineral removal from copper concentrates**”, donde se



ejecuta una pre oxidación para realizar una flotación selectiva, en estas pruebas se aprovecha dicha propiedades de velocidad de oxidación de los minerales de cobre, las cuales siguen el siguiente orden: calcosina> tennantita> enargita> covelita> calcopirita.



**Figura 4.1:** Flotación Selectiva de Concentrados de cobre



**Figura 4.2:** Maquina de Flotación Marca Essa



**Figura 4.3: Fotografía de los productos de flotación**

#### 4.3.1 Exploratorio N° II-01

En esta prueba no se utilizó ningún reactivo oxidante. Las condiciones operativas se muestran en la Tabla 4.1.

**Tabla 4.1: Condiciones de flotación – Exploratoria N° II-01**

	Tiempo (min)	pH	ORP	RPM	REACTIVOS ADICIONADOS (g/TM)				
					C.A.	H2O2	Z-6	MIBC	
Molienda	5								
Acondicionamiento I	30	7.6	120	950.0	500				
Acondicionamiento II	5	7.5	92.0	750.0			10	10	
Flotación Rougher	5	7.5	85.0	750.0					
<b>TOTALES</b>	<b>45</b>				<b>500</b>		<b>10</b>	<b>10</b>	

Peso de Alimento : 1000 g. Granulometría : 100% -m 200 Tyler % Sólidos : 30	<b>OBSERVACIONES:</b> Flotación Directa de cobres grises (Tennantita y Tetraedrita)
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Los resultados obtenidos se muestran en el balance metalúrgico en la Tabla 4.2.

**Tabla 4.2:** Balance metalúrgico Exploratoria II-01

Productos	BALANCE METALÚRGICO							
	PESO		LEYES (%)			RECUPERACIONES (%)		
	(g)	(%)	As	Cu	Sb	As	Cu	Sb
Concentrado	346.5	34.82	3.900	32.040	0.967	44.56	37.19	44.90
Relave	648.5	65.18	2.593	28.910	0.634	55.44	62.81	55.10
Cabeza Calculada	995.0	100.00	3.048	30.000	0.750	100.00	100.00	100.00
Cabeza Ensayada			3.098	29.865	0.782			
% RSD			1.1	0.3	3.0			

### 4.3.2 Exploratorio N° II-02

En esta prueba se utilizó el peróxido de hidrógeno (H<sub>2</sub>O<sub>2</sub>). Las condiciones operativas se muestran en la Tabla 4.3.

**Tabla 4.3:** Condiciones de flotación – Exploratoria N° II-02

	Tiempo (min)	pH	ORP	RPM	REACTIVOS ADICIONADOS (g/TM)				
					C.A.	H2O2	Z-6	MIBC	
Molienda	5								
Acondicionamiento I	30	7.4	120	950	500				
Acondicionamiento II	30	5.7	450	750		1500		10	
Acondicionamiento III	5	5.7	450	750			10		
Flotación Rougher	5	5.7	450	750					
TOTALES	75				500	1500	10	10	

Peso de Alimento : 1000 g.	OBSERVACIONES: Flotación Directa de cobres grises (Tennantita y Tetraedrita)
Granulometría : 100% -m 200 Tyler	
% Sólidos : 30	

Los resultados obtenidos se muestran en el balance metalúrgico en la Tabla 4.4.

**Tabla 4.4:** Balance metalúrgico Exploratoria II-02

Productos	BALANCE METALÚRGICO							
	PESO		LEYES (%)			RECUPERACIONES (%)		
	(g)	(%)	As	Cu	Sb	As	Cu	Sb
Concentrado	268.9	27.06	1.202	31.110	0.379	10.83	28.25	13.15
Relave	725.0	72.94	3.669	29.300	0.928	89.17	71.75	86.85
Cabeza Calculada	993.9	100.00	3.002	29.790	0.779	100.00	100.00	100.00
Cabeza Ensayada			3.098	29.865	0.782			
% RSD			2.2	0.2	0.2			

Con estos resultados de las Exploratorias II-01 y II-02, podemos afirmar que existe efectos significativos al tratar de oxidar la superficie de los cobres grises ya que la recuperación de arsénico y antimonio son afectados directamente por el uso de peróxido de hidrógeno. Las leyes de As en el concentrado, entre la primera y segunda prueba son de 3.900% y 1.202%, estos resultados nos inclinan a continuar pruebas de tipo flotación inversa.

#### 4.4 Flotación Selectiva – Evaluando agente oxidante

Para estas pruebas se considera una evaluación exploratoria para determinar el uso de hipoclorito de sodio ó peróxido de hidrógeno para utilizar como agente oxidante en la flotación inversa de cobres grises, por recomendaciones del proveedor de reactivos, se utilizó el hostaflot 3403 para complementar al Xantato Z-6.

##### 4.4.1 Exploratorio N° II-03

En esta prueba se utilizó el peróxido de hidrógeno (H<sub>2</sub>O<sub>2</sub>). Las condiciones operativas se muestran en la Tabla 4.5. La flotación inversa se realizó hasta 15 minutos de flotación.

**Tabla 4.5:** Condiciones de flotación – Exploratoria N° II-03

	Tiempo (min)	pH	ORP	RPM	REACTIVOS ADICIONADOS (g/TM)				
					C.A.	H2O2	Z-6	Host. 3403	MIBC
Molienda	5								
Acondicionamiento I	30	7.4	120	950	500				
Acondicionamiento II	30	5.7	450	750		1500			
Acondicionamiento III	5	5.7	450	750			20	31	10
Flotación Rougher I	5	5.6	450	750					
Flotación Rougher II	5	5.6	400	750			5		
Flotación Rougher III	5	5.6	400	750			5		
<b>TOTALES</b>	<b>85</b>				<b>500</b>	<b>1500</b>	<b>30</b>	<b>31</b>	<b>10</b>

Los resultados obtenidos se muestran en el balance metalúrgico en la Tabla 4.6.

**Tabla 4.6:** Balance metalúrgico Exploratoria II-03

Productos	BALANCE METALÚRGICO							
	PESO		LEYES (%)			RECUPERACIONES (%)		
	(g)	(%)	As	Cu	Sb	As	Cu	Sb
Concentrado Cu (cp)	629.5	63.14	<b>0.997</b>	<b>29.210</b>	<b>0.233</b>	20.61	62.19	18.77
Relave (Conc. CGRs)	367.5	36.86	<b>6.577</b>	<b>30.420</b>	<b>1.727</b>	<b>79.39</b>	<b>37.81</b>	<b>81.23</b>
<b>Cabeza Calculada</b>	<b>997.0</b>	<b>100.00</b>	<b>3.054</b>	<b>29.656</b>	<b>0.784</b>	<b>100.00</b>	<b>100.00</b>	<b>100.00</b>
Cabeza Ensayada			3.098	29.865	0.782			

% RSD	1.0	0.5	0.2
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#### 4.4.2 Exploratorio N° II-04

En esta prueba se utilizó el hipoclorito de sodio (NaClO). Las condiciones operativas se muestran en la Tabla 4.7. La flotación inversa se realizó hasta 15 minutos de flotación.

**Tabla 4.7:** Condiciones de flotación – Exploratoria N° II-04

	Tiempo (min)	pH	ORP	RPM	REACTIVOS ADICIONADOS (g/TM)				
					C.A.	NaClO	Z-6	Host. 3403	MIBC
Molienda	5								
Acondicionamiento I	30	7.2	120	950	500				
Acondicionamiento II	30	12.8	-20	750		2000			
Acondicionamiento III	5	12.7	95	750			20	31	10
Flotación Rougher I	5	12.7	100	750					
Flotación Rougher II	5	12.6	95	750			5		
Flotación Rougher III	5	12.6	80	750			5		
<b>TOTALES</b>	<b>85</b>				<b>500</b>	<b>2000</b>	<b>30</b>	<b>31</b>	<b>10</b>

Peso de Alimento : 1000 g.	OBSERVACIONES: Flotación Inversa de cobres grises (Tennantita y Tetraedrita)
Granulometría : 100% -m 200 Tyler	
% Sólidos : 30	

Los resultados obtenidos se muestran en el balance metalúrgico en la Tabla 4.8.

**Tabla 4.8:** Balance metalúrgico Exploratoria II-04

Productos	BALANCE METALÚRGICO							
	PESO		LEYES (%)			RECUPERACIONES (%)		
	(g)	(%)	As	Cu	Sb	As	Cu	Sb
Concentrado Cu (cp)	712.4	71.46	<b>0.580</b>	<b>30.300</b>	<b>0.145</b>	13.78	72.42	13.23
Relave (Conc. CGRs)	284.5	28.54	<b>9.088</b>	<b>28.890</b>	<b>2.382</b>	<b>86.22</b>	<b>27.58</b>	<b>86.77</b>
Cabeza Calculada	<b>996.9</b>	<b>100.00</b>	<b>3.008</b>	<b>29.898</b>	<b>0.783</b>	<b>100.00</b>	<b>100.00</b>	<b>100.00</b>
Cabeza Ensayada			3.098	29.865	0.782			
% RSD			2.1	0.1	0.1			

Con estos resultados de las Exploratorias II-03 y II-04, se aprecia que el hipoclorito de sodio tiene un mejor efecto en comparación del peróxido de hidrógeno, la leyes de arsénico en la exploratoria II-04 es de 9.088% mientras que en la exploratoria II-03 es 6.577%.

Las recuperaciones obtenidas en estas dos exploratorias, son de carácter significativo, ya que lo que tratamos de buscar una flotación inversa donde quede

deprimido el mayor contenido de arsénico y antimonio en la menor masa posible, con el uso de hipoclorito la masa es 28.54%, mientras que con el peróxido de hidrógeno llegó a 36.86%.

Considerando la utilización del hipoclorito de sodio, se realizó una prueba exploratoria a la muestra con su granulometría natural a las condiciones mostradas en la Tabla 4.9.

**Tabla 4.9:** Condiciones Operativas Exploratoria N° II-05

	Tiempo (min)	pH	ORP	RPM	REACTIVOS ADICIONADOS (g/TM)				
					C.A.	NaClO	Z-6	Host. 3403	MIBC
Molienda	0								
Acondicionamiento I	30	7.2	120	950	500				
Acondicionamiento II	30	12.8	-15	750		2000			
Acondicionamiento III	5	12.7	90	750			20	31	10
Flotación Rougher I	5	12.5	85	750					
Flotación Rougher II	5	12.5	84	750			5		
Flotación Rougher III	5	12.5	81	750			5		
<b>TOTALES</b>	<b>80</b>				<b>500</b>	<b>2000</b>	<b>30</b>	<b>31</b>	<b>10</b>

Peso de Alimento : 1000 g.	OBSERVACIONES: Flotación Inversa de cobres grises (Tennantita y Tetraedrita)
Granulometría : Natural (82.40% -m200 Tyler)	
% Sólidos : 30	

Los resultados obtenidos se muestran en el balance metalúrgico en la Tabla 4.10.

**Tabla 4.10:** Balance metalúrgico Exploratoria II-05

Productos	BALANCE METALÚRGICO							
	PESO		LEYES (%)			RECUPERACIONES (%)		
	(g)	(%)	As	Cu	Sb	As	Cu	Sb
Concentrado Cu	578.8	58.12	<b>0.715</b>	<b>29.170</b>	<b>0.188</b>	13.79	57.02	13.97
Relave	417.1	41.88	<b>6.205</b>	<b>30.510</b>	<b>1.607</b>	<b>86.21</b>	<b>42.98</b>	<b>86.03</b>
<b>Cabeza Calculada</b>	<b>995.9</b>	<b>100.00</b>	<b>3.014</b>	<b>29.731</b>	<b>0.782</b>	<b>100.00</b>	<b>100.00</b>	<b>100.00</b>
Cabeza Ensayada			3.098	29.865	0.782			

% RSD	1.9	0.3	0.0
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Revisando los resultados de las Exploratorias II-04 y II-05, apreciamos que el grado de liberación entre realizar una remolienda al 100%-m 200Tyler y de no realizarla, presenta resultados significativos, ya que no realizar una remolienda conlleva a tener un relave con mayor contenido de masa, reduciendo la leyes de As de 9.088% a 6.205% lo cual no es un resultado favorable para lo que se trata de obtener.

#### 4.5 Flotación Inversa - Cinética

Se ha ejecutado una prueba de cinética para evaluar el mejor tiempo de flotación a la mejor prueba obtenida (Exploratoria N° II-04). Las condiciones operativas de esta flotación inversa tipo cinética se muestran en la Tabla 4.11.

**Tabla 4.11:** Condiciones operativas de Cinética de Flotación

	Tiempo (min)	pH	ORP	RPM	REACTIVOS ADICIONADOS (g/TM)				
					C.A.	NaClO	Z-6	Host. 3403	MIBC
Molienda	5								
Acondicionamiento I	30	7.2	120	950	500				
Acondicionamiento II	30	12.8	-15	750		2000			
Acondicionamiento III	5	12.7	95	750			20	31	10
Cinetica de Flotación	9	12.5		750			5		
	15	12.5		750			5		
	18	12.5		750			5		
<b>TOTALES</b>	<b>112</b>				<b>500</b>	<b>2000</b>	<b>35</b>	<b>31</b>	<b>10</b>

Peso de Alimento : 1000 g.	OBSERVACIONES: Cinetica de Flotación Inversa de cobres grises (Tennantita y Tetraedrita)
Granulometría : 100% -m 200 Tyler	
% Sólidos : 30	

El balance metalúrgico de esta prueba de flotación inversa tipo cinética se muestra en la Tabla 4.12, su balance acumulado se muestra en la Tabla 4.13 y sus curvas de cinética de flotación inversa se presentan en la Figura 4.4.



**Tabla 4.12:** Balance Metalúrgico de Cinética de Flotación Inversa

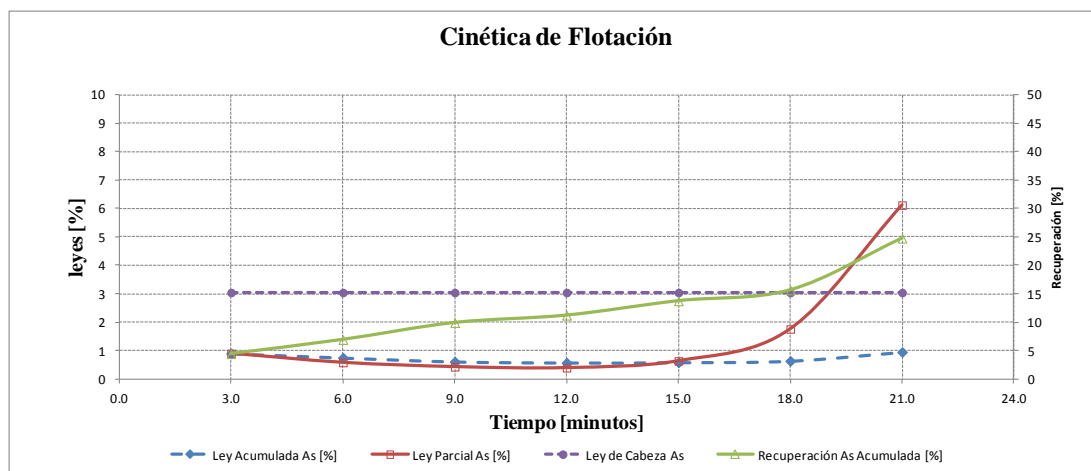
Productos	BALANCE METALURGICO							
	PESO		LEYES (%)			RECUPERACIONES (%)		
	(g)	(%)	As	Cu	Sb	As	Cu	Sb
Conc. Cu 3.0	149.7	15.0	0.897	22.860	0.189	4.42	11.42	3.61
Conc. Cu 6.0	131.2	13.1	0.578	30.550	0.197	2.50	13.38	3.30
Conc. Cu 9.0	211.2	21.1	0.427	32.690	0.119	2.97	23.05	3.21
Conc. Cu 12.0	101.0	10.1	0.392	32.610	0.115	1.30	10.99	1.48
Conc. Cu 15.0	121.5	12.2	0.634	32.210	0.122	2.54	13.06	1.89
Conc. Cu 18.0	33.1	3.3	1.757	31.000	0.368	1.92	3.43	1.55
Conc. Cu 21.0	45.2	4.5	6.118	30.050	0.992	9.11	4.53	5.72
Relave Final	205.9	20.6	11.097	29.290	3.016	75.25	20.13	79.24
Cab. Calculada	998.8	100.0	3.040	29.993	0.785	100.00	100.00	100.00
Cab. Ensayada			3.098	29.865	0.782			

% RSD	1.3	0.3	0.2
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**Tabla 4.13:** Balance Acumulado de Cinética de Flotación Inversa.

Productos	ACUMULADOS							
	PESO		LEYES (%)			RECUPERACIONES (%)		
	(g)	(%)	As	Cu	Sb	As	Cu	Sb
Conc. Cu 3.0	149.7	15.0	0.897	22.860	0.189	4.42	11.42	3.61
Conc. Cu 6.0	280.9	28.1	0.748	26.452	0.193	6.92	24.80	6.91
Conc. Cu 9.0	492.1	49.3	0.610	29.129	0.161	9.89	47.85	10.11
Conc. Cu 12.0	593.1	59.4	0.573	29.722	0.153	11.19	58.85	11.60
Conc. Cu 15.0	714.6	71.5	0.583	30.145	0.148	13.73	71.91	13.49
Conc. Cu 18.0	747.7	74.9	0.635	30.183	0.158	15.65	75.33	15.04
Conc. Cu 21.0	792.9	79.4	0.948	30.175	0.205	24.75	79.87	20.76



**Figura 4.4:** Curvas de Cinética de Flotación Inversa

De la Tabla 4.13, podemos apreciar que la flotación selectiva de cobres grises no logra nuestro propósito de obtener un concentrado con leyes de arsénico menor a 0.5 %, sin embargo el proceso de pre oxidación nos da muchos indicios de poder optimizarlo.

#### 4.6 Flotación Inversa - Acumulada

Se ha ejecutado una prueba acumulada con 2 Kg de muestra, tomando 15 minutos de flotación, tomando de referencia la flotación inversa tipo cinética y utilizando los mejores parámetros obtenidos en la Exploratoria N° II-04, el balance metalúrgico presentado en la Tabla 4.14, confirma los resultados de la exploratoria N° II-04, replicando con valores muy similares a los obtenidos en dicha prueba. El relave (concentrado de cobres grises) fue utilizado para realizar una lixiviación alcalina.

**Tabla 4.14:** Balance Metalúrgico – Flotación Inversa Acumulada

Productos	BALANCE METALÚRGICO							
	PESO		LEYES (%)			RECUPERACIONES (%)		
	(g)	(%)	As	Cu	Sb	As	Cu	Sb
Concentrado Cu (cp)	1412.8	70.81	<b>0.588</b>	<b>30.122</b>	<b>0.149</b>	13.42	71.59	13.45
Relave (Conc. CGRs)	582.4	29.19	<b>9.202</b>	<b>28.998</b>	<b>2.326</b>	<b>86.58</b>	<b>28.41</b>	<b>86.55</b>
Cabeza Calculada	<b>1995.2</b>	<b>100.00</b>	<b>3.102</b>	<b>29.794</b>	<b>0.784</b>	<b>100.00</b>	<b>100.00</b>	<b>100.00</b>
Cabeza Ensayada			3.098	29.865	0.782			
% RSD			0.1	0.2	0.2			

#### 4.7 Lixiviación Alcalina – Relave (Conc. CGRs)

Se realizó la lixiviación alcalina al concentrado de cobres grises del producto de flotación inversa acumulada, para lo cual se consideró una adición de 70 gramos de NaSH y 80 gramos con adición de NaOH, realizando una cinética a diferentes tiempos para observar la extracción para este tipo de muestra. Los parámetros de trabajo de temperatura de pulpa, granulometría de muestra y velocidad de agitación se mantuvieron constantes, tal como se indican en la Tabla 4.15.

**Tabla 4.15:** Parámetros de Exploratoria N° II-06

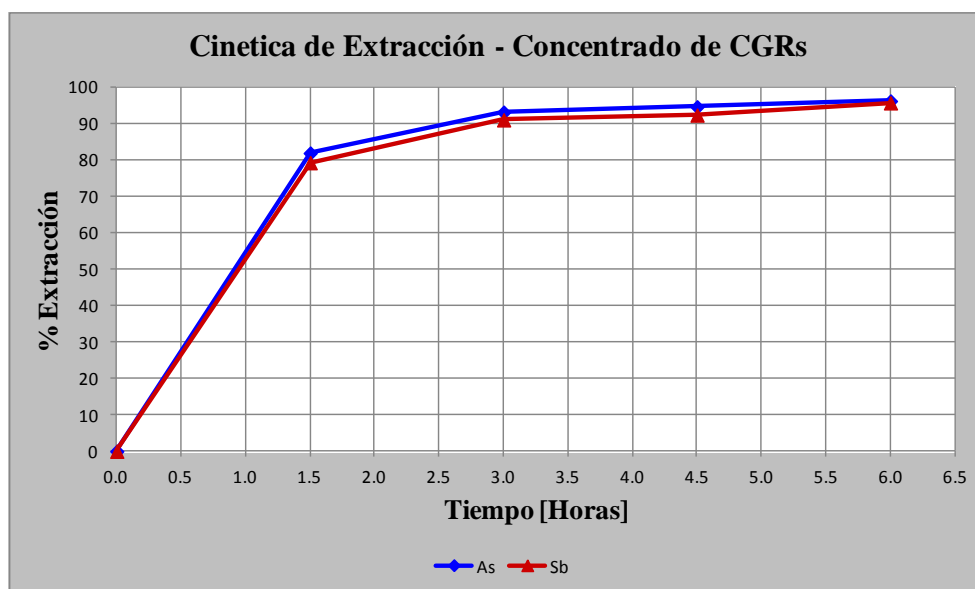
Tipo de Muestra	: Concentrado de CGRs (Flotación Selectiva Acumulada)
Granulometría	: Natural (100% -m 200 Tyler)
Peso de Muestra	: 100 g.
% Sólidos	: 30
NaSH (70 %)	: 70 g
NaOH (99 %)	: 80 g
Tiempo Lixiviación	: 1.5, 3.0, 4.5 y 6.0 horas
Temperatura	: 90 °C
Agitación	: 300 rpm

Los rипios obtenidos de cada prueba fueron filtrados, lavados y secados a temperatura controlada de 100 °C para su posterior análisis químico por As, Sb y Cu. Con estos resultados se realizó un balance metalúrgico, el cual se presenta en la Tabla 4.16.

**Tabla 4.16:** Balance Metalúrgico – Lixiviación Alcalina Conc. CGRs

MUESTRA	Relación Mol.S/As	Tiempo (horas)	LEYES [%]						% EXTRACCIÓN	
			CABEZA			RIPIO			As	Sb
			As	Cu	Sb	As	Cu	Sb		
Conc. Flot. (1.5)	14	1.5	9.202	28.998	2.326	1.834	31.09	0.531	81.88	79.25
Conc. Flot. (3.0)	14	3.0	9.202	28.998	2.326	0.701	31.43	0.231	93.11	91.01
Conc. Flot. (4.5)	14	4.5	9.202	28.998	2.326	0.554	31.15	0.198	94.58	92.33
Conc. Flot. (6.0)	14	6.0	9.202	28.998	2.326	0.392	31.12	0.112	96.18	95.68

Esta prueba de lixiviación alcalina del concentrado de cobre grises, ha obtenido resultados con extracciones a diferentes tiempos de As y Sb. Las curvas de Cinética de Extracciones de As y Sb se presentan en la Figura 4.5.



**Figura 4.5:** Curvas de Cinética de Extracción – Exploratoria N° I-06

#### 4.8 Balance General Calculado – Segundo Esquema

Como objetivo del Segunda Esquema, se realizó una serie de flotaciones de tipo exploratoria para tratar de obtener un concentrado rico en As y Sb mediante una flotación selectiva de cobres grises, logrando obtener los mejores resultados con la Exploratoria N° II-04. Luego se realizó una prueba acumulativa con los parámetros de la Exploratoria N° II-04, logrando obtener dos productos con las leyes mostradas en el Tabla 4.17.

**Tabla 4.17:** Leyes de la Flotación Acumulada

Productos de Flotación	% Peso	Leyes [%]		
		As	Cu	Sb
Concentrado Cu (cp)	70.81	0.588	30.12	0.149
Relave (Concentrado CGRs)	29.19	9.202	29.00	2.326

Con el relave (Concentrado CGRs), se ha logrado concentrar una buena cantidad de arsénico y antimonio. Dicha muestra fue llevada al proceso de lixiviación alcalina reduciendo considerablemente sus leyes de estos elementos contaminantes. En la Tabla 4.18 se muestran las leyes del concentrado de CGRs antes y después de ser lixiviado.

**Tabla 4.18:** Leyes de concentrado de cobres grises.

Muestra	% Peso	Leyes [%]		
		As	Cu	Sb
Relave (Conc. CGRs) - Sin Lixiviación	29.19	9.202	29.00	2.326
Relave (Conc. CGRs) - Con Lixiviación	26.18	0.392	31.12	0.112

Se realizó un balance con el cálculo ponderado de las leyes de concentrado de cobres grises lixiviado y el concentrado de calcopirita, llegando a obtener los resultados mostrados en la Tabla 4.19.

**Tabla 4.19:** Leyes de Concentrado Final - Segundo Esquema

Producto Final	% Peso	Leyes [%]		
		As	Cu	Sb
Conc. Cu	70.81	0.588	30.122	0.149
Relave (Conc. CGRs) - Con Lixiviación	26.18	0.392	31.120	0.112
<b>Conc. Cu Total - Segundo Esquema</b>		<b>0.535</b>	<b>30.391</b>	<b>0.139</b>

Con el Segundo Esquema se ha logrado obtener un concentrado final con 0.535% de arsénico y 0.139% de antimonio. Este resultado no está dentro de los valores de nuestro objetivo, el cual debió estar por debajo de 0.5% en arsénico.

## **CAPITULO V**

### **ANÁLISIS DE RESULTADOS**

La caracterización química de la muestra (concentrado de cobre) indica que la muestra en estudio presenta leyes de arsénico y antimonio con valores de 3.098 % y 0.782 % respectivamente, estos contaminantes afectan significativamente el valor comercial de los concentrados de cobre.

Del estudio mineralógico realizado, se aprecia que el mayor porcentaje de contenido en la muestra (concentrado de cobre) se encuentra mineralizado como calcopirita con un 78.5%, seguido de los cobres grises como la tennantita y tetraédrica con 6%, siendo estos los principales portadores de arsénico y antimonio.

La distribución granulométrica que se realizó a la muestra (concentrado de cobre) como parte de la caracterización física, presenta un 82.4 % -m 200 Tyler y 55.21 % -m 400 Tyler.

### 5.1 Primer Esquema (Lixiviación Alcalina)

Con las pruebas exploratorias del Primer Esquema (Lixiviación Alcalina), se pudo comprobar que el medio debe de mantener una alta alcalinidad, de esta manera podemos evitar la hidrólisis del sulfuro, tal como podemos apreciar en las pruebas exploratorias N° I-01, N° I-02, N° I-04 y N° I-05, logrando obtener una extracción máxima de arsénico de 99.14% (Muestra 1 - Exploratoria N° I-05) en un tiempo de lixiviación de 6 horas y con una relación molar azufre/arsénico de  $S/As = 42$ , en esta prueba la adición inicial de hidróxido de sodio (NaOH) para mantener un alta alcalinidad fue de 80 gramos (342.9 g/l).

Para el primer esquema, se ha logrado comprobar que la granulometría no es un factor que afecte significativamente al proceso de lixiviación alcalina para esta muestra de concentrado de cobre. Con los resultados obtenidos en la Exploratoria N° I-3 con extracciones de arsénico  $> 96\%$ , se llega a la conclusión que para este proceso solo se requiere utilizar la muestra a su granulometría natural (82.40% -m 200 Tyler).

En la prueba Exploratoria I-06, se muestra que el proceso de lixiviación alcalina llevada en laboratorio puede ejecutarse en 3 horas, ya que en aquel tiempo se ha logrado una extracción de As y Sb de 93.23 % y 92.32% respectivamente, con leyes de As y Sb de 0.213% y 0.061% respectivamente. La relación molar azufre/arsénico para esta prueba fue de  $S/As = 30$ .



Se ha logrado un avance considerable con respecto al proceso plantado en el Primer Esquema de lixiviación alcalina de arsénico y antimonio contenidos en los concentrados de cobres, sin embargo aun podemos enumerar algunas propuestas para continuar investigando:

- Optimizar el consumo de reactivos de Hidrosulfuro de Sodio (NaSH) e hidróxido de sodio (NaOH).
- Evaluar el tratamiento de la solución lixiviada rica en arsénico y antimonio para re-utilizar el remanente de los reactivos de NaSH y NaOH con miras a una recirculación.
- Realizar la estabilización del arsénico de  $As^{3+}$  a  $As^{5+}$ , podría realizarse utilizando semillas de escorodita.
- Disposición de los elementos contaminantes

## **5.2 Segundo Esquema (Flotación / Lixiviación)**

Con las pruebas exploratorias del Segundo Esquema (Flotación / Lixiviación) N° II-01 y II-02, se logra determinar que la muestra de concentrado de cobre es más dócil a la oxidación de cobres grises (deprimir Tennantita y Tetraedrita), motivo por el cual la flotación selectiva se direcciona a una flotación inversa, teniendo en cuenta que la especie de interés son los cobres grises para poder realizar un proceso siguiente de remoción de arsénico por lixiviación alcalina.

Los resultados de las exploratorias N° II-03 y N° II-04 indican que el mejor reactivo oxidante viene a ser el hipoclorito de sodio, el cual afecta directamente al pH de la pulpa elevándola hasta 12.7, dicho pH mejora la flotación de la calcopirita deprimiendo a los cobres grises, los cuales están superficialmente oxidados.

Los resultados obtenidos en la exploratoria N° II-05 demuestran que realizar la flotación con la muestra a granulometría natural no es el camino adecuado, ya que la recuperación de As se mantienen aproximadamente 86%, sin embargo las leyes de los concentrados de cobres aumentan de 0.580% hasta 0.715% con respecto a la mejor prueba (Exploratoria II-04). Esto afecta directamente al objetivo de nuestras pruebas de obtener un concentrado final de  $< 0.5\%$  de As.

Las extracciones obtenidas en la lixiviación alcalina del producto de flotación deprimido (concentrado de cobres grises) han sido satisfactorias, reduciendo el contenido de arsénico de 9.202 % hasta 0.392 %, lo cual se traduce en un 96.18 % de extracción de arsénico. El mismo comportamiento se presencia para el antimonio, logrando una extracción de Sb = 95.68 %. Cabe resaltar que en este proceso hay una pérdida promedio de 10% en masa, esto puede justificarse con la disolución total de As y Sb presentes en esta muestra altamente concentrada con cobres grises.

Realizando el balance General de la Segundo Esquema (Flotación / Lixiviación), el promedio ponderado del concentrado limpio de arsénico del proceso de Flotación más el concentrado del proceso de Lixiviación, se obtiene un Concentrado Final de Cobre con contenidos de: Cu = 30.391%, As = 0.535% y Sb = 0.139 %.

En el presente informe se ha obtenido resultados que pueden considerarse como indicios para realizar una investigación a detalle para lograr realizar una flotación selectiva de cobres grises contenidos en concentrados de cobre (calcopirita). La pre oxidación ejecutada aun tiene muchos factores por estudiar, por lo que se podría indicar:

- Realizar pruebas considerando concentraciones de NaClO, tiempo de oxidación para tener una mejor panorama de este proceso de pre oxidación de cobres grises.
- Revisar literaturas para poder ejecutar pruebas de lixiviación directa sin la etapa de pre oxidación.
- Analizar un conjunto de pruebas de flotación directa e inversa con el efecto del potencial redox.

## **CONCLUSIONES**

Con las leyes finales de la muestra (concentrado de cobre) obtenidas en el primer esquema (Lixiviación Alcalina), se ha logrado cumplir con el objetivo de este informe, el cual consistía en obtener un concentrado de cobre final con contenidos de arsénico inferiores a 0.5%.

Con las leyes finales de la muestra (concentrado de cobre) obtenidas en el segundo esquema (Flotación / Lixiviación), no se logro cumplir con el objetivo planteado (contenido de arsénico < 0.5%). Sin embargo el sub proceso de lixiviación alcalina para el concentrado de cobres grises si lograron resultados satisfactorios.

El proceso de lixiviación alcalina puede ejecutarse en recipientes cerrados, ya que trabajar de esta manera mejora la operación y ayuda a la cuantificación de la adición de los reactivos.

Realizar la remoción de arsénico y antimonio aumenta la ley del concentrado de cobre.

Con los resultados obtenidos en estas pruebas de investigación tipo exploratorio ejecutadas en el presente informe, se puede afirmar que el camino ya recorrido nos está dando buenos indicios para continuar con pruebas de optimización que permitan llegar a conclusiones mucho más solidas, las cuales determinaran realizar este proceso a nivel industrial.

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### **HYDROMETALLURGY: Selective leaching of arsenic from enargite in NaHS–NaOH media**

William Tongamp, Yasushi Takasaki, Atsushi Shibayama. Volume 101, Issues 1–2, February 2010, Pages 64–68

**MINERALS ENGINEERING: A critical review of surface properties and selective flotation of enargite in sulphide systems**

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**MINERALS ENGINEERING: A review of copper–arsenic mineral removal from copper concentrates**

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## **ANEXOS**

Anexo N° 01: HIDROMETALURGIA, Arsenic removal from copper ores and concentrates through alkaline leaching in NaHS media

Anexo N° 02: HIDROMETALURGIA, Selective leaching of arsenic from enargite in NaHS–NaOH media

Anexo N° 03: MINERALS ENGINEERING, A critical review of surface properties and selective flotation of enargite in sulphide systems

Anexo N° 04: MINERALS ENGINEERING, A review of copper–arsenic mineral removal from copper concentrates

Anexo N° 05: MINERALS ENGINEERING, Selective leaching of arsenic and antimony from a tetrahedrite rich complex sulphide concentrate using alkaline sulphide solution





# Arsenic removal from copper ores and concentrates through alkaline leaching in NaHS media

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## ABSTRACT

Removal of arsenic impurity in ores and concentrates containing copper (Cu) through alkaline leaching in NaHS media was investigated in this work. Samples containing Cu from 10 to 40 wt.% and arsenic from 0.8 to 14 wt.% with enargite ( $\text{Cu}_3\text{AsS}_4$ ) as main arsenic bearing mineral were used as starting materials and all leaching tests were conducted at 80 °C under normal atmospheric pressure. Solution and/or slurry potential and pH were maintained consistently below  $-500$  mV (SHE) and above 12.5 respectively with the addition of NaHS and NaOH, creating a reducing environment for arsenic dissolution and conversion of  $\text{Cu}_3\text{AsS}_4$  to  $\text{Cu}_2\text{S}$ . Pulp density ranged from 100 to 1000 g/L, NaHS and NaOH reagents were added at 50–200 g/L each and leaching time varied from 10 min to 10 h.

Characterization of solid samples (original and leach residue) by XRD and XRF analyses and chemical analysis of both solid and solution samples by ICP analysis showed that  $\text{Cu}_3\text{AsS}_4$  in the starting material was completely decomposed or transformed to  $\text{Cu}_2\text{S}$  and arsenic released into solution as As (III)/ $\text{As}^{3+}$  ions ( $\text{Na}_3\text{AsS}_3$ ). Over 90% of arsenic in the starting materials was removed within 1–3 h for materials with arsenic content from 1 to 4 wt.% and within 3–6 h for materials with arsenic content over 4–10 wt.%. Dissolution and analysis of leach residues obtained after leaching by ICP indicated that arsenic in the starting materials has been reduced in all cases to below 0.5 wt.%. In all test conditions dissolution of Cu and Fe into solution was not detected, indicating selective leaching of arsenic. NaHS application for removal of arsenic in Cu-ores and/or concentrates was demonstrated in this work and further research is in progress to develop a process to include treatment of arsenic leached into solution.

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## 1. Introduction

Arsenic and antimony impurities in copper ores and/or deposits that usually affect the final concentrate purity occur most commonly in the minerals; enargite ( $\text{Cu}_3\text{AsS}_4$ ), tennantite ( $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ ), tetrahedrite ( $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ ) which are normally associated with pyrite ( $\text{FeS}_2$ ), covellite ( $\text{CuS}$ ), chalcocite ( $\text{Cu}_2\text{S}$ ), and digenite ( $\text{Cu}_9\text{S}_5$ ), and may coexist in small quantities in chalcocite ( $\text{Cu}_2\text{S}$ ) and bornite ( $\text{Cu}_5\text{FeS}_4$ ). (Lattanzi et al., 2008; Filippou et al., 2007; Baláz and Achimovičová, 2006a; Guo and Yen, 2005; Welham, 2001). These minerals are economically attractive; however, the content of arsenic and antimony effectively reduces their economic value due to requirements for additional treatment options for the containment of hazardous emissions from pyrometallurgical processing, and the negative effect of arsenic and antimony on conductivity and ductility of refined copper is noted widely in literature (Mihajlovic et al., 2007; Filippou et al., 2007; Baláz and Achimovičová, 2006a; Viñals et al., 2003; Padila et al., 1998).

Separation of ores containing arsenic and antimony (enargite, tetrahedrite, and tennantite) from other copper/iron sulfides such as; chalcocite ( $\text{Cu}_2\text{S}$ ), covellite ( $\text{CuS}$ ), chalcocite ( $\text{Cu}_2\text{S}$ ), bornite ( $\text{Cu}_5\text{FeS}_4$ ), and pyrite ( $\text{FeS}_2$ ) by selective flotation to obtain concentrates with arsenic content below 0.5 wt.% for feed to smelters is reported by many researchers (Filippou et al., 2007; Senior et al., 2006; Guo and Yen, 2005; Kantar, 2002; Fornasiero et al., 2001; Pauporté and Schuhmann, 1996; Menacho et al., 1993). However, as demand for copper continues to grow resulting in a decline in copper deposits with low arsenic and antimony impurities, the focus will now be directed on the treatment of copper ores and/or concentrates with high enargite, tennantite, and tetrahedrite contents. Unfortunately, the high content of arsenic reduces the economic value of the copper resource due to environmental issues associated with treatment by pyrometallurgical processing as additional facilities are required for containing arsenic. Also the cost of treating such materials may not be economically feasible; therefore, a more cost effective and environmentally friendly process for the removal of arsenic prior to pyrometallurgical processing for copper could be achieved by hydrometallurgical processing as discussed in the preceding paragraphs.

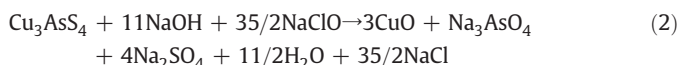
Many researchers discuss possible dissolution and/or leaching of arsenic bearing minerals in copper resources and their findings are

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available in literature. Filippou et al. (2007), Viñals et al. (2003) and Herreros et al. (2002) discuss the many treatment options and provide an overall review of many different leaching reagents or media used under varying experimental conditions by different researchers, but with the same purpose to remove arsenic from copper bearing ores or concentrates. Leaching of enargite ( $\text{Cu}_3\text{AsS}_4$ ) and other materials containing arsenic in media such as chloride, sulfide, and ammonical solutions with tests being conducted at higher pressures and temperatures, and the use of bacteria (bio-leaching) are reported by many of these researchers (Filippou et al., 2007; Padilla et al., 2005; Viñals et al., 2003; Herreros et al., 2002; Canales et al., 2002; Welham, 2001; Gajam and Raghavan, 1983; Dutrizac and MacDonald, 1972). Generally arsenic leaching rates in the systems listed above are slow and require longer reaction times. To increase reaction rates in such systems, leaching is normally conducted in high acid concentrations and at high pressure and temperature environments. Other hydrometallurgical processes for arsenic removal from copper ores and concentrates to obtain clean copper resource for feed to pyrometallurgical processing are currently being investigated by many researchers.

The removal of arsenic from enargite can be achieved by alkaline leaching of concentrates in sodium sulfide ( $\text{Na}_2\text{S}$ ) solutions containing high  $\text{S}^{2-}$  under highly alkaline ( $\text{OH}^-$  ( $\text{NaOH}$ )) reducing conditions with  $\text{Cu}_3\text{AsS}_4$  converted or transformed to  $\text{Cu}_2\text{S}$  as represented by Reaction (1) below. Such a treatment option by selectively removing arsenic into solution and separating from  $\text{Cu}_2\text{S}$  is reported by many researchers (Curreli et al., 2009; Filippou et al., 2007; Baláž and Achimovičová, 2006a,b; Delfini et al., 2003; Baláž et al., 2000). And in sodium hypochlorite solutions under alkaline oxidizing conditions,  $\text{Cu}_3\text{AsS}_4$  is transformed or converted to  $\text{CuO}$  as represented by Reaction (2).



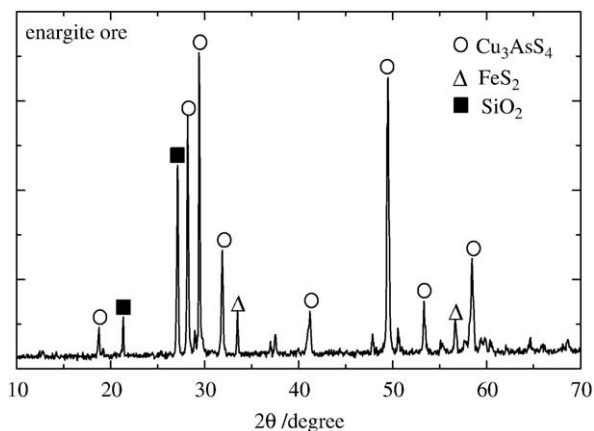
A review on enargite oxidation, including its many other properties, is clearly discussed by Lattanzi et al. (2008) and Delfini et al. (2003). Recently, the transformation of  $\text{Cu}_3\text{AsS}_4$  to  $\text{CuO}$  in an oxidizing alkaline medium consisting of  $\text{ClO}^-$  ( $\text{NaOCl}$ –sodium hypochlorite) and  $\text{OH}^-$  ( $\text{NaOH}$ –sodium hydroxide) solutions and the soluble arsenic forming  $\text{AsO}_4^{3-}$ , to be separated from  $\text{CuO}$  has been reported (Viñals et al., 2003; Mihajlovic et al., 2007; Curreli et al., 2005; Jackson, 1986) showing that arsenic could be removed at much faster rates.

As a contribution to the development of a hydrometallurgical process for the treatment of copper ores and concentrates containing enargite as the carrier of arsenic, in the current work we discuss the effect of certain parameters in leaching of enargite in alkaline media. Sodium hydrosulfide ( $\text{NaHS}$ ) as leaching medium, creating a high reducing environment to obtain solution potentials  $< -500$  mV and  $\text{NaOH}$  to have solution  $\text{pH} > 12.5$  and prevent hydrolysis of sulfide ions responsible for substitution of arsenic in enargite was investigated in this work. The parameters including pulp density, slurry temperature, sulfur/arsenic ( $\text{S}/\text{As}$ ) molar ratio, and leaching time, have been

**Table 1**

Main chemical and phase compositions in Cu-ores/concentrate samples with arsenic impurity from various sources.

Sample	As (%)	Cu (%)	Fe (%)	Main composition
(1) Cu conc.	0.81	26.62	25.40	$\text{CuFeS}_2$ , $\text{FeS}_2$
(2) Cu conc.	0.95	22.60	18.17	$\text{CuFeS}_2$ , $\text{FeS}_2$
(3) Cu conc.	1.67	11.49	9.71	$\text{CuFeS}_2$ , $\text{FeS}$
(4) Cu conc.	3.11	33.46	14.34	$\text{FeS}_2$ , $\text{Cu}_2\text{FeSiS}_4$
(5) Enargite ore	8.32	33.71	16.34	$\text{Cu}_3\text{AsS}_4$ , $\text{CuFeS}_2$
(6) Mixture (1) + (5)	3.00	25.84	21.04	–
(7) Mixture (2) + (5)	3.00	25.69	21.08	–



**Fig. 1.** Characteristic X-ray diffraction pattern of enargite ore (sample (5)) with arsenic content at 8.32 wt.% and  $\text{Cu}_3\text{AsS}_4$  at about 43%.

investigated. Our findings show that complete removal of arsenic from enargite ore, Cu-concentrates containing enargite, and blends of the two materials can be achieved within 3–6 h at 80 °C under normal atmospheric pressure. The results also indicate that under high stirring rates, complete arsenic removal can be achieved for slurry or pulp densities as high as 1000 g/L.

## 2. Experimental

### 2.1. Samples

Copper ores and concentrate samples used in this work have been obtained from different sources or locations with differing amounts of copper and arsenic ranging from 10 to 40 wt.% and 0.8 to 14 wt.% for the two elements respectively, containing mainly enargite as the main carrier of arsenic in its structure. Ore samples were first prepared by crushing and grinding followed by sizing of both ores and concentrates to obtain size ranging from 35 to 75 mm for the leaching experiments. Samples with arsenic content below 1.0 wt.% were also blended with enargite ore with arsenic content over 8.0 wt.% to obtain a composite with arsenic content of 3.0 wt.%. Specific sample information including chemical analysis and phase distributions of all samples is given in Table 1 and a characteristic X-ray diffraction pattern of the enargite ore used is shown in Fig. 1. Enargite (sample (5)) having 8.32 wt.% arsenic will contain up to 43.7% enargite, assuming all arsenic is from enargite ( $\text{Cu}_3\text{AsS}_4$ ), and its copper content should give about 21 wt.% Cu since pure enargite normally contains 19.1% arsenic and 48.3% copper. A higher value of copper at 33% suggests that the enargite ore contains other copper bearing minerals, however, the contents are below detection limit and do not appear on the X-ray diffraction pattern.

Sodium hydrosulfide ( $\text{NaHS}$ : 70% purity) and sodium hydroxide ( $\text{NaOH}$ : 90% purity) reagents were supplied by Wako Chemicals, Japan for the preparation of high alkaline medium for conversion of  $\text{Cu}_3\text{AsS}_4$  to  $\text{Cu}_2\text{S}$ .

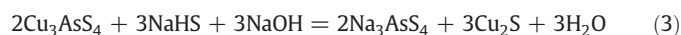
### 2.2. Experimental setup

All leaching experiments were conducted in a 200 mL Teflon beaker fully enclosed with a thermometer fixed for monitoring temperature and gas exhaust pipe as cooling system to prevent solution evaporation. The solution volume for leaching experiment was 100 mL for pulp density ranging from 100 to 600 g/L, and 50 mL for pulp density at 1000 g/L. The Teflon beaker was fully immersed in a water bath placed on a hot plate with magnetic stirrer.  $\text{NaHS}$  as leaching media and  $\text{NaOH}$  to maintain high pH and prevent sulfur hydrolysis were added at 50–200 g/L. After adjusting temperature to

the set point, solid feed containing arsenic was introduced into the solution and the slurry was stirred continuously with a magnetic stirrer at 500–750 rpm. The slurry temperature was varied from one experiment to another from 30 to 95 °C to evaluate effect of temperature. However, most tests were conducted at 80 °C and the leaching time was varied from 10 min to 10 h. At the end of each experimental run, the solids were separated from solution by filtration. The filtrate and the residue were analyzed for their chemical and mineralogical compositions.

### 2.3. The leaching mechanism

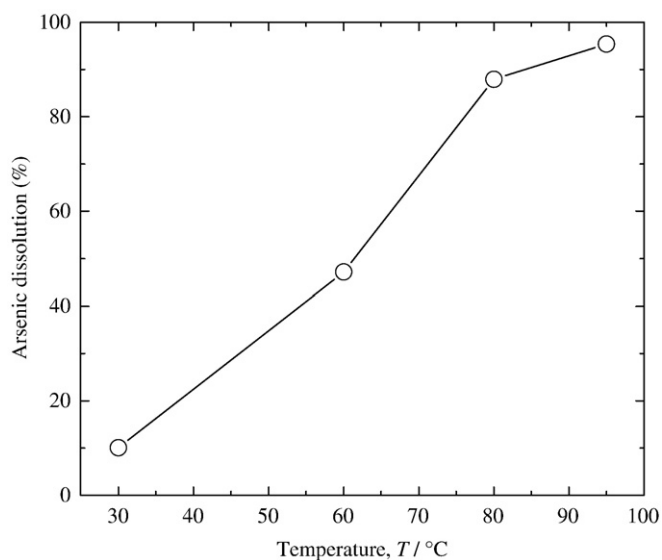
The transformation or leaching mechanism of enargite ( $\text{Cu}_3\text{AsS}_4$ ) to  $\text{Cu}_2\text{S}$  in NaHS and NaOH media can be represented by Reaction (3) below. The dissociation of NaHS added as a leaching medium can be represented by Reaction (4), which further dissociates to provide  $\text{S}^{2-}$  as shown by Reaction (5) in the presence of  $\text{OH}^-$  (NaOH). Therefore, maintaining high pH in high alkaline region ( $>12.5$ ) prevents the hydrolysis of the  $\text{S}^{2-}$  ions to  $\text{HS}^-$ , and maintains a high concentration of  $\text{S}^{2-}$  ions to dissolve arsenic from  $\text{Cu}_3\text{AsS}_4$ .



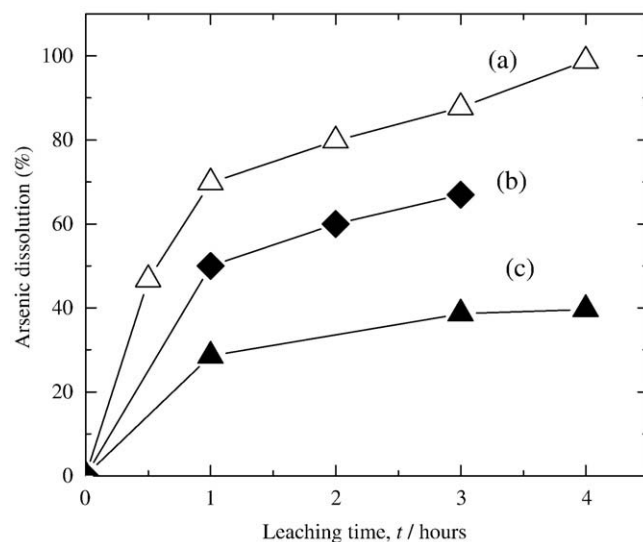
The stoichiometric requirements according to Reaction (3), show that 1 mol of arsenic would require 1.5 mol of sulfur ( $\text{S}/\text{As} = 1.5$ ) for dissolution of arsenic from enargite. The transformation of  $\text{Cu}_3\text{AsS}_4$  to  $\text{Cu}_2\text{S}$  as represented by Reaction (3) in NaHS media is similar to that represented by Reaction (1) for  $\text{Na}_2\text{S}$ . NaHS was chosen as reagent for this work due to its application in copper flotation and higher sulfur content (2 to 3 times higher).

### 2.4. Characterization and analyses

X-ray powder diffraction (XRD) analysis was carried out using Rigaku, RINT-2200/PC system with a  $\text{CuK}\alpha$  irradiation source ( $\lambda = 1.5405 \text{ \AA}$ ) at 40 kV and 50 mA for starting samples and residues after leaching to observe changes in phase formations. Samples were analyzed in a continuous scan mode between  $10^\circ$  and  $70^\circ 2\theta$ . Slurry



**Fig. 2.** Dissolution behavior of arsenic from Cu-concentrate (sample 3) at different temperatures. Leaching time was fixed at 3 h, pulp density at 500 g/L with NaHS ( $\text{S}/\text{As} = 12.3$ ) and NaOH additions at 100 g/L.



**Fig. 3.** Effect of NaHS and NaOH concentrations on arsenic dissolution as a function of leaching time at 80 °C and pulp density of 500 g/L. (a) Both NaHS/NaOH additions at 100 g/L ( $\text{S}/\text{As} = 12.3$ ); (b) NaOH addition at 50 g/L and NaHS addition at 100 g/L ( $\text{S}/\text{As} = 12.3$ ); (c) NaHS addition at 50 g/L and NaOH addition at 100 g/L ( $\text{S}/\text{As} = 6.1$ ).

solution pH and potential were measured both at the beginning and end of each leaching experiment using laboratory Eh/pH meters to observe changes and relate the Eh and pH conditions to enargite transformation. Analyses of filtrates and residues after dissolution in  $\text{HCl}/\text{HNO}_3$  (3:1) were carried out using an inductively coupled plasma (ICP-AES/OES) atomic/optical emission spectrometer, SPS-3000 (Seiko Instruments Inc.) to monitor dissolution and/or distribution of As, Cu and Fe during leaching.

## 3. Results and discussion

### 3.1. The effect of temperature

Initial evaluation of arsenic leaching was performed using Cu-concentrate (sample 3) with arsenic content of 1.67 wt.% for 3 h at temperatures ranging from 30 to 95 °C. The results obtained are shown in Fig. 2. Pulp density and NaHS additions were kept constant at 500 g/L and 100 g/L respectively with NaOH addition at 100 g/L. At this pulp density and NaHS addition, the ratio of sulfur to arsenic ( $\text{S}/\text{As} = \text{mol/mol}$ ) is 12.3 and that of sulfur to copper ( $\text{S}/\text{Cu} = \text{mol/mol}$ ) is 4.5. At 30 °C, the arsenic dissolution reached only 10% after 3 h. However, as the temperature is increased, the arsenic dissolution increases significantly and reaches over 47% at 60 °C, 88% at 80 °C, and over 95% at 95 °C. The main objective in this work is to find optimum conditions to reduce arsenic content in all samples to below 0.5 wt.%, a requirement for smelters treating materials containing arsenic.

For this sample, arsenic dissolution of up to 70% is required to reduce its content from 1.67 wt.% to below 0.5 wt.%, which according to Fig. 2, has been achieved within 3 h at 80 °C, but at a very high  $\text{S}/\text{As}$  ratio of 12.3 which is over 8 times stoichiometric requirement ( $\text{S}/\text{As} = 1.5$ ) as indicated by Reaction (3). Analysis of leach residue obtained after leaching at 80 °C for 3 h showed arsenic content of 0.22 wt.%. Based on this result, all leaching experiments were conducted at 80 °C and leaching times varied from 10 min to 10 h.

### 3.2. The effect of NaHS and NaOH concentration

The effect of both NaHS and NaOH during leaching of Cu-concentrate (sample 3) with arsenic content at 1.67 wt.% while keeping temperature constant at 80 °C, pulp density at 500 g/L and varying leaching time from 30 min to 4 h is shown in Fig. 3. At 100 g/L

each of NaHS and NaOH additions ( $S/As = 12.3$ ), arsenic dissolution rapidly increases to 70% in the first 1 h and further increases to over 85% within 3 h and near complete dissolution is achieved in 4 h. The result shows that arsenic content in this sample could be reduced to below 0.5 wt.% within 1–2 h at 80 °C and with NaHS–NaOH additions of 100 g/L (Fig. 3(a)).

However, dissolution of arsenic significantly decreases when either NaHS or NaOH addition is reduced to 50 g/L. Retaining NaHS addition at 100 g/L ( $S/As = 12.3$ ) and reducing NaOH addition to 50 g/L (Fig. 3(b)), overall dissolution of arsenic only reaches 70% in 3 h. Reducing NaHS addition to 50 g/L ( $S/As = 6.1$ ) while retaining NaOH addition at 100 g/L (Fig. 3(c)), overall dissolution of arsenic does not exceed 40% under the same conditions within 4 h. This result indicates that at 500 g/L pulp density and leaching temperature of 80 °C, concentration of both NaHS and NaOH of at least 100 g/L ( $S/As = 12.3$ ) is required to reduce arsenic content in the sample to below 0.5 wt.% within 1–4 h. The stoichiometric requirement for sulfur per mole of arsenic ( $S/As$ ) as indicated by Reaction (3) is 1.5. However, sample (3) is a copper concentrate sample with chalcopyrite ( $CuFeS_2$ ) and iron sulfide ( $FeS$ ) as main constituents, and high  $S/As$  ratio requirement indicates that arsenic is difficult to dissolve as it may be contained in the other copper and iron sulfides that do not easily dissolve. Also a decrease in NaOH addition to 50 g/L resulted in a decrease of slurry pH to below 12.3 from a high of pH over 13, and this could be attributed to a decrease of  $S^{2-}$  ions in solution due to hydrolysis of  $S^{2-}$  to  $HS^-$  as pH approaches pH 12 (Delfini et al., 2003). In most tests the slurry pH and potential (Eh vs. SHE) measured throughout all leaching experiments showed pH values ranging consistently over 12.5–13.5 and Eh values ranging between  $-500$  and  $-550$  mV. The measured Eh and pH values in this region of the (copper–sulfur–arsenic–water) on the Eh–pH diagrams correspond to  $Cu_2S$  and  $S^{2-}$  as dominant phases and/or species indicating that a transformation of  $Cu_3AsS_4$  to  $Cu_2S$  can be theoretically achieved (Mihajlovic et al., 2007; Curreli et al., 2005; Jackson, 1986).

### 3.3. The effect of pulp density

The effect of pulp density from 100 to 600 g/L was investigated to determine the highest pulp density at which arsenic content in the samples could be successfully reduced to below 0.5 wt.% within 6 h of leaching time, while keeping NaHS/NaOH additions at 100 g/L and leaching temperature constant at 80 °C. As shown in Fig. 4, at 600 g/L ( $S/As = 10.2$ ), the leaching rate is slightly lower than at

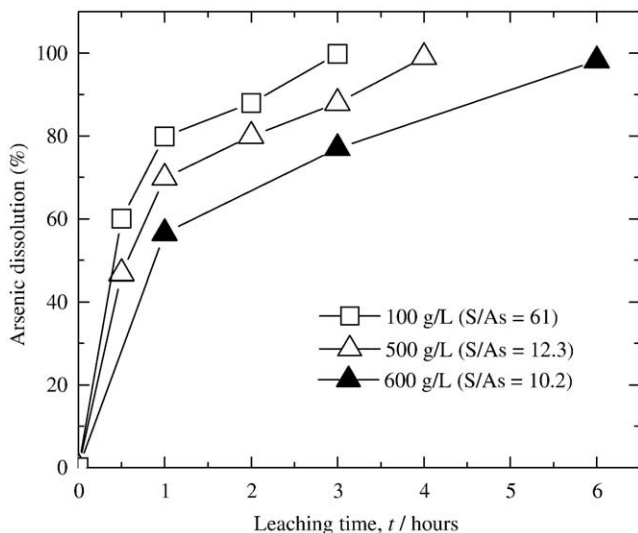


Fig. 4. Dissolution behavior of arsenic from Cu-concentrate (sample (3)) at different pulp densities as a function of leaching times at 80 °C. Additions of NaHS and NaOH were kept constant at 100 g/L each.

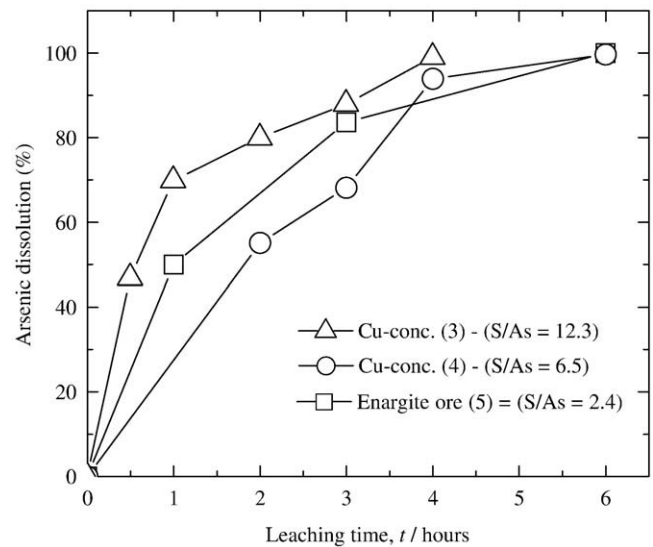


Fig. 5. Arsenic dissolution as a function of leaching time for both concentrate and enargite ore samples at 80 °C. Pulp density, and NaHS and NaOH additions were kept constant at 500 g/L and 100 g/L respectively.

500 g/L ( $S/As = 12.3$ ) and arsenic dissolution reaches 70% after 2 h, but, it is also clear that arsenic content can be reduced to below 0.5 wt.% within 3 h and complete dissolution could be achieved within 6 h. A much higher rate of arsenic dissolution is achieved for a lower pulp density at 100 g/L ( $S/As = 61$ ), but at a very high sulfur/arsenic ratio of 61. Up to 80% arsenic dissolution is achieved within 30 min and complete removal of arsenic is achieved in 3 h. This result shows that under similar leaching conditions of NaHS, NaOH additions and temperature at 80 °C a high dissolution of arsenic can be achieved at relatively high pulp densities, but, with  $S/As$  molar  $> 10$  which is more than 8 times stoichiometric requirement ( $S/As = 1.5$ ) to reduce arsenic content to  $< 0.5$  wt.% within 6 h.

### 3.4. The effect of arsenic content on leaching

The arsenic dissolution behavior of other copper ore and concentrate samples were investigated while maintaining leaching conditions of temperature, pulp density, and NaHS and NaOH additions at 80 °C, 500 g/L, and 100 g/L respectively and varying leaching time from 30 min to 6 h. Fig. 5 shows arsenic dissolution of Cu-concentrate (sample (4)) with arsenic content of 3.11 wt.% ( $S/As = 6.5$ ) and enargite ore (sample (5)) with arsenic content of 8.32 wt.% ( $S/As = 2.4$ ) and both results compared to that of sample (3) ( $S/As = 12.3$ ) as discussed in Sections 3.2 and 3.3 above.

Target arsenic dissolutions for each of the samples used in this work to reduce arsenic content to below 0.5 wt.% as computed and actual arsenic dissolution results obtained from 4 to 6 h of leaching are shown in Table 2. Samples (1) and (2) due to low arsenic content would require from 40 to 50% dissolution of arsenic to obtain a product with arsenic content below 0.5 wt.%. However, both samples were not treated separately but blended with sample (5) to prepare samples (6) and (7) respectively. The results show that over 98% of arsenic in sample (3) was dissolved within 4 h and arsenic dissolution for samples (4) and (5) reached 90–98% from 4 to 6 h. Analysis of the leach residues by ICP obtained after dissolution for arsenic content corresponds well with filtrate or leach solution analysis discussed in sections above with arsenic content in all leach residues remaining below 0.5 wt.%.

Fig. 6 shows arsenic dissolution behavior of sample (7) [enargite ore (sample (5)) + Cu-conc. sample (1)] with arsenic content at 3.0 wt.%. Pulp density of the blended sample was varied at 500–1000 g/L and NaHS addition was varied accordingly to maintain  $S/As$  molar ratio at 6.7

**Table 2**

Analysis of solid samples for arsenic distribution both before and after leaching of samples with varying amounts of arsenic content.

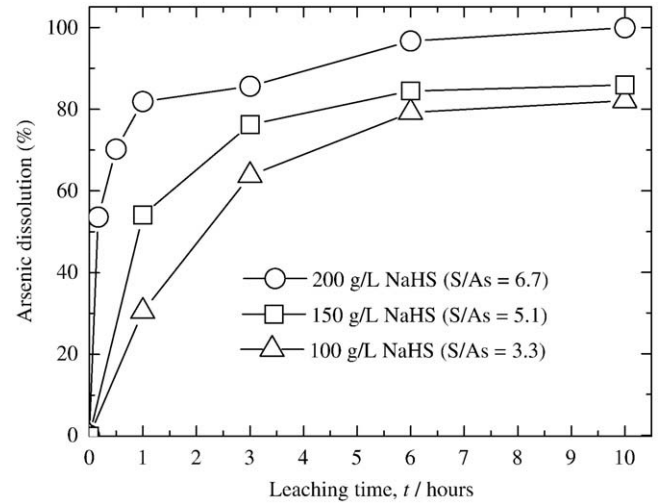
Sample	Arsenic content (wt.%)		As dissolution (%)	
	Original sample	Leach residue	Target	Actual
(1) Cu conc.	0.81	–	38.27	–
(2) Cu conc.	0.95	–	47.37	–
(3) Cu conc.	1.67	0.35	70.06	79.04
(4) Cu conc.	3.11	0.40	83.92	87.14
(5) Enargite ore	8.32	0.50	93.99	93.99
(6) Mixture (1) + (5)	3.00	0.30	83.33	90.00
(7) Mixture (2) + (5)	3.00	0.30	83.33	90.00

Leaching conditions: pulp density at 500 g/L, NaHS and NaOH additions at 100 g/L each, temperature and time at 80 °C and 4 h respectively.

(–) No separate leaching experiments conducted.

in solution. This result is discussed together with that of sample (5). At 3.0 wt.% arsenic, a total dissolution of 83% is required to reduce arsenic content to below 0.5 wt.% as compared to enargite, requiring 94% arsenic dissolution. It is interesting to note that arsenic dissolution of sample (7) at 1000 g/L achieved dissolution of up to 80% in the first 1 h, and proceeds slowly until over 95% of arsenic is dissolved into solution in 6 h. The same sample at 500 g/L also undergoes a rapid dissolution in the first 1 h and reaches over 80% dissolution in 6 h. Original enargite (sample (5)) as discussed in previous sections, achieves complete dissolution of arsenic within 6 h. These results together with solids residue analysis given in Table 2 clearly indicate that arsenic in individual samples, enargite ore, or samples with low arsenic content blended with samples with high arsenic content can be successfully treated, even at very high pulp density such as 1000 g/L within 6 h of leaching at 80 °C.

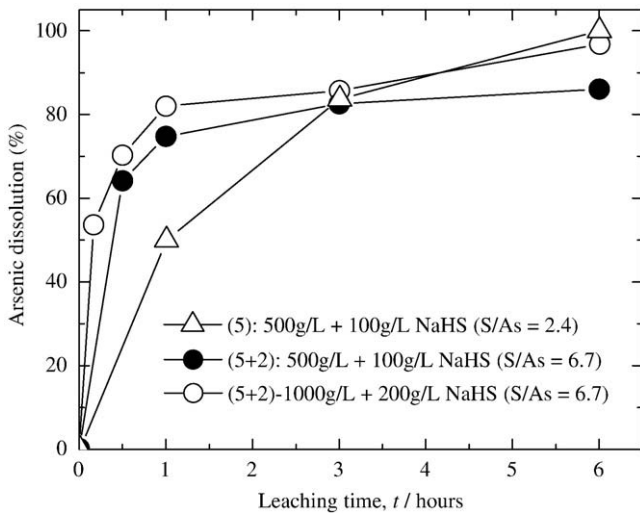
Varying addition of NaHS and NaOH to observe arsenic dissolution of sample (7) with a pulp density of 1000 g/L was performed and the results are shown in Fig. 7. At 200 g/L NaHS addition ( $S/As = 6.7$ ) over 80% of arsenic is dissolved in 1 h and reaches over 95% in 6 h and total dissolution is achieved in 10 h. Decreasing NaHS addition to 150 g/L ( $S/As = 5.1$ ) and 100 g/L ( $S/As = 3.4$ ), the arsenic dissolution is reduced accordingly and reaches 70–80% in 6 h, after which it remains consistent at prolonged leaching up to 10 h. This result suggests that an  $S/As$  molar ratio of at least 6 is required from a stoichiometric requirement of  $S/As = 1.5$  (Reaction (3)) to reduce arsenic content



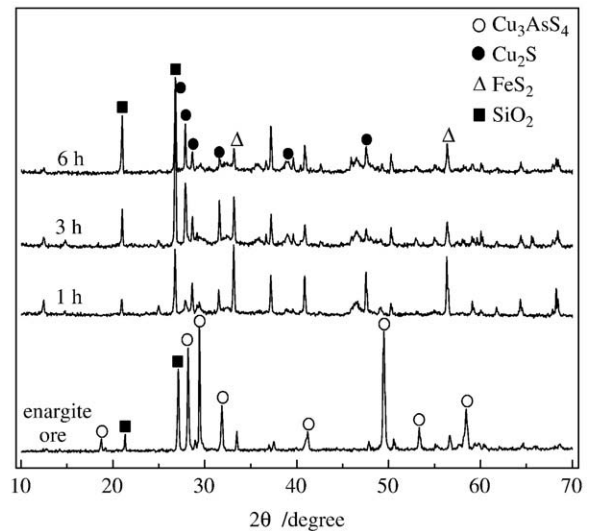
**Fig. 7.** Arsenic leaching behavior of blended sample (7) with arsenic content at 3.0 wt.% at a very high pulp density of 1000 g/L. Effect of NaHS and NaOH addition on arsenic dissolution as a function of leaching time at 80 °C was investigated and aggressive stirring at 650–750 rpm was performed to keep sample evenly dispersed in slurry.

from 3.0 wt.% to below 0.5 wt.% for the Cu-concentrate samples mixed with enargite ore within 6 h.

X-ray diffraction analysis of starting enargite ore (sample (5)) with arsenic content of 8.32 wt.% and compared to leach residues obtained after leaching for different times (1, 3, 6 h) is shown in Fig. 8. The figure clearly shows near complete disappearance of characteristic peaks of  $Cu_3AsS_4$  from leach residues obtained after 1 h. This data correspond well with arsenic dissolution profile for enargite (sample (5)) in Fig. 5. On the other hand, characteristic peaks of  $Cu_2S$  clearly appear from residues obtained after 1 h leaching and their intensity increases significantly as leaching progresses. Transformation of  $Cu_3AsS_4$  to  $Cu_2S$  in NaHS media represented by Reaction (3) above is supported by these results. X-ray diffraction patterns for other samples did not show peaks of enargite due to low content of enargite in the Cu-concentrate samples and non-appearance of  $CuFeS_2$  peaks in solid residue after leaching enargite ore indicates that amount of  $CuFeS_2$  if present is below detection limit. Solution analysis does not show copper or iron dissolution indicating only conversion of  $Cu_3AsS_4$  to  $Cu_2S$ , so other copper and iron sulfide minerals if present



**Fig. 6.** Arsenic dissolution as a function of leaching time for enargite ore (sample (5)) with arsenic content of 8.32 wt.% and that of sample (5+2) blended mixture with arsenic content at 3.0 wt.%. Pulp density of mix sample was increased to 1000 g/L and leaching was conducted at 80 °C. NaOH addition was the same as that of NaHS and aggressive stirring at 650–750 rpm was performed to keep sample evenly dispersed in slurry.



**Fig. 8.** X-ray diffraction pattern of original enargite ore (sample (5)) and the leach residues obtained after leaching for different times at 80 °C. Pulp density, and NaHS and NaOH additions were kept constant at 500 g/L and 100 g/L respectively.

remain un-dissolved. Molar ratio of S/As during leaching of enargite ore (8.32 wt.% arsenic) at pulp density of 500 g/L and NaHS addition of 100 g/L was 2.4, which was over stoichiometric requirement ( $S/As = 1.5$ ) giving high arsenic dissolution within 6 h, but, we saw a significant decrease in arsenic dissolution when S/As molar ratio was reduced to below 2.0.

#### 4. Conclusions

The removal of arsenic as an impurity in copper ores and concentrates containing enargite ( $Cu_3AsS_4$ ) by leaching in NaHS and NaOH media was investigated in this work. The results obtained and discussed herein can be summarized as follows;

- The leaching of samples containing arsenic at 80 °C under normal atmospheric pressure showed that arsenic can be reduced to below 0.5 wt.% within 1–3 h for samples with arsenic content less than 4.0 wt.% and within 3–6 h for samples with arsenic content ranging from 8.0 to 10.0 wt.%.
- Mole sulfur ( $S^{2-}$ ) required per arsenic mole (S/As) for  $Cu_3AsS_4$  conversion to  $Cu_2S$  varied for different samples. Cu-concentrate samples with arsenic content less than 4.0 wt.% showed that complete arsenic dissolution can be achieved at S/As molar ratio above 12. For a blended sample, an S/As molar ratio above 6.0 was required to completely dissolve arsenic into solution. Similarly, leaching of enargite ore showed that S/As molar ratio of 2.0 was able to completely dissolve arsenic. The S/As molar ratio used was consistently above the stoichiometric requirement of  $S/As = 1.5$ .
- It was also demonstrated that over 98% of arsenic in samples treated can be removed, even for pulp densities as high as 1000 g/L within 6 h.
- Under all leaching conditions of temperature, pulp density, NaHS and NaOH concentrations, dissolution of Cu and Fe from the samples was not detected in the leach solutions, but their contents in the solids slightly increased due to the dissolution of arsenic.
- The enargite phase ( $Cu_3AsS_4$ ) was transformed to  $Cu_2S$  as a result of reduction of  $As^{5+}$  in enargite being reduced to  $As^{3+}$  ( $Na_3AsS_4$ ) by  $S^{2-}$  offered by NaHS. X-ray diffraction patterns and solution pH/potential values consistent at over 12.5 and from  $-500$  to  $-550$  mV (vs. SHE) respectively correspond well with these results.
- Blending of Cu-concentrate with arsenic content below 1.0 wt.% and enargite ore with arsenic content over 8.0 wt.% for leaching gives promising results. Over 90% of arsenic dissolution was achieved within 6 h for sample leached at very high pulp density of 1000 g/L.

Arsenic in Cu-ores and concentrates can be successfully removed by leaching in NaHS/NaOH media as shown by the results in this work. Complete removal of arsenic at 1000 g/L gives a positive indication that a process can be put together to treat Cu-resources with high arsenic content. More work will be done to investigate options for treatment of solutions with dissolved arsenic and can be incorporated into the leaching process.

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## Selective leaching of arsenic from enargite in NaHS–NaOH media

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Leaching kinetics

### ABSTRACT

The dissolution kinetics of arsenic from enargite ( $\text{Cu}_3\text{AsS}_4$ ) was investigated in sodium hydrosulfide (NaHS) solution of concentration range 0.68 M–1.35 M  $\text{S}^{2-}$  and 1.25 M  $\text{OH}^-$  (NaOH) in the temperature range from 298 K to 363 K. The kinetic equation from evaluation of experimental data using several heterogeneous and pseudo-homogeneous reaction models was found to be  $1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha) = kt$  and from the Arrhenius plot, using  $k$  values determined experimentally, an activation energy of  $70.26 \pm 4.74$  kJ/mol was obtained. This result indicates that the rate-determining process for the reaction between  $\text{Cu}_3\text{AsS}_4$  and NaHS is controlled by product layer diffusion process. Characterization of solid samples by XRD and chemical analysis by ICP showed that  $\text{Cu}_3\text{AsS}_4$  was transformed to  $\text{Cu}_2\text{S}$  and complete removal of arsenic into solution can be achieved within 60 to 120 min.

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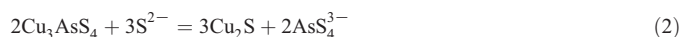
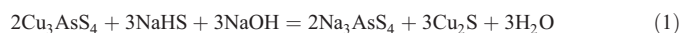
### 1. Introduction

Enargite ( $\text{Cu}_3\text{AsS}_4$ ) and tennantite ( $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ ) are the main minerals with high arsenic content that associate with copper and iron sulfides [covellite ( $\text{CuS}$ ), chalcocite ( $\text{Cu}_2\text{S}$ ), chalcopyrite ( $\text{CuFeS}_2$ ), Bornite ( $\text{Cu}_5\text{FeS}_4$ ), pyrite ( $\text{FeS}_2$ )] and are normally recovered by flotation and offered as copper resource to smelters for copper recovery. However the high content of arsenic effectively reduces value of the copper resource due to environmental implications of toxic arsenic that require additional processing steps for containment of arsenic. As demand for copper continues to grow, the need to source copper from all resources including those that contain high arsenic is necessary and as such more economical and environmentally friendly processing options will be sought. Reviews on copper resources containing enargite are covered widely in literature by many researchers (Lattanzi et al., 2008; Filippou et al., 2007; Mihajlovic et al., 2007; Baláž and Achimovičová, 2006a; Guo and Yen, 2005; Viñals et al., 2003; Welham, 2001; Padila et al., 1998).

For copper ores and concentrates with high arsenic contained as enargite for feed to smelters, first, separation by flotation to obtain a clean concentrate with arsenic content <0.5 wt.% and a dirty reject mainly containing enargite by employing slurry potential and pH control with depressants and activators can be achieved and is discussed in literature (Filippou et al., 2007; Senior et al., 2006; Guo and Yen, 2005; Kantar, 2002; Fornasiero et al., 2001; Pauporté and Schuhmann, 1996; Menacho et al., 1993). In the second case involving leaching, the transformation of enargite to  $\text{CuO}$  or  $\text{Cu}_2\text{S}$  by selectively dissolving

arsenic into solution with sodium hypochlorite ( $\text{NaClO}$ ) or sodium sulfide ( $\text{Na}_2\text{S}$ ) in alkaline solutions with NaOH gives very promising results (Lattanzi et al., 2008; Mihajlovic et al., 2007; Filippou et al., 2007; Baláž and Achimovičová, 2006a,b; Curreli et al., 2005; Delfini et al., 2003; Viñals et al., 2003; Delfini et al., 2003; Baláž et al., 2000; Jackson, 1986). Other hydrometallurgical treatment options through chloride and sulfates leaching, or in ammonical solutions and at elevated temperatures and pressures is reported elsewhere in literature (Filippou et al., 2007; Viñals et al., 2003; Canales et al., 2002; Herreros et al., 2002; Dutrizac and MacDonald, 1971).

In a recent study, Tongamp et al. (2009) have introduced sodium hydrosulfide (NaHS) as a leaching media for the conversion of enargite ( $\text{Cu}_3\text{AsS}_4$ ) to  $\text{Cu}_2\text{S}$  in NaHS–NaOH solution. They have shown that near complete removal of arsenic (>99%) in enargite can be achieved within 4 to 6 h even for very high pulp density at 1000 g/L and have proposed Reaction (1) as overall reaction to represent conversion of  $\text{Cu}_3\text{AsS}_4$  to  $\text{Cu}_2\text{S}$  in NaHS–NaOH media. NaHS dissociates to provide  $\text{S}^{2-}$  to substitute arsenic in enargite and NaOH addition maintains high alkaline environment, preventing hydrolysis of  $\text{S}^{2-}$  to  $\text{HS}^-$  and allow Reaction (1) to proceed. This reaction mechanism could be simplified to show direct role of  $\text{S}^{2-}$  ions offered by NaHS in the conversion of enargite or leaching of arsenic according to Reaction (2).



The behavior of enargite conversion in NaHS media is very similar to that of sodium sulfide ( $\text{Na}_2\text{S}$ ) (Filippou et al., 2007; Baláž and Achimovičová, 2006a,b; Delfini et al., 2003; Baláž et al., 2000), however, selection of NaHS was based on its application in copper flotation

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and also its higher sulfur content (~43%) per unit mole NaHS as compared to Na<sub>2</sub>S (~13%) since leaching of arsenic from enargite is a function of sulfur [S<sup>2-</sup>] concentration.

In the current study, the effects of particle size, slurry stirring rate, NaHS concentration and temperature were investigated to study the reaction kinetics of enargite in NaHS–NaOH media and identify the rate-determining process for Cu<sub>3</sub>AsS<sub>4</sub> in NaHS–NaOH media.

## 2. Experimental

### 2.1. Materials

The enargite ore sample (Mt Jinga, Taiwan) was first prepared by crushing/milling and sizing to obtain four size ranges: –125 + 100 μm, –100 + 75 μm, –75 + 32 μm, and –32 μm. Chemical composition of main elements was: 3.5 to 4.0 wt.% As, 12.0 to 12.6 wt.% Cu, and 20 to 24 wt.% Fe (Table 1) and X-ray diffraction pattern showed Cu<sub>3</sub>AsS<sub>4</sub>, SiO<sub>2</sub>, and FeS<sub>2</sub> as main mineral constituents, shown in Fig. 1. The *d*-spacing values for enargite and corresponding 2θ degrees are 3.22Å(28.58°), 3.21Å(28.68°), 3.07Å(30.12°), 2.84Å(32.85°), 1.85Å(56.38°) and they correspond well with the peaks identified in Fig. 1 and the *d*-spacing values calculated from the XRD pattern are 3.28Å(28°), 3.18Å(29°), 2.91Å(32°) and 1.86Å(56°). Assuming all arsenic is hosted as enargite, the ore sample contains up to 20.5 wt.% enargite and will contain about 9.4 wt.% copper, a slightly higher value over 12 wt.% Cu could be due to presence of other copper bearing minerals.

Sodium hydrosulfide (NaHS, 70% purity) and sodium hydroxide (NaOH, 90% purity) chemical grade reagents supplied by Wako Chemicals, Japan were used to prepare NaHS–NaOH alkaline solution for leaching of arsenic or conversion of Cu<sub>3</sub>AsS<sub>4</sub> to Cu<sub>2</sub>S.

### 2.2. Leaching

A 200 ml Teflon beaker fully enclosed with a thermometer fixed for monitoring temperature, exhaust line to prevent solution evaporation, and opening for sampling was used for all leaching experiments. Into the beaker, 150 ml leaching solution (50 to 100 g/L (0.68 to 1.35 M) NaHS + 50 g/L (1.25 M) NaOH) was introduced, adjusted temperature to required test temperature from 298 to 363 K and added 1.0 g of enargite sample. All tests for kinetic study were performed for 120 min and at varying stirring rate from 360 to 550 rpm. A 5 ml sample was continuously drawn from the leach slurry at specified time intervals (5, 10, 20, 30, 60, 90, and 120 min) for analysis of dissolved arsenic. Solid samples after experimental run were separated from solution for both chemical and phase analyses.

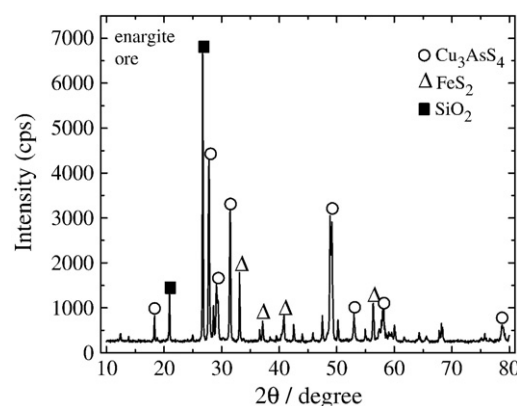
### 2.3. Characterization and chemical analyses

X-ray diffraction (XRD) measurements were performed by using Rigaku, RINT-2200/PC system with a Cu Kα irradiation source (λ = 1.5405 Å) at 40 kV and 50 mA. Samples were analyzed in a continuous scan mode between 10° and 80° 2θ. Slurry solution pH and potential were measured for every test using laboratory Eh/pH meters. All solution analysis was conducted using an Inductively Coupled Plasma (ICP-AES/OES) atomic/optical emission spectrometer, SPS-3000 (Seiko Instruments Inc.).

**Table 1**

Chemical contents for the enargite ore separated into different size fractions.

Size fraction (μm)	Chemical analysis (wt.%)		
	As	Cu	Fe
–75 + 32	3.65	12.32	23.37
–100 + 75	3.68	12.19	21.20
–125 + 100	3.91	12.53	20.10



**Fig. 1.** Characteristic X-ray diffraction pattern of enargite ore with arsenic content of 3.65 wt.%.

## 3. Results and discussion

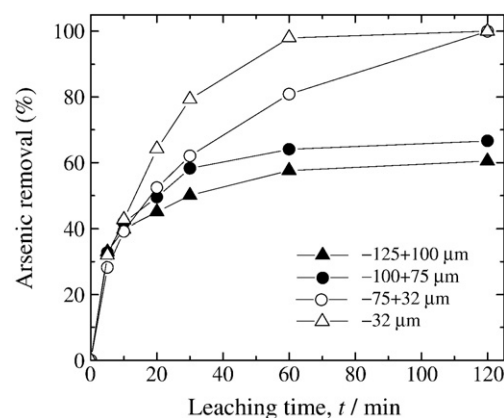
### 3.1. Effect of particle size

At fixed reagent concentration (100 g/L (1.35 M) NaHS + 50 g/L (1.25 M) NaOH) and slurry temperature (353 K), arsenic leaching behavior of 1.0 g enargite sample in 150 ml solution for the four size fractions was investigated. According to Fig. 2, arsenic leaching from all the four size fractions rapidly reached up to 40% in the first 10 min. As leaching is progressed, arsenic removal from –32 μm proceeds faster reaching 80% in 30 min and complete arsenic removal observed within 60 min. The –75 + 32 μm fraction also proceeds faster reaching 80% in 60 min and over 99% in 120 min. However, arsenic removal for –100 + 75 μm and –125 + 100 μm proceeds slowly and remains consistently below 60% throughout the 120 min leaching period. The result generally indicates higher arsenic removal for the smaller size fraction which is attributed to by increased surface area of the sample.

### 3.2. Effect of NaHS concentration

The leaching profile of the –75 + 32 μm enargite fraction in NaHS solution of different concentrations; 50 (0.68 M), 75 (1.01 M), 100 g/L (1.35 M) + 50 g/L (1.25 M) NaOH for 120 min is shown in Fig. 3.

Slurry temperature and stirring rate were fixed at 353 K and 550 rpm respectively. At 100 g/L (1.35 M) NaHS addition, over 99% arsenic is removed within 120 min, however, the leaching rate decreases when NaHS concentration is reduced to 75 (1.01 M) and 50 g/L (0.68 M), reaching up to 85% and 55% for the two NaHS concentrations respectively in 120 min. Low arsenic removal at 50 and 75 g/L NaHS



**Fig. 2.** Leaching arsenic from enargite ore of different size fractions at 353 K and slurry stirred at 550 rpm for 120 min. NaHS concentration at 100 g/L (1.35 M) and NaOH at 50 g/L (1.25 M).



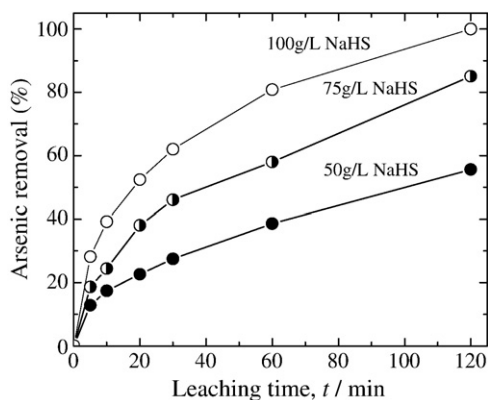


Fig. 3. Leaching arsenic from enargite ore ( $-75 + 32 \mu\text{m}$ ) in NaHS–NaOH solution with varying NaHS concentrations at 353 K, stirring rate 550 rpm for 120 min. NaOH concentration fixed at 50 g/L (1.25 M).

addition could be attributed to by hydrolysis of  $\text{S}^{2-}$  ions to  $\text{HS}^-$  ions as in both cases pH values decreased from 13.7 for 100 g/L NaHS addition to below pH 12.7 and pH 12.3 for 75 and 50 g/L NaHS respectively. For tests at 100 g/L NaHS addition, the slurry pH and potential (Eh vs. SHE) remained consistently over 13.5 and Eh values ranging from  $-500$  to  $-550$  mV.

The measured Eh and pH values in this region of the (copper–sulfur–arsenic–water) on the Eh–pH diagrams correspond to  $\text{Cu}_2\text{S}$  and  $\text{S}^{2-}$  as dominant phases and/or species indicating that a transformation of  $\text{Cu}_3\text{AsS}_4$  to  $\text{Cu}_2\text{S}$  can be theoretically achieved, however, on reduction of NaHS concentration, slurry pH was observed to decrease approaching pH 12, this could attribute to decrease in arsenic dissolution due to low  $\text{S}^{2-}$  concentration from reduced addition and hydrolysis of  $\text{S}^{2-}$  to  $\text{HS}^-$  (Mihajlovic et al., 2007; Curreli et al., 2009; Delfini et al., 2003; Jackson, 1986).

### 3.3. Effect of stirring rate

The leaching behavior of arsenic in 100 g/L (1.35 M) NaHS + 50 g/L (1.25 M) NaOH for the 1.0 g sample ( $-75 + 32 \mu\text{m}$  fraction) at 353 K under three different stirring rates is shown in Fig. 4. The result clearly shows an increase in arsenic leaching rate with increase in slurry stirring speed. At 550 rpm, over 99% of arsenic removal is achieved within 120 min; however, on decrease in stirring speed arsenic removal proceeds slower and reaches 89 and 82% in 120 min for 360 and 200 rpm respectively. This result suggests that the leaching of

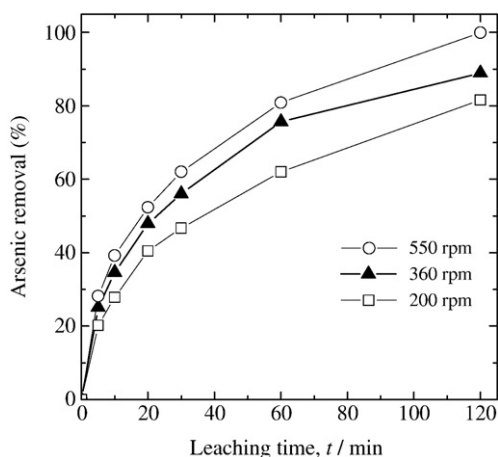


Fig. 4. Leaching arsenic from enargite ore ( $-75 + 32 \mu\text{m}$ ) in 100 g/L (1.35 M) NaHS + 50 g/L (1.25 M) NaOH solution at different stirring rates. Temperature was kept constant at 353 K for 120 min.

enargite in NaHS–NaOH media is of diffusion control, since a chemical reaction controlled process would show not much effect of stirring speed on the leaching rate.

### 3.4. Effect of temperature

The influence of temperature on arsenic dissolution was investigated by conducting experiments at: 298 K to 363 K using the  $-75 + 32 \mu\text{m}$  enargite fraction while keeping reagent concentrations fixed at 100 g/L (1.35 M) NaHS + 50 g/L (1.25 M) NaOH and the results obtained are shown in Fig. 5.

These data show that temperature exerts the most significant effect on arsenic dissolution rate. At 298 K, arsenic dissolution reached only 13% in 30 min and shows no improvement after that. Increasing temperature to 313 K, arsenic dissolution reaches 20% in the first 30 min and reaches 36% in 120 min. Further increase in temperature to 333, 343, 353 and 363 K, arsenic dissolution significantly increases reaching over 99% in 120 min for sample leached at 353 K and over 99% in 90 min for sample leached at 363 K.

Characteristic X-ray diffraction pattern of the enargite ore sample and the leached residue sample obtained after 120 min in 100 g/L (1.35 M) NaHS + 50 g/L (1.25 M) NaOH solution at 353 K is given in Fig. 6. Characteristic peaks of  $\text{Cu}_3\text{AsS}_4$  ( $d$ -spacing values) and corresponding  $2\theta$  degrees;  $3.22\text{\AA}$ ( $28.58^\circ$ ),  $3.21\text{\AA}$ ( $28.68^\circ$ ),  $3.07\text{\AA}$  ( $30.12^\circ$ ),  $2.84\text{\AA}$ ( $32.85^\circ$ ),  $1.85\text{\AA}$ ( $56.38^\circ$ ) are completely removed from the original sample and clear peaks of  $\text{Cu}_2\text{S}$  appear in the leached residue. The same authors (Tongamp et al. (2009)) have obtained similar results with enargite ore containing higher arsenic content at  $>8$  wt.%, and the XRD peaks correspond well with arsenic dissolution data and the reaction mechanisms (1) and (2).

### 3.5. Leaching kinetics

The rate of reaction between solid particles and leaching reagent could be determined by a non-catalytic heterogeneous model such as diffusion through the fluid film, diffusion through product layer, or one involving surface chemical reaction. Experimental results obtained at different temperatures in this work have been evaluated using several kinetic models;  $1 - (1 - \alpha)^{1/3}$  and  $1 - (1 - \alpha)^{2/3}$  (interface/surface chemical reaction control models) and diffusion controlled mechanisms;  $1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha)$  and  $(1 - 2/3\alpha) - (1 - \alpha)^{2/3}$ . The diffusion controlled models were observed to produce good linearity and data from current work was analyzed using the shrinking core model or rate expression represented by Eq. (3) below:

$$1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha) = kt \quad (3)$$

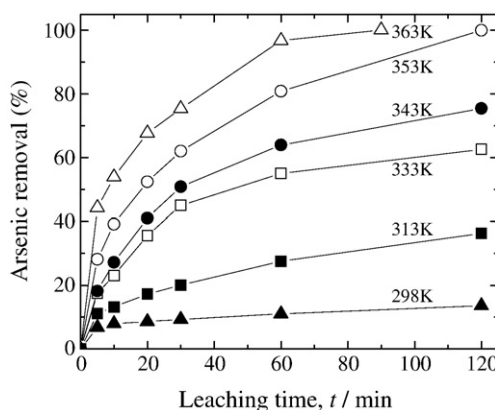
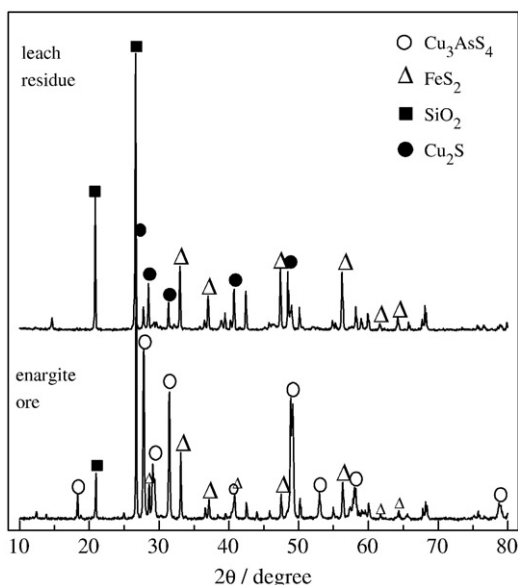


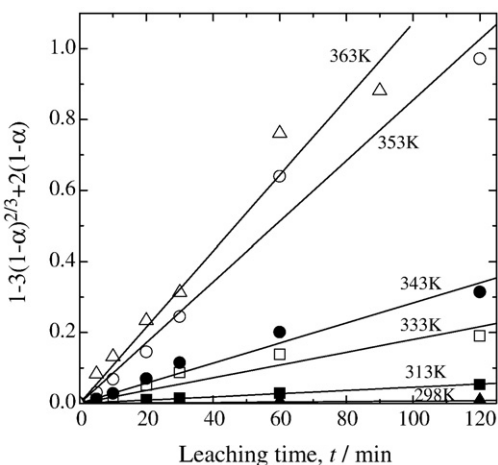
Fig. 5. Leaching arsenic from enargite ore ( $-75 + 32 \mu\text{m}$ ) at different temperatures in a 100 g/L (1.35 M) NaHS and 50 g/L (1.25 M) NaOH solution. Temperature at 353 K for 120 min and stirring rate fixed at 550 rpm.



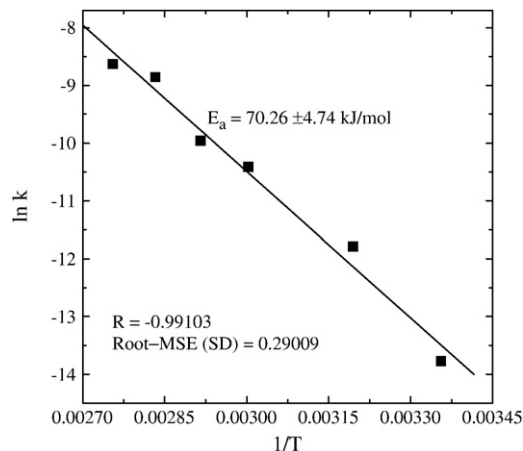
**Fig. 6.** X-ray diffraction pattern of original enargite ore used for the kinetic study and the leach residue obtained after leaching for different 120 min at 353 K. NaHS and NaOH additions were kept constant at 100 g/L respectively.

In the expression,  $k$  is the linear kinetic constant,  $t$  is the reaction time and  $\alpha$ , represents fraction arsenic removed from enargite. A linear relationship from the plot of reaction time ( $t$ ) versus  $1-3(1-\alpha)^{2/3}+2(1-\alpha)$  could confirm this model and Fig. 7 clearly supports the kinetic model chosen for linearization of the experimental results, giving correlation coefficients for the linear plots drawn through the origin consistently over 0.9 and nearing 1.0 for experiments above 313 K, confirming that leaching of arsenic from enargite in NaHS–NaOH solution is controlled by the diffusion mechanism as controlling step. Kinetic constant values from Fig. 7 were used to construct an Arrhenius plot for determination of activation energy as shown in Fig. 8, giving an excellent linear dependency of the kinetic constant with temperature. From the slope of the straight line in this figure, the activation energy was determined as  $70.26 \pm 4.74$  kJ/mol.

Baláz et al. (2000) report activation energy of 62 kJ/mol for enargite leaching in (100 g/L  $\text{Na}_2\text{S}$  + 50 g/L NaOH) from 333 to 363 K, this was achieved with the aid of mechanochemical activation of the enargite sample prior to leaching. With the aid of high-energy planetary mill, Baláz and Achimovičová (2006a,b) achieved a much higher activation energy of 182 kJ/mol for enargite in  $\text{Na}_2\text{S}$ –NaOH solution. Viñals et al.



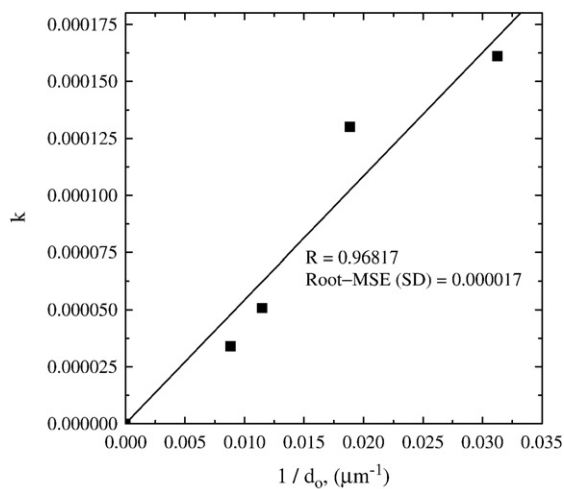
**Fig. 7.** Linearization of the experimental data (Fig. 5) of arsenic leaching from enargite ore in NaHS–NaOH solution using the chosen kinetic model ( $kt=1-3(1-\alpha)^{2/3}+2(1-\alpha)$ ).



**Fig. 8.** Arrhenius plot for arsenic leaching from enargite ore in NaHS–NaOH solution constructed from linear kinetic constant ( $k$ ) values from plots in Fig. 7.

(2003) report activation energy of 58 kJ/mol for enargite dissolution in NaClO–NaOH solution from 293 to 333 K. Mihajlovic et al. (2007) report activation energy of 30 kJ/mol for enargite concentrate dissolved in NaClO–NaOH solution from 298 to 333 K but 38 kJ/mol for isothermal roasting of the same enargite sample. Padilla et al. (2005) (65 kJ/mol), Welham (2001), (40 kJ/mol), Herreros et al. (2002) (14–21 kJ/mol), Dutrizac and MacDonald (1971) (55 kJ/mol) report varying activation energies for enargite dissolution in sulfate and chloride solutions.

Further investigations to confirm applicability of the kinetic model ( $1-3(1-\alpha)^{2/3}+2(1-\alpha)$ ), Eq. (3) by obtaining plots for linearity between kinetic constants ( $k$ ) obtained from experiment for the different size fractions and varying NaHS concentrations against inverse of initial particle size and sulfide concentrations respectively was performed. A plot of kinetic constant ( $k$ ) versus inverse of initial particle size ( $1/d_o$ ) shows a linear relationship with correlation coefficient at 0.96817 as shown in Fig. 9 supporting application of the kinetic model used in this work. Fig. 10 shows plot of  $(1-3(1-\alpha)^{2/3}+2(1-\alpha))$  versus time ( $t$ ) for tests conducted at different NaHS concentrations producing excellent linear relationship with correlation coefficients all above 0.99. A plot of  $\log k$  versus  $\log [S^{2-}]$  as shown in Fig. 11 produced a good linear relationship with correlation coefficient of 0.9873. A plot of the kinetic model ( $1-3(1-\alpha)^{2/3}+2(1-\alpha)$ ) versus time ( $t$ ) for leaching performed at different slurry stirring rates represented in Fig. 4 also produced excellent linear relationship giving correlation coefficients above 0.99.



**Fig. 9.** Arsenic leaching rate dependency on the initial particle size of enargite ore in 100 g/L (1.35 M) NaHS and 50 g/L (1.25 M) NaOH solution. Leaching temperature was fixed at 353 K for 120 min and stirring rate at 550 rpm.

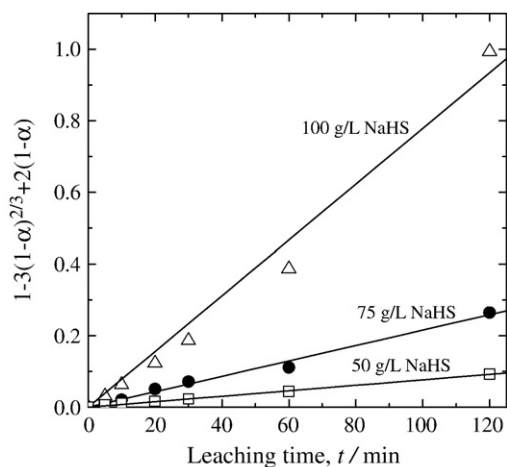


Fig. 10. Linearization of the experimental data (Fig. 3) of arsenic leaching from enargite ore in NaHS–NaOH solution at different NaHS concentrations for  $-75 + 32 \mu\text{m}$  fraction using the chosen kinetic model  $kt = 1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha)$ .

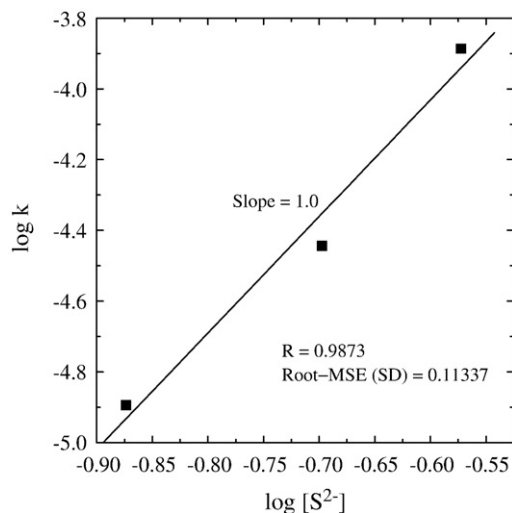


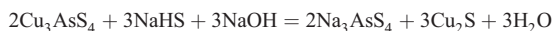
Fig. 11. A plot of the rate constant as a function of sulfide ion  $[S^{2-}]$  concentration during leaching of arsenic from enargite in NaHS–NaOH solution. Leaching temperature was fixed at 353 K for 120 min and stirring rate at 550 rpm.

As discussed in Section 3.2 above regarding NaHS addition and depicted by Reactions (1) and (2),  $S^{2-}$  ions offered by NaHS and its concentration and availability as  $[S^{2-}]$  plays main role in leaching or arsenic or conversion of enargite ( $\text{Cu}_3\text{AsS}_4$ ) to  $\text{Cu}_2\text{S}$ .

#### 4. Conclusion

The results presented for the current study can be summarized as follows;

- (1) Selective leaching of arsenic from enargite ( $\text{Cu}_3\text{AsS}_4$ ) and subsequent formation of  $\text{Cu}_2\text{S}$  in NaHS–NaOH system occurs according to the reaction:



- (2) The kinetics of arsenic leaching from enargite in NaHS–NaOH solution was well represented by the diffusion controlled model;  $kt = 1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha)$  and the activation energy was calculated to be  $70.26 \pm 4.74 \text{ kJ/mol}$ .

- (3) Linear dependency of experimental kinetic constant on the inverse of initial particle size and excellent linear relationship from plot of  $\log k$  versus  $\log [S^{2-}]$  with a slope of 1.0 confirms the applicability of the kinetic model chosen for the analysis of experimental data in this work.

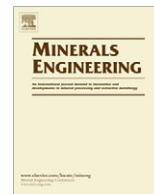
- (4) Increasing slurry stirring rate from 200 rpm to 550 rpm subsequently increased arsenic dissolution indicating the dissolution of arsenic is of diffusion mechanism. Linearization of this data using the chosen model produced excellent linear relationship.

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## A critical review of surface properties and selective flotation of enargite in sulphide systems

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### ABSTRACT

Arsenic contained in sulphides such as enargite, tennantite and arsenopyrite can represent a significant penalty element in base metals production. There are significant economic advantages to achieving a separation of arsenic bearing minerals at an early stage in processing, but to date no feasible widely applicable commercial method of separation at the flotation stage has been developed. This review focuses on the current state of knowledge in the selective flotation of enargite, commonly found in association with non-arsenic copper sulphide mineralisation. Due to its similar flotation properties with many other copper sulphides, enargite is typically recovered together with the copper minerals, producing a high arsenic bulk concentrate which is costly and problematic to process. Special consideration is given to the various approaches used in the study of the surface chemistry of enargite in different environments, and the implications for the flotation of enargite. Developments in the various approaches in the selective flotation of enargite are critically reviewed and discussed.

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### 1. Introduction

Arsenic can occur naturally in elemental form, but more commonly as a compound in several mineral types which include copper arsenic sulphides such as enargite ( $\text{Cu}_3\text{AsS}_4$ ) and tennantite ( $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ ), and associated arsenic-bearing minerals such as arse-

nopyrite ( $\text{FeAsS}$ ). It is a highly toxic inorganic pollutant, responsible for serious environmental and human health problems in several parts of the world. Specifically, arsenic emissions from downstream processing such as smelting must be captured and rendered inert for safe disposal. Such treatments are expensive and significant financial penalties are increasingly imposed to process concentrate containing typically more than 0.2 wt% arsenic. Arsenic in final copper concentrates is also undesirable in copper metal production. For example, arsenic is known to be detrimental

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to properties of copper metal such as electrical conductivity and annealability, both of which are critical for electrical copper (Biswas and Davenport, 1994; Cordova et al., 1997).

There are significant economic advantages to achieving a separation of arsenic bearing minerals at an early stage in processing, but to date no feasible widely applicable commercial method of separation at the flotation stage has been developed. Compared to other sulphide mineral types, relatively limited research has been carried out on the selective flotation of enargite and methods of achieving an effective separation from non-arsenic copper sulphides.

This review focuses on enargite, which is the main form of copper arsenic mineralisation in many deep epithermal copper–gold deposits (Filippou et al., 2007). It is commonly associated with copper sulphides such as chalcopyrite ( $\text{CuFeS}_2$ ) and chalcocite ( $\text{Cu}_2\text{S}$ ). All these minerals are significant in the formation of copper sulphide ore mineralisation and are economically important sources of copper.

The main difference between copper arsenic sulphides and other arsenic minerals is that the former can represent significant economic forms of copper mineralisation in their own right. Therefore, it is not just their separation from other copper sulphides that is important, but also their recovery for further processing to extract, where possible, the copper.

The purpose of this paper is to present a review of current developments in the research into separation of enargite from other minerals in copper sulphide flotation systems. This includes characterisation of surface oxidation and various approaches to achieving selectivity in flotation of enargite and copper sulphide minerals.

## 2. Surface properties and floatability of enargite

### 2.1. Surface potential

Castro and Honores (2000) used microelectrokinetic (zeta potential) measurements, rest potentials of enargite electrodes and Hallimond tube flotation tests to investigate the surface properties and floatability of enargite. Zeta potential was found to be negative ( $-21$  mV to  $-47$  mV) in the pH range 2.5–12.0 with no isoelectric point. Potential peaks were found at about pH 5.5 and 11.0 (Fig. 1). They argued that these peaks could be due to the presence of arsenate ions ( $\text{AsO}_4^{3-}$ ) dissolved from the mineral surface. This was tested by investigating the effect of adding sodium arsenate ( $\text{Na}_3\text{AsO}_4$ ).

The presence of arsenate ions was found to make the zeta potential less negative across the pH range, but a new peak at pH

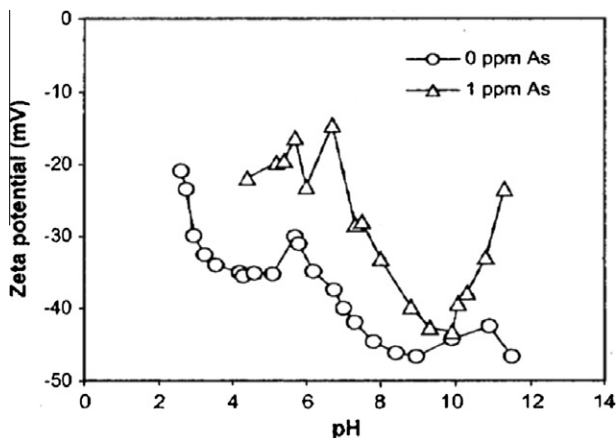


Fig. 1. Zeta potential of enargite as a function of pH in the presence and absence of arsenate ions in  $10^{-3}$  M  $\text{NaNO}_3$  supporting electrolyte (Castro and Honores, 2000).

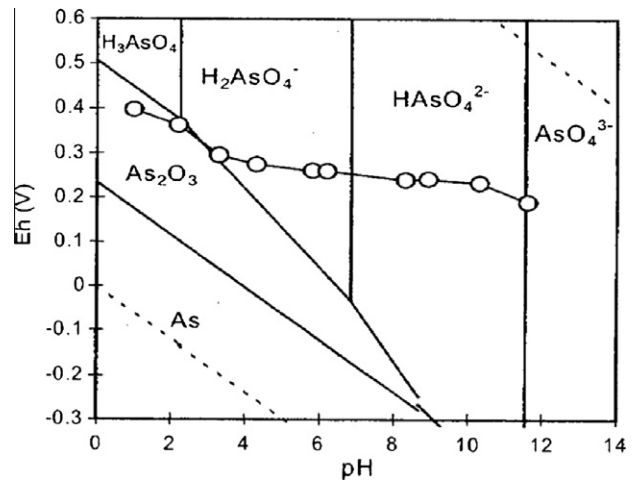


Fig. 2. Rest potentials of the enargite electrode in aqueous solution as a function of pH, plotted on the thermodynamic equilibrium diagram for the As–H<sub>2</sub>O system at  $10^{-3}$  M As (25 °C) (Castro and Honores, 2000).

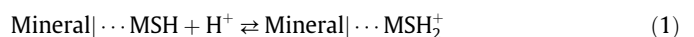
6.5 was seen. Comparing with data for the hydrolysis of arsenate and thio-arsenate ions reported in the literature (Schwedt and Rieckhoff, 1996) the potential peaks were found to correspond well with these pK values. From this study it was suggested that the negative zeta potential of enargite may be due to the presence of negatively charged thio-arsenate species formed from acids such as  $\text{H}_3\text{AsO}_4$ ,  $\text{H}_3\text{AsO}_3\text{S}$ ,  $\text{H}_3\text{AsO}_2\text{S}_2$  and  $\text{H}_3\text{AsOS}_3$ .

By comparing rest potentials with the  $E_h$ –pH diagrams of the As–H<sub>2</sub>O system and enargite (Fig. 2) it was proposed that dissolution of enargite and formation of arsenate ions may occur in alkaline conditions, while in acidic conditions a surface layer of arsenic trioxide would be expected. This behaviour is the opposite of what is seen for copper sulphides, which form an oxide layer under alkaline conditions and undergo dissolution under acidic conditions.

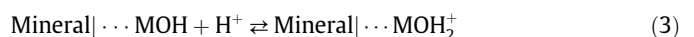
Hallimond tube studies using isopropyl xanthate showed good floatability at pH 10.0 even at very low collector concentrations. Oxidation by pre-treatment with  $\text{NaClO}$  at pH 11.0 was found to have only a slight depressant effect. This was interpreted to mean that thio-arsenate groups at the surface contribute to the good floatability of enargite and increase in resistance to oxidation compared to other copper sulphides. The good flotation response at high pH was thought to occur because collector adsorption on active sites at the mineral surface was unaffected by the increasingly negative zeta potential seen with increasing pH. Dissolution and hydrolysis of thio-arsenate and arsenate ions followed by re-adsorption at the mineral surface was proposed as the mechanism for the formation of negative surface charge observed in the zeta potential measurements.

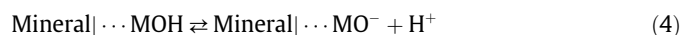
Fullston et al. (1999a) studied the surface oxidation of enargite and tennantite by investigating the dissolution of the minerals and changes in zeta potential under different oxidising conditions. Samples were conditioned at pH 11.0 in the presence of either nitrogen or oxygen gas prior to the zeta potential and dissolution measurements.

The mechanism of oxidation and formation of surface charge was proposed to be one of protonation or deprotonation of either metal sulphide surfaces



or metal hydroxides



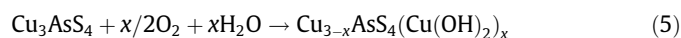


at the mineral surface as illustrated by the reactions above. It was argued that changes in pH and redox conditions caused the formation of a surface oxide layer on a metal-deficient (hence sulphur-rich) mineral surface, resulting in the observed changes in zeta potential. The extent of copper dissolution and formation of oxidation products on the mineral surface was found to increase with more oxidising conditions. It was also found that the dissolution of copper was greater than that of arsenic.

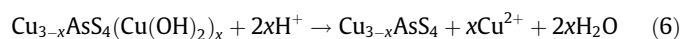
The process of oxidation in a low pH environment was proposed to be as follows. Initially, dissolution of metal ions takes place leaving a metal-deficient or sulphur-rich mineral surface. With continuing oxidation the sulphide groups oxidise to form polysulphide or elemental sulphur. Under conditions of high pH in an oxygenated environment this process is one of metal hydrolysis on the mineral surface and in solution followed by precipitation of metal hydroxide on the metal-deficient surface.

The following reactions were proposed to occur on the enargite (and tennantite) surface.

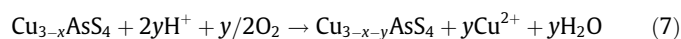
Oxidation at pH 9.0:



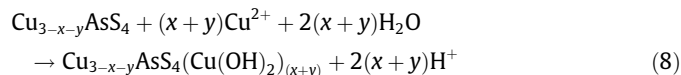
Dissolution of copper hydroxide during the acid titration:



Dissolution of copper from the mineral lattice at low pH values:



Precipitation of copper hydroxide during the base titration:



In a follow-up study by Fullston et al. (1999b) the surface oxidation of enargite and tennantite was investigated using X-ray photoelectron spectroscopy (XPS), with the same conditioning methods as the previous study. After conditioning, the mineral surface was found to be lightly oxidised, where the presence of a thin surface oxidation layer was shown by the detection, using XPS, of the non-oxidised mineral beneath. The main oxidation product was found to be a copper oxide/hydroxide layer, with an associated sulphur-rich phase comprised of a metal-deficient sulphide/polysulphide, and also arsenic oxide/hydroxide and sulphite species. From the XPS analysis arsenic sulphides, mainly  $\text{As}_4\text{S}_4$  and  $\text{As}_2\text{S}_3$ , were found to be the major arsenic sulphide species at the enargite surface, but were minor species at the tennantite surface and also in the bulk of both minerals.

Castro and Baltierra (2005) used an experimental and thermodynamic approach to study the surface chemistry of enargite as a function of pH. Zeta potential measurements as a function of pH were conducted for two different electrolytes, 0.001 M KCl and 0.001 M  $\text{NaNO}_3$ . In both cases zeta potential was found to be negative across the pH range studied, with no isoelectric point found.

The magnitude of the zeta potential was found to become increasingly negative with increasing pH. These results were interpreted in terms of adsorption of the hydrolysis products of the As–Cu–S–H<sub>2</sub>O system formed at the mineral surface. Potential valleys observed at pH 4.5 and 9.0 were interpreted as indicative of the adsorption of ions such as  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$ . Peaks at pH 5.5 for both electrolytes, pH 11.0 for KCl and pH 9.5 for  $\text{NaNO}_3$ , were also observed. Zeta potential reversal observed in the presence of copper ions was explained in terms of the formation and adsorption of copper-hydroxyl complexes such as  $\text{Cu}(\text{OH})^+$  by hydrolysis, and precipitation of a surface layer of copper hydroxide.

Fullston et al. (1999c) investigated the zeta potential of several copper sulphide minerals as a function of pH and oxidising conditions. It was found that variation in zeta potential with changes in pH and extent of oxidising conditions were consistent with the formation of a copper hydroxide layer on a metal-deficient, sulphur-rich mineral surface. The extent of copper hydroxide layer formation was found to increase as the mineral was subject to more oxidising conditions.

The zeta potential measurements were interpreted to mean that dissolution of the copper hydroxide surface layer takes place as pH decreases below about pH 8.0, while increasing pH results in the precipitation of a copper hydroxide surface layer above pH 6.0. In the case of acid titration followed by base titration, hysteresis between the acid and base zeta potential titration curves is seen where the mineral was prepared under oxidising conditions, but not when reducing conditions were used. This is attributed to the precipitation of copper sulphide on the mineral surface. The hysteresis was explained as the result of greater copper hydroxide precipitation with increasing pH, with the additional copper coming from increased metal dissolution at low pH.

From this study the minerals were ranked for oxidation in order of high to low: chalcocite > tennantite > enargite > bornite > covellite > chalcopyrite. It was concluded that separation by flotation of enargite and tennantite from the other copper sulphides, by exploiting differences in their susceptibility to oxidation, could be possible if chalcocite were not present.

## 2.2. Electrochemical investigations

Given that the industrial process of froth flotation of sulphide minerals is fundamentally electrochemical in nature, an understanding of the electrochemical properties of sulphide minerals is an essential part of an investigation of surface properties and behaviour in the flotation environment. Various authors have carried out investigations to characterise the surface properties of enargite using electrochemical methods.

As well as chemical oxidative pre-treatments, discussed in a later section, electrochemical oxidation is an important technique to investigate mineral surface reactivity under controlled conditions.

In an investigation of the electrochemical oxidation and reduction of natural enargite (Asbjornsson et al., 2004a), Asbjornsson et al. studied the surface reactivity of enargite in acid solution using cyclic voltammetry and chronoamperometry coupled with XPS, Raman spectroscopy and inductively coupled plasma-atomic emission spectrometry (ICP-AES).

The presence of  $\text{Cu}^{\text{II}}$  species associated with sulphate ( $\text{SO}_4^{2-}$ ) and chloride ( $\text{Cl}^-$ ) ions at the enargite surface, at potentials greater than +440 mV SHE, was reported. The ion concentration increased with increasing potential. Oxidation of arsenic to  $\text{As}^{\text{III}}$  at potentials less than +840 mV SHE was noted, as well as detection of small amounts of  $\text{As}^{\text{V}}$  above this range.

Interestingly, in the oxidative potential range an active–passive transition was reported at potentials around +540 mV SHE, believed to be the result of formation of elemental sulphur and sulphate, as well as  $\text{Cu}^{\text{II}}$  and  $\text{As}^{\text{III}}/\text{As}^{\text{V}}$  species. Formation of  $\text{H}_2\text{S}$ , arsine and elemental copper due to electrochemical reduction was also reported. The latter was demonstrated by the loss of an enargite Raman signal at increasingly negative potentials, a phenomenon attributed to the formation of elemental copper at the mineral surface.

Pauporté and Schuhmann (1996) used techniques including electrochemical impedance spectroscopy (EIS) and voltammetry to study the electrochemistry of natural enargite under alkaline conditions. It was concluded from the EIS data that in the potential range +140 to +440 mV SHE the observed variation in impedance

was consistent with the formation and dissolution of a surface layer.

Voltammetric studies were used to compliment the EIS data. Scans were carried out in the potential range  $-360$  to  $+640$  mV SHE. The voltammetry results showed the formation of current peaks in the anodic scan direction that decreased in magnitude over three successive scans. A model was proposed to explain the observed behaviour. It was suggested that a two-step reaction was involved, with the formation of a surface product of copper involving the transfer of one or more electrons, followed by the formation of a soluble species. However the authors did not specify the compound or compounds represented by the surface product or soluble species. It was concluded that the EIS and voltammetric behaviour resulted from the same processes.

In a study of enargite by electrochemical methods, Cordova et al. (1997, 1996) used a number of techniques to understand the reactions at the enargite electrode surface in solutions of different pH values. These methods included open circuit potential, stationary polarisation, cyclic voltammetry and electrochemical impedance spectroscopy.

It was found that under anodic conditions (positive applied potential)  $\text{Cu}^{2+}$  ions are initially released into solution leaving a metal-deficient surface where arsenic and sulphur remain. It was suggested the surface is probably composed of  $\text{AsS}_4$  or  $\text{Cu}_{3-x}\text{AsS}_4$ . As oxidation continues this surface gradually becomes a passivating layer, causing a decrease in the oxidation rate. This is similar to the mechanisms of oxidation proposed by Fullston et al. (1999a) in their zeta potential study.

Under cathodic conditions it was proposed that electro reduction produces  $\text{S}^{2-}$  species and the formation of a surface layer composed of  $\text{As}_2\text{S}_2$  and  $\text{Cu}_2\text{S}$  species. At increasingly negative potentials  $\text{As}_2\text{S}_2$  is partly reduced to metallic arsenic although it was reported that no metallic copper could be found.

Studies were also carried out under the same conditions but in the presence of  $10^{-4}$  M xanthate. It was concluded that in the potential range where a surface film is not formed ( $-460$  to  $+140$  mV SHE) no collector was adsorbed. A mechanism was suggested where xanthate takes part in the formation of the surface film during oxidation and is incorporated in it.

Guo and Yen (2008) investigated the electrochemical behaviour of natural and synthetic enargite using open circuit potential, stationary polarisation and cyclic voltammetry. Changes in solution pH, scan direction, scan rate and scan range were found to alter the electrochemical behaviour significantly. Interestingly, enargite was found to be insensitive to the presence of dissolved oxygen with little effect on the electrochemical behaviour observed.

The main effect of pH was observed to be an increase in the applied potential needed to oxidise enargite as pH is decreased. This was interpreted to mean enargite more readily forms a passivation layer in neutral or alkaline pH. It was found to be most stable at neutral or alkaline pH at about  $40$  mV SHE. However, passivation of the surface may occur over the range  $-660$  to  $+1070$  mV SHE.

The main oxidation product formed on the mineral surface was found to be copper hydroxide ( $\text{Cu}(\text{OH})_2$ ) where the applied potential was less than  $+570$  mV SHE. At potentials above  $+760$  mV SHE elemental sulphur is also formed. At high rates of oxidation  $\text{Cu}_2\text{O}$  was found to be the main hydrophilic product formed, rather than  $\text{Cu}(\text{OH})_2$ .

These findings are interesting in light of previous work (Asbjornsson et al., 2004a) discussed earlier, which reported the presence of  $\text{Cu}^{\text{II}}$  species, associated with sulphate and chloride, at the surface, at potentials greater than  $+440$  mV SHE. No mention of copper hydroxide or oxide formation was made.

In a related study (Asbjornsson et al., 2004b) tennantite ( $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ ) was investigated using the same methods. In this case under oxidising potentials of  $+340$  mV SHE the formation of

elemental sulphur was observed, and at  $+840$  mV SHE the formation of arsenic (III) and (V) oxides, was observed. This is similar behaviour to that observed by these authors for enargite.

Velásquez and co-workers (Velásquez et al., 2000b) used cyclic voltammetry (CV) to control the redox potential applied to a natural enargite surface in an alkaline solution. Surface composition under different applied potentials was analysed using XPS, SEM, EDX and EIS. A previous study by the same authors (Velásquez et al., 2000a) in which CV and XPS were used to characterise natural enargite, provides verification of the XPS results.

From the CV results two oxidation peaks in the positive sweep direction were observed, at  $+340$  and  $+840$  mV SHE. Surface composition analysis by XPS was reported to show a gradual decrease in Cu concentration with respect to As and S from  $+190$  to  $+440$  mV SHE. At  $+740$  mV SHE complete oxidation of the mineral surface resulted in the formation of  $\text{CuO}$ ,  $\text{As}_2\text{O}_3$ ,  $\text{As}_2\text{O}_5$ ,  $\text{CuSO}_4$  and  $\text{Cu}(\text{OH})_2$ .

This is an interesting finding in light of the more recent results discussed above (Asbjornsson et al., 2004a; Guo and Yen, 2008) where both  $\text{CuSO}_4$  and  $\text{Cu}(\text{OH})_2$  are identified as oxidation products, but only at higher potentials (above  $+740$  mV SHE). This contrasts with the findings of Guo and Yen (2008) where  $\text{Cu}(\text{OH})_2$  is found below  $+570$  mV SHE and  $\text{Cu}_2\text{O}$  formation occurs at higher rates of oxidation. In addition, Guo and Yen (2008) do not identify  $\text{CuSO}_4$  formation. This suggests further work is needed to resolve these discrepancies, clarify the mechanism of oxidation and identify the surface species that are formed.

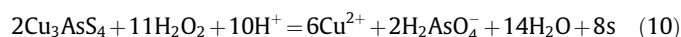
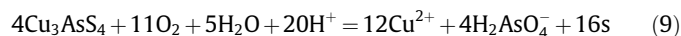
Subsequent cycling of the applied potential in the negative sweep direction (Velásquez et al., 2000b) over the range  $+840$  to  $-610$  mV SHE found oxide, hydroxide and sulphate species are no longer present as  $+440$  mV SHE is reached. This would appear to be consistent with the observation of progressive dissolution of Cu at low but increasingly positive potentials, followed by precipitation of copper compounds above about  $+740$  mV SHE. The authors contend that the oxidation species formed on the enargite surface are only stable at high applied potentials but do not specify a threshold potential at which this stability transformation takes place. Additionally they argue that the Cu concentration at the mineral surface is dependent only on applied potential, and not sweep direction (Velásquez et al., 2000a).

Further examination of the mineral surface was carried out using SEM and EDX (Velásquez et al., 2000b) to characterise morphology and composition. It was reported that at  $+740$  mV SHE the surface is covered by a very thin heterogeneous oxidised layer. From this layer protrude surface structures formed from nucleation sites which are thought to be composed of oxide, hydroxide and sulphate material.

### 2.3. Chemical oxidation

One method that has been investigated for its effectiveness in achieving a separation of various copper sulphide minerals by flotation is that of oxidative pre-treatment to cause selective oxidation at the mineral surface. Fornasiero et al. (2001) investigated the selective oxidation of the mineral surfaces in solution, or oxidation followed by selective dissolution of the surface products formed, as a pre-treatment stage to achieve separation of enargite and tennantite from chalcopyrite, chalcocite and covellite. This will be discussed further in a later section.

Sasaki et al. (2010) focussed on the effects of oxidative treatments at the mineral surface, comparing the physical and chemical response of enargite, tennantite and chalcopyrite. The procedure involved oxidising the minerals with  $\text{H}_2\text{O}_2$  and oxygen gas at pH values of 2, 5 and 11. XPS was used to identify the species present at the mineral surface. These authors found in the case of enargite that elemental sulphur was formed by oxidative dissolution. The proposed reactions by which this occurs are shown below.



The evidence for this was given as a significant increase after oxidation at pH 2.0 in the proportion of elemental sulphur relative to total sulphur, as was seen in the XPS results for the  $\text{S}_{2p}$  spectrum. In another study, elemental sulphur was also found on the enargite surface by Raman spectroscopy after electrochemical oxidation at pH 1.0 (Asbjornsson et al., 2004a). In terms of copper, the predominant species in un-oxidised enargite was of the  $\text{Cu}^{\text{I}}$  form, with evidence of formation of  $\text{Cu}^{\text{II}}$  compounds following oxidation at  $\text{pH} \geq 5.0$  (Sasaki et al., 2010), most likely hydroxide rather than oxides or sulphate forms due to the high solubility of copper sulphates and oxides (Welham, 2001).

#### 2.4. Contact angle

The preceding discussion indicates that much attention has been given to the nature of the surface species present under oxidising or reducing conditions produced by various methods. In order to better understand the potential effects of these treatments on the floatability of the mineral, the surface wettability has been studied directly by means of contact angle measurements.

Guo and Yen (2001) studied the effects of applied potential, pH, collector type and concentration on the wettability of enargite in the presence of collector under electrochemical control. Xanthate oxidation and dixanthogen reduction on the mineral surface were also studied.

Fig. 3 shows the effect of applied potential for natural enargite. Below  $-250$  mV SCE ( $-10$  mV SHE) the contact angle was zero. The surface became hydrophobic above  $-200$  mV SCE ( $+40$  mV SHE) with a contact angle of  $90^\circ$  from  $-150$  to  $+850$  mV SCE ( $+90$  to  $+1090$  mV SHE). Changes in pH were found to have no significant effect on the contact angle magnitude. The net effect was to increase what Guo and Yen termed the “floatable potential range”.

Where collector type was investigated, natural enargite was found to have a wider floatable potential range of about 125 mV using PAX (potassium amyl xanthate) compared to SIPX (sodium isopropyl xanthate). Increasing the collector concentration, in this case PAX, showed both an increase in the floatable potential range width of about 70 mV, and an increase in contact angle of about  $10^\circ$  over the floatable potential range.

In addition Guo and Yen (2001) investigated xanthate oxidation and dixanthogen formation on the enargite surface, and reduction of dixanthogen to xanthate by cathodic polarisation. Dixanthogen formation was found to occur at similar potentials to those at which the surface became hydrophobic.

Guo and Yen (2002) extended the investigation of xanthate oxidation and dixanthogen formation carried out by Guo and Yen (2001). Ultraviolet (UV) spectroscopy applied to hexane extracts

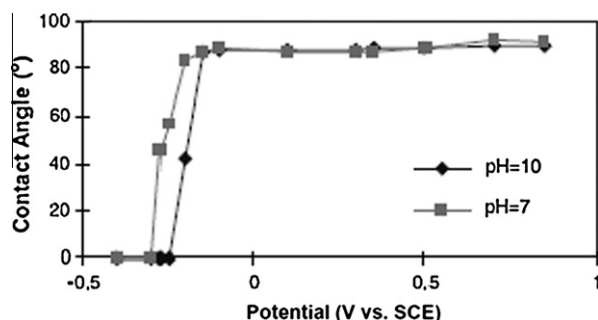


Fig. 3. Effect of applied potential on contact angle of natural enargite at pH 10.0 and 7.0 (Guo and Yen, 2002).

of the bulk solution and the solution surrounding the mineral surface confirmed the formation of dixanthogen on the mineral surface.

An important difference in these studies to those previously discussed is that the effects of the presence of flotation collectors in solution are investigated. In addition attempts were made to characterise the oxidation of xanthate and formation of dixanthogen on the enargite surface. From these findings it is possible to draw some correlations between applied potential and the transition of the mineral surface from hydrophilic to hydrophobic in the presence of a collector. The results of these studies indicate that a threshold potential exists where this transition takes place. Further evidence can be found in the work of Senior et al. (2006) where such an effect was demonstrated for a number of sulphide mineral types.

However no published work has yet been found where a thorough review of the mineral surface chemistry has been carried out, using quantitative techniques such as XPS, to characterise the species formed at the mineral surface.

### 3. Single mineral flotation studies

Although arsenic more commonly occurs in mineral form, certain ore deposits are known to contain elemental arsenic. Bruckard et al. (2007) investigated the flotation of metallic (or elemental) arsenic, citing a lack of research in the area. A synthetic ore composed of 5% arsenic metal and 95% quartz was used in flotation tests carried out over a pH range of 5–12 and an  $E_h$  range of  $-500$  to  $+500$  mV SHE.

The flotation recovery was determined under two conditions. In the first selected pH values between pH 5 and 12 were used. Natural  $E_h$  ranged from  $+237$  mV SHE at pH 5 to  $-45$  mV SHE at pH 12. In the second, the flotation response was determined at selected  $E_h$  values between  $-500$  and  $+500$  mV SHE for pH values of 6 and 10.

Metallic arsenic was shown to have little floatability in the absence of collector. Using 40 g/t KEX, a typical flotation response of up to 95% recovery after 8 min, with about 5% quartz recovery was seen. Tests conducted over a range of pH values at natural  $E_h$  showed a flotation recovery of 95–85% in the pH range 5–10, then falling slowly to 53% at pH 12.

The effect of pulp potential was investigated by varying the pulp  $E_h$  at fixed pH values of 6 and 10. At pH 6 a strong flotation response was found in the  $E_h$  range  $+125$  to  $+275$  mV SHE, with a peak recovery of about 95%. In the  $E_h$  range  $+300$  to  $+400$  mV SHE a transition from strong to poor floatability was observed, with an upper limiting potential, defined as the potential at which recovery is 50%, between  $+325$  and  $+375$  mV SHE.

At pH 10 a strong flotation response at all  $E_h$  values tested between  $-300$  and  $+225$  mV SHE was found, with an upper limiting potential between  $+250$  and  $+300$  mV SHE. No lower limiting potential was found in the range tested. A typical pulp potential versus recovery curve is shown in Fig. 4.

Senior et al. (2006) investigated the flotation response of enargite using an artificial ore, composed of 10% natural enargite and 90% quartz, determined for a range of  $E_h$  values between  $-500$  and  $+500$  mV SHE and for pulp pH values of 8 and 11. Pulp potential was controlled by adding dilute solutions (2.5% w/v) of laboratory grade sodium hypochlorite ( $\text{NaClO}$ ) and sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ).

To identify pulp pH and  $E_h$  conditions where effective separation of enargite could be achieved, the experimental flotation response of enargite was compared with data for chalcocite ( $\text{Cu}_2\text{S}$ ), chalcopyrite ( $\text{CuFeS}_2$ ) and cuprite ( $\text{Cu}_2\text{O}$ ), sourced from the CSIRO Minerals databank on the pulp potential dependence of the flotation response for these minerals. A number of differences according to pulp potential conditions were identified that offered potential for exploitation.



The single mineral studies revealed a threshold potential for enargite below which it does not float and above which it does. For a pH of 8, this was found to be about  $-75$  mV SHE and at pH 11 about  $-25$  mV SHE. Threshold potential was defined as that at which recovery of the mineral of interest is 50%. Data for the effects of pulp potential on the flotation response of other copper mineral types was reported. For chalcocite, at pH 8 a lower threshold of about  $-155$  mV SHE was found to exist, above which it floats, while no upper limiting potential was reported. However at pH 11 threshold potentials at about  $-155$  and  $+270$  mV SHE was reported, between which chalcocite floats strongly.

These results are in agreement with the findings of Heyes and Trahar (1979) who reported that at pH 8 and 11 flotation of chalcocite was not observed below  $-200$  mV SHE, there was a transition to complete floatability between  $-200$  and  $-100$  mV SHE, while at pH 8 no upper limiting potential was observed. However at pH 11 a second limiting potential between about  $+200$  and  $+300$  mV SHE was reported above which chalcocite does not float.

Chalcopyrite was similar (Senior et al., 2006) at pH 8 to chalcocite but the lower limiting threshold potential was about  $+160$  mV SHE. No upper limiting potential was reported up to  $+360$  mV SHE, which was the limit of the range studied. No data was reported for other pH values.

Cuprite was reported to differ from the other mineral types in that no lower limiting potential was observed and a strong flotation response in reducing conditions down to  $-400$  mV SHE exists at pH 11. In addition an upper limiting potential of about  $+290$  mV SHE was found. Based on these findings a number of possible separations that might be achieved by exploiting the observed differences in flotation response were proposed.

In the case of chalcopyrite, considered representative of the copper-iron sulphides, it was concluded (Senior et al., 2006) that separation from enargite is possible in the potential range  $-25$  to  $+50$  mV SHE at pH 8 where enargite floats strongly but chalcopyrite does not. Although no data was reported the authors concluded that the threshold potential would not be likely to change significantly with pH and so a similar separation could be possible at pH 11.

Where selective flotation of enargite from the copper sulphide minerals is concerned, represented in this study by chalcocite, it was concluded that the threshold potentials at pH 8 are not sufficiently different for an adequate separation to be achieved, but that this is not the case at pH 11. Under these conditions two possible  $E_h$  ranges were found to exist where separation might be achieved. The first is between about  $-150$  and  $-75$  mV SHE where chalcocite

floats, and the second is above about  $+270$  mV SHE where enargite floats but chalcocite does not.

Where separation from copper oxides such as cuprite is concerned, it was found that selectivity is possible in two potential ranges. Cuprite was found to float at potentials below about  $-150$  mV SHE while enargite does not. Conversely above about  $+290$  mV SHE it was observed that enargite will float but cuprite does not.

Since the behaviour of cuprite is similar to chalcocite, where both minerals display a poor flotation response under oxidising conditions, it was concluded that separation of enargite from both these minerals should be possible in a single flotation step. It should be pointed out that these conclusions were based on data obtained from single mineral studies. No work was carried out to take into account the effects of interactions between different mineral types that might affect the flotation results in mixed mineral systems.

#### 4. Selective flotation of enargite

##### 4.1. Selective flotation reagents

Various studies have been carried out to investigate the potential for selective flotation of arsenic-bearing copper minerals using either chemical reagents that act as depressants, or use of oxidising and reducing agents to control electrochemical conditions of the flotation pulp, that is, pulp  $E_h$  control. By far most of the selective depressant work has focussed on arsenopyrite, but other mineral types have also been investigated. However, the number of studies involving the separation of copper arsenic sulphides, in particular enargite and tennantite, from non-arsenic copper sulphides, is limited.

Kydros et al. (1993) used sodium dithionite and sodium sulphite as arsenopyrite depressants in the treatment of a bulk auriferous concentrate in acidic media. It was reported that the use of sodium dithionite led to slight activation of pyrite, possibly due to the coverage of its surface with a sulphur-containing hydrophobic layer. Selective depression of arsenopyrite in the presence of sodium dithionite and sodium sulphite was found.

Tapley and Yan (2003) considered the effects of magnesium–ammonium mixture (MAA) with pH control, pre-aeration and potassium permanganate on pyrite–arsenopyrite separation, achieving successful depression of arsenopyrite. However no mechanism of action was proposed. Abeidu and Almahdy (1980) reported the use of arsenic triiodide ( $AsI_3$ ) followed by the addition of magnesia mixture to depress chalcopyrite and arsenopyrite for separation from pyrite in the manufacture of sulphuric acid. Magnesia mixture was prepared using  $MgCl_2 \cdot 6H_2O$ ,  $NH_4Cl$  and  $NH_4OH$  dissolved in distilled water. The proposed mechanism of depression was reported as based on the selective adsorption of arsenite ions ( $As^{3+}$ ) onto the chalcopyrite surface to form insoluble copper arsenides ( $Cu_3As$ ,  $Cu_3As_2$ ). Since iron ( $Fe^{2+}$  and  $Fe^{3+}$ ) does not form stable arsenides, pyrite was not affected. Since  $As^{3+}$  is readily oxidisable to  $As^{5+}$  it forms a stable complex anion  $[AsO_4]^{3-}$  on the chalcopyrite surface which, along with the original arsenate sites on the arsenopyrite surface, react with the magnesia mixture to form strongly hydrophilic layers of the form  $AsO_4NH_4Mg \cdot 6H_2O$ . This surface layer inhibits collector adsorption on the chalcopyrite and arsenopyrite surfaces and facilitates the separation of pyrite.

Tajadod and Yen (1997a) investigated the surface properties and flotation characteristics of enargite and chalcopyrite in the presence of a xanthate collector, using sodium cyanide (NaCN) and potassium permanganate ( $KMnO_4$ ) as depressants. Their effects on pre-adsorbed xanthate desorption from the mineral surfaces and the effects of sodium cyanide and potassium permanganate pre-conditioning on xanthate adsorption were investigated.

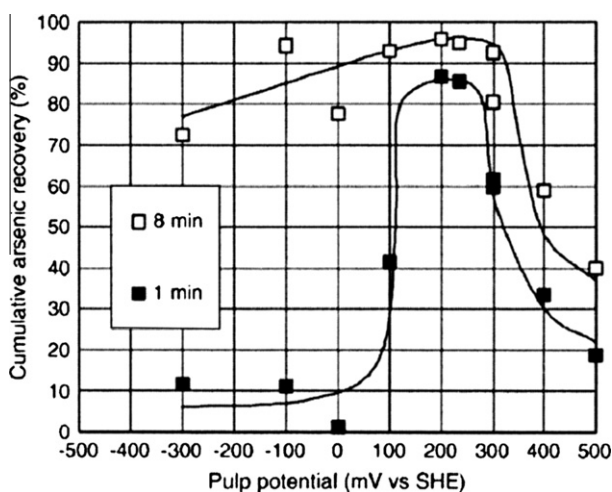


Fig. 4. Cumulative arsenic metal recovery after 1 min and 8 min flotation with 40 g/t KEX as a function of pulp potential at pH 6 (Bruckard et al., 2007).

It was found that xanthate adsorption was more rapid on enargite than chalcopyrite. The effect of sodium cyanide on xanthate desorption was greatest for enargite, while the effect on chalcopyrite was minimal. Pre-conditioning with sodium cyanide followed by xanthate addition further reduced the final xanthate adsorption density. The effects of potassium permanganate on pre-adsorbed xanthate were found to be similar to those of sodium cyanide. After pre-conditioning with potassium permanganate followed by xanthate addition the adsorption density was found to be higher. Selective flotation by depression of enargite with sodium cyanide achieved no more than a partial separation, with about 70% of the arsenic rejected, but at the expense of about 45% of the copper.

Despite concluding that sodium cyanide is a suitable depressant for enargite and reducing arsenic content of copper concentrates, the high associated copper losses were recognised. Such high losses are not sustainable in industrial applications. In addition, no consideration is given to achieving a separation in the more complex multi-mineral systems that generally exist in practice.

In a related study (Tajadod and Yen, 1997b) a number of other methods to achieve a separation of enargite from chalcopyrite by flotation were investigated. This included the effects of sodium sulphide ( $\text{Na}_2\text{S}$ ), oxidation by pulp aeration, and magnesium–ammonium mixture addition on xanthate adsorption density and mineral floatability.

Neither conditioning with sodium sulphide or pulp aeration was found to give sufficient difference in adsorption density to produce an effective separation. Flotation tests showed without any conditioning at pH 9, enargite and chalcopyrite showed similar floatability with recoveries of 71% and 81% respectively. Conditioning with  $\text{Na}_2\text{S}$  reduced the flotation recoveries to 58% and 26% for enargite and chalcopyrite. In comparison, after two hours conditioning by aeration only, recoveries were reported as 32% and 46% respectively. In contrast, conditioning with MAA reduced recoveries of enargite and chalcopyrite from 71% and 81% to 15% and 80% respectively, while aeration combined with MAA gave 12% and 79% respectively.

Sodium sulphide ( $\text{Na}_2\text{S}$ ) conditioning and oxidation by pulp aeration were found to be ineffective in achieving a separation of enargite and chalcopyrite. Using MAA mixture and aeration as the conditioning step, xanthate adsorption on the enargite surface was significantly inhibited. A separation efficiency of arsenic from non-arsenic minerals of 50% was found to be possible. Where sodium sulphide was used as the chalcopyrite depressant a separation efficiency of 22.7% was found, while using aeration to oxidise the enargite gave a separation efficiency of less than 15%. Separation efficiency in this case was defined as the copper recovery minus the arsenic recovery.

The specificity of MAA for enargite was explained (Tajadod and Yen, 1997b) as the oxidation of the arsenic sites at the enargite surface to form a stable complex anion  $[\text{AsO}_4]^{3-}$  which has a great affinity for the MAA. As a result the compound  $\text{AsO}_4(\text{NH}_4)\text{Mg}\cdot 6\text{H}_2\text{O}$  is formed, which is strongly hydrophilic and acts to block xanthate adsorption. As this compound formation is specific to the arsenic sites chalcopyrite is not affected and there is no inhibition of xanthate adsorption on its surface.

Based on these results it was concluded that it is possible to achieve a separation of enargite from chalcopyrite by froth flotation of a copper concentrate using MAA as an enargite depressant.

Yen and Tajadod (2000) compared two methods of separation of enargite from chalcopyrite by flotation, pulp potential control and depression of enargite by conditioning with MAA. At a potential of  $-10$  mV SHE enargite could be recovered by flotation while chalcopyrite remained depressed. Enargite recovery was best in the range  $-145$  to  $+14$  mV SHE, while for chalcopyrite this range was  $-160$  to  $+100$  mV SHE.

Xanthate adsorption on enargite decreased with increasing MAA concentration with a reduction of 76% reported. No decrease for chalcopyrite was found at any MAA concentration. Flotation tests found that enargite recovery decreased with increased MAA concentration, falling below 15%, while chalcopyrite was not affected. In the pH range 7.0–9.0 enargite recovery was below 15% while chalcopyrite was unaffected at 80–82%. As the pH increased from 9 to 11, this reduced to about 47%, with a further small decrease for enargite. In addition it was reported that if the minerals were aerated for 10 min prior to conditioning a further 2.3% decrease in enargite recovery was observed, while chalcopyrite was unaffected. It was concluded that selective flotation of enargite from chalcopyrite could be achieved using either pulp potential control or depression of enargite by conditioning with MAA prior to collector addition.

Castro et al. (2003) also investigated the depressant effects of MAA on enargite in the recleaner stage of copper ore flotation over a pH range of 7–10 and a MAA dosage range of 1.8–10.8 kg/t. A limited depressant effect was observed with the best result reported at pH 10 and a MAA dosage rate of 2.5 kg/t, resulting in an arsenic recovery of about 55%. However, when the dose rate was increased to 7 kg/t, no depression was observed. It was theorised that where a mineral surface is already coated by collector, adsorption of magnesium and ammonium ions to form a magnesium ammonium arsenate complex ( $\text{AsO}_4\text{NH}_4\text{Mg}\cdot 6\text{H}_2\text{O}$ ) at the mineral surface is limited. In this case the reported results contradict the findings of Yen and Tajadod (2000). Depression was not observed in the pH range 7–9 using 1.8–10.8 kg/t magnesia mixture. An important step appears to be pre-aeration of the pulp. According to Dai et al. (2005) in a study of the Garson Ni–Cu ore, magnesia mixture does not depress gersdorffite ( $\text{NiAsS}$ ) without pre-aeration. Yen and Tajadod (2000) incorporated pre-aeration of the flotation pulp whereas this step was not used by Castro et al. (2003).

#### 4.2. Selective oxidation

Fornasiero and co-workers (Fornasiero et al., 2001) investigated the separation of enargite and tennantite from chalcopyrite, chalcocite and covellite in mixed mineral systems using selective oxidation of the mineral surfaces in solution, or oxidation followed by selective dissolution of the surface products formed. Mixed mineral flotation tests were carried out using six two-mineral systems comprised of enargite and tennantite with each of the copper sulphide minerals. Conditioning was carried out under non-oxidising conditions with  $\text{N}_2$  gas at pH 5.0 and 11.0, and under oxidising conditions with  $\text{O}_2$  gas and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) as an oxidising agent at pH 5.0 and 11.0. Collector was added at the end of conditioning. Ethylene diamine tetra-acetic acid (EDTA) addition at pH 11.0 was used to selectively remove surface oxidation products.

After conditioning with  $\text{N}_2$  at pH 5.0 all minerals displayed a high flotation recovery without selectivity. However at pH 11.0, separation of chalcopyrite from tennantite, chalcopyrite from enargite and covellite from tennantite were significantly improved. Separation of chalcocite from enargite and chalcocite from tennantite were also improved but to a lesser extent. Separation of covellite from enargite was essentially unchanged from that seen at pH 5.0. Moreover, it was found that for the covellite-tennantite system the arsenic bearing mineral was depressed, while for all other mineral pairs the reverse was true. Thus for this system covellite was recovered preferentially, whereas for the other three systems enargite and tennantite were recovered preferentially.

It was concluded from the variation observed in separation efficiency that in any real complex multi-mineral flotation system it would not be possible to achieve the desired result of an efficient separation of copper sulphides from copper arsenic sulphides.

Conditioning with  $O_2$  at pH 5.0 resulted in higher recovery of non-arsenic minerals and so gave a good separation, particularly for the mineral systems containing enargite. Recoveries ranged from 47% to 82% for the non-arsenic minerals and from 40% to 53% for the arsenic minerals. At pH 11.0 depression of all minerals was reported with maximum recoveries lower than 20%.

Where EDTA was added after conditioning and before collector addition at pH 11.0, flotation recoveries and mineral separation were dependent on concentration. Without EDTA a thick layer of surface oxide species was present resulting in low flotation recoveries. In the chalcocite–tennantite system the optimum separation of arsenic and non-arsenic species was observed at an EDTA concentration of  $2 \times 10^{-5}$  mol dm $^{-3}$ . At high EDTA concentrations surface oxidation products were removed from both mineral species resulting in high recoveries but little selectivity.

It was concluded that higher flotation recoveries of non-arsenic minerals resulted from greater collector adsorption and less surface oxide and hydroxide species than on enargite and tennantite, suggesting that the surface oxidation layer inhibited collector adsorption on the surface of enargite and tennantite. Thus, the observed results were due to a greater extent of surface oxidation of the arsenic minerals compared to the non-arsenic minerals. It is this surface oxidation layer that inhibits the adsorption of collector molecules onto the mineral surface resulting in decreased recovery of arsenic minerals. Arsenic oxides were found to be more stable than copper oxides at pH 5.0, and dissolve less than copper oxides when EDTA was added to the system at pH 11.0. The extent of oxide dissolution was found to be dependent on EDTA concentration and, when combined with the different rates of arsenic and copper oxide dissolution, control of arsenic and non-arsenic mineral recovery could be achieved by varying this concentration.

Huch (1994) developed and patented a method to separate chalcocite from enargite using froth flotation, whereby a pre-conditioning step incorporating an oxidising agent, preferably hydrogen peroxide, was used to treat a concentrate containing these minerals. An optimum pulp oxidation reduction potential of +50 to +200 mV (no reference standard given) was described. In this application it is considered that the mechanism of separation is the preferential oxidation and depression of the more easily oxidised mineral, chalcocite, while enargite is recovered to concentrate.

In both cases the oxidation step was carried out before collector addition so that the formation of a surface oxide layer acts to prevent or reduce collector adsorption and increase flotation selectivity. The success of this approach therefore depends on two factors. First, sufficiently different rates of oxidation between the mineral types present for an oxide layer to form on one species and not another, and second, precise control of the oxidation to ensure only the target species is oxidised.

These findings provide a useful insight into the mechanisms by which the surface reactions of the mineral species studied can be controlled by altering the solution conditions under which flotation is carried out. It demonstrates that potential exists to achieve useful separations of arsenic and non-arsenic copper mineral species through an understanding of the behaviour of each of these minerals under different conditions. By controlling the formation and dissolution of surface oxidation species it has been shown that it is possible to alter the adsorption of collector molecules at the mineral surface and hence vary the flotation recovery that can be achieved. In this way selective mineral recovery was achieved in simple two mineral systems.

#### 4.3. Pulp potential control

Pulp potential in the flotation of sulphide minerals is not a new concept and the use of  $E_h$  measurement and its interpretation has been practiced by researchers for more than thirty years. Despite

the long-term research interest, its use in industrial flotation applications has been limited, according to Chander (2003). Woods (2003) concluded that in laboratory applications the monitoring and control of electrochemical potential has led to improvements in development of flotation strategies. In the separation of arsenic bearing copper sulphides from other copper sulphides control of  $E_h$  to achieve selectivity in flotation has shown promising results in recent years.

In a study of separation of enargite from chalcopyrite using pulp potential control, Guo and Yen (2005) investigated the surface oxidation and flotation response using cyclic polarisation, contact angle measurements and microflotation tests.

Chalcopyrite was found to oxidise more quickly at a lower potential than enargite, the difference possibly due to different electrical conductivity. Resistance of 1 cm $^3$  samples of chalcopyrite (2–3  $\Omega$ ) and enargite (1000  $\Omega$ ) was reported. Enargite was found to show formation of a passivation layer at potentials below +90 mV SHE, giving some resistance to oxidation. Contact angle varied with potential, as shown in Fig. 5 for a  $7 \times 10^{-4}$  M PAX solution at pH 10.0.

The lower hydrophobicity (or smaller contact angle) observed for chalcopyrite was explained in terms of the surface oxidation products that form at different applied potentials. Hydrophobic species such as  $S^0$  that form at low potentials (+140 to +340 mV SHE) become further oxidised to hydrophilic species such as  $SO_3^{2-}$  and  $SO_4^{2-}$  at potentials above +440 mV SHE. In contrast the hydrophobic oxidation products formed on the enargite surface persist up to a potential of +990 mV SHE.

Using a lower PAX concentration ( $7 \times 10^{-5}$  M PAX solution at pH 10.0) the contact angle for chalcopyrite was much smaller than for enargite and the difference between them was greater at potentials above +440 mV SHE, suggesting a more effective separation could be achieved under these conditions (Fig. 6).

Flotation tests showed the best selectivity was obtained with  $7 \times 10^{-5}$  M PAX solution at pH 10.0 at a potential of +740 mV SHE, with 93.4% enargite recovered to concentrate and 92.6% chalcopyrite recovered to tailings, as shown in Fig. 7.

Kantar (2002) investigated the flotation characteristics of enargite using hydrogen peroxide and sodium sulphide to control the potential of the system. It was found that under oxidising conditions enargite was capable of collectorless flotation, due to the formation of elemental sulphur on the surface. In contrast under reducing conditions collectorless flotation was not possible, due to the formation of CuO. In the presence of xanthate, floatability was strongly dependent on the solution potential with maximum enargite recovery close to 100% at potentials between +150 and +270 mV SHE, and decreasing rapidly above or below this range.

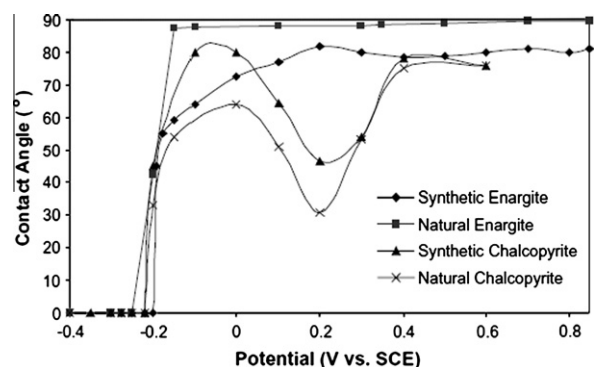


Fig. 5. Effect of pulp potential on contact angle in  $7 \times 10^{-4}$  M PAX at pH 10 (Guo and Yen, 2005).

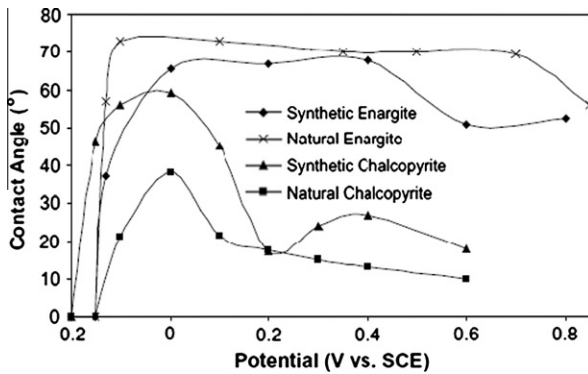


Fig. 6. Effect of pulp potential on contact angle in  $7 \times 10^{-5}$  M PAX at pH 10 (Guo and Yen, 2005).

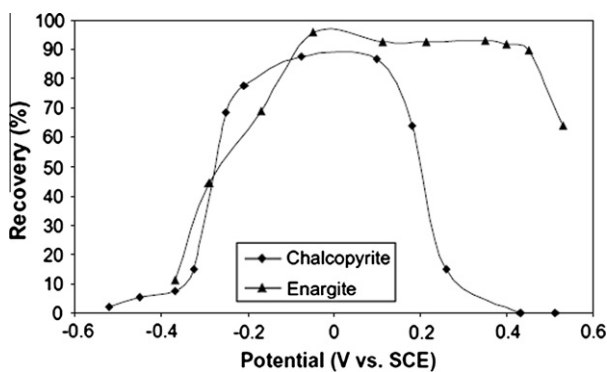


Fig. 7. Effect of pulp potential on flotation recovery in  $7 \times 10^{-5}$  M PAX solution at pH 10 (Guo and Yen, 2005).

Senior and co-workers (Senior et al., 2006) investigated the floatability of enargite as a function of pulp potential and pH to determine if its flotation behaviour was sufficiently different to other copper minerals for flotation separation to be achieved.

Single mineral flotation studies found a threshold potential of about  $-75$  mV SHE at pH 8.0 and  $-25$  mV SHE at pH 11.0 above which enargite floats and below which it does not. Threshold potential was defined as that potential at which the recovery after 1 min is 50%. The transition from non-floatability to strongly floating took place over a range of about  $-150$  to  $-50$  mV SHE at pH 8.0. At pH 11.0 the threshold potential was found to be about  $-25$  mV SHE (Fig. 8).

However the authors' state this difference may be due to scatter in the data and whether it is in fact a real difference is uncertain, although theoretically the threshold potential should change with pH, since it is related to the oxidation potential.

This transition is similar to that reported by Guo and Yen (2005) in the range of about  $-150$  to  $+100$  mV SHE at pH 10.0. Using the same definition as Senior et al., a threshold potential of about  $-10$  mV SHE at pH 10.0 was found, which is in reasonable agreement with Senior et al. (2006), given the stated level of uncertainty.

Guo and Yen (2006) found good flotation of enargite in the potential range of  $+190$  to  $+740$  mV SHE in a  $7 \times 10^{-5}$  M PAX solution. Smith and Bruckard (2007) used controlled-potential flotation to separate tennantite from chalcopyrite and bornite. The separation was made on a bulk copper–arsenic concentrate after reducing the pulp potential to about  $-150$  mV SHE at pH 12 and floating the tennantite from the other copper minerals.

The flotation behaviour of arsenic metal with ethyl xanthate as a function of pulp pH and pulp potential was studied by Bruckard et al. (2007). It was found that metallic arsenic has no natural flo-

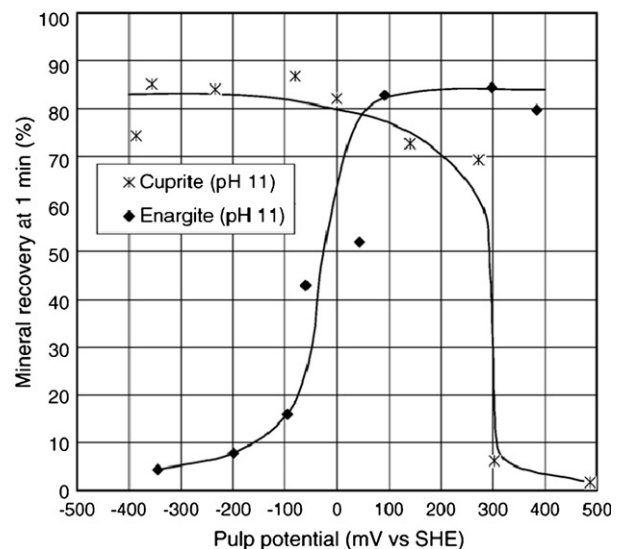
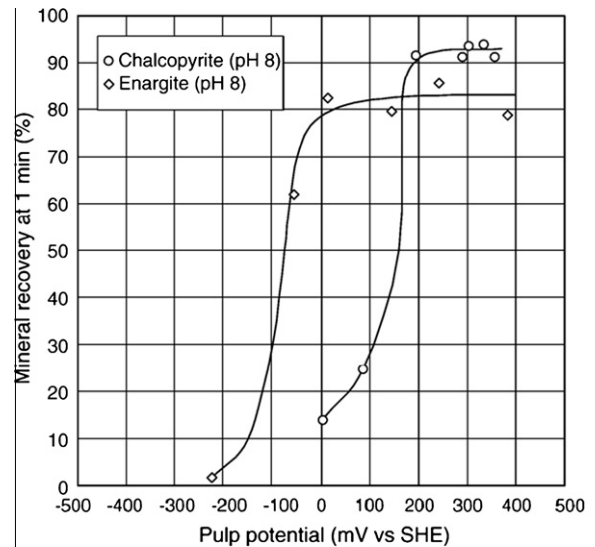


Fig. 8. Enargite flotation recovery as a function of pulp potential at pH 11 and pH 8 (Senior et al., 2006).

atibility but floats readily (up to 95% recovery in 8 min) over a wide range of pH and  $E_h$ . In a detailed study of the electrochemical behaviour of enargite (Guo and Yen, 2008) a passivation layer was found to form over a broad potential range ( $-660$  to  $+1070$  mV SHE). The main oxidation product found on the mineral surface were copper hydroxide ( $\text{Cu}(\text{OH})_2$ ) below  $+570$  mV SHE. At potentials above  $+760$  mV SHE elemental sulphur was also formed.

Bruckard et al. (2010) investigated the feasibility of arsenic reduction using controlled potential flotation to produce both low-arsenic and high-arsenic concentrates. This was incorporated as a first treatment step in a proposed three-stage beneficiation process for arsenic-bearing copper ores. The second stage used low temperature roasting of the high-arsenic concentrate to produce a calcine for smelting. In the final stage the fume product is immobilised in a low temperature ceramic for disposal. It was shown that a net economic benefit can be achieved.

## 5. Summary

Zeta potential studies have been used to propose a mechanism of enargite oxidation at high pH involving dissolution and

hydrolysis of thio-arsenate and arsenate ions followed by re-adsorption at the mineral surface and precipitation of metal hydroxides on the metal-deficient surface. At low pH dissolution of metal ions takes place leaving a metal-deficient or sulphur-rich mineral surface. With continuing oxidation the sulphide groups oxidise to form polysulphide or elemental sulphur. The differences between copper sulphides and copper arsenic sulphides suggest the potential for flotation separation taking place in alkaline environments by exploiting differences in their susceptibility to oxidation.

Electrochemical techniques coupled with surface analysis have been used by a number of authors to investigate the chemical species formed on the enargite surface under oxidising (anodic) and reducing (cathodic) conditions. Under anodic conditions the formation of species including copper sulphate or hydroxide and elemental sulphur has been reported. Although there is broad agreement between these studies, some disagreement exists about the nature of oxidation product formed. It is not clear whether copper hydroxide or oxide species, or  $\text{Cu}^{\text{II}}$  species associated with sulphate and chloride, are the main oxidation products. However, there seems to be good agreement that the main oxidation mechanism is one of progressive dissolution of Cu at low but increasingly positive potentials, followed by precipitation of copper compounds above about +740 mV SHE. An active-passive transition in the oxidative potential range was reported at potentials around +540 mV SHE, which correlates with the formation of an oxidative surface layer. This mechanism of surface layer formation also appears to be significant in the adsorption of xanthate collectors and in the application of controlled potential flotation of enargite. Chemical oxidation as a selective oxidative pre-treatment of the mineral surfaces produced similar results to electrochemical oxidation, with the formation of elemental sulphur and  $\text{Cu}^{\text{II}}$  compounds, most likely hydroxides.

Contact angle measurements further develop the idea of collector adsorption dependency on the formation of an oxide surface layer, and form a link between the fundamental studies of surface oxidation and flotation of enargite. It has been shown that there is a threshold potential range (of about –250 to –150 mV SHE) where contact angle sharply increases from 0° to 90° as applied potential increases.

Single mineral studies provide further support for a threshold potential below which enargite does not float. It was shown that enargite will become floatable as pulp potential increases through about –75 mV SHE, depending on pH. This threshold is different from threshold potentials for flotation of non-arsenic copper sulphides, suggesting it is possible to achieve selective flotation of enargite by careful control of pulp potential.

Investigations of the selective flotation of As-minerals has focused on arsenopyrite and on enargite only in recent years. The main mechanisms of achieving enargite selectivity involve the use of selective flotation reagents, selective oxidation and control of pulp potential. Conditioning with reagents such as sodium cyanide and sodium sulphide has shown limited success, with generally poor separation efficiency and high copper losses. The use of MAA to depress enargite has shown mixed results, with some authors reporting good selectivity while other studies fail to give the same results. However methodological differences may explain these differences. Selective oxidation of the mineral surface to influence collector adsorption using a pre-conditioning step has been shown to be effective in separating enargite from non-arsenic copper sulphides. Typically, hydrogen peroxide or similar oxidising reagents are used and can be combined with pulp aeration using air or oxygen gas. Pulp potential control as a method for achieving selective flotation of arsenic minerals and in particular enargite has received increasing attention recently, and promising results have been reported. However, more work must be done both to under-

stand the fundamental mechanisms that underpin a successful separation, and to further develop a process more readily applicable to industrial separation. In addition the use of other potentially more selective flotation collectors, other than the traditional default standard of xanthates, has been neglected in the literature concerning enargite, and deserves investigation. In combination with a well developed method of pulp potential control, there is the potential for worthwhile developments towards the ultimate goal of achieving a robust industrial separation process.

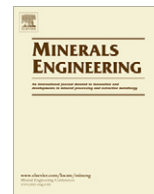
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## A review of copper–arsenic mineral removal from copper concentrates

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### ABSTRACT

Arsenic is a toxic and volatile element that has little commercial use. This is causing some concern to copper smelters as they are obliged to dispose of arsenic materials produced as a by-product to the smelting process in accordance with ever tightening environmental guidelines. The onus is to move back to concentrate producers to remove toxic elements, such as arsenic, earlier in the concentrate supply chain.

The common copper–arsenic bearing minerals in copper ores, enargite ( $\text{Cu}_3\text{AsS}_4$ ) and tennantite ( $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ ), contain significant amounts of copper; 48.4% and 51.6% respectively. Removal of these minerals from the concentrate removes valuable metal, hence income. There is a dearth of literature concerning the selective removal of enargite and tennantite from sulphide ores, but there are reports on some success using either chemical oxidation or potential control. These methodologies have been applied to ores from mines as they deepen where arsenic levels in concentrate are becoming prohibitive. In this paper copper–arsenic mineral removal from copper concentrates is reviewed.

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### 1. Introduction

Arsenic is a naturally occurring element widely distributed through the Earth's crust. It is mainly produced as a by-product of base metals smelting, in particular copper, lead, cobalt and nickel concentrates. The major use of arsenic was as arsenic trioxide ( $\text{As}_2\text{O}_3$ ), formerly used as a wood preservative but its use was phased out in 2003 following concerns about the effects of arsenic exposure to human health. Current uses of arsenic are as a component of Gallium–Arsenide (GaAs) semi-conductors, as an additive to lead in car batteries, as an anti-friction agent in bearings and it has glassmaking applications. The requirement to store or dispose safely of this product has led to many smelters introducing penalties for concentrates that contain amounts above a base limit. China, the world's largest producer of arsenic in 2007, has imposed an upper limit of 5000 ppm arsenic for concentrates entering that country (USGS, 2008).

In copper ores, arsenic is often contained within tennantite ( $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ ) or enargite ( $\text{Cu}_3\text{AsS}_4$ ). These copper–arsenic minerals contain 51.6% and 48.4% copper respectively, so they tend to float similarly to other copper sulphide minerals, reporting to the concentrate. With smelters having to dispose of arsenic products in accordance with environmental regulations, they are becoming more selective in the concentrates they buy, and imposing financial penalties for excessive arsenic levels on concentrates when

appropriate. Development of an economical method of removing arsenic bearing minerals earlier in the beneficiation stream is becoming increasingly more important.

### 2. Arsenic sulphide mineralogy

Within the Andean Porphyry Copper deposits, Chile, chalcopyrite and pyrite are the primary sulphides, but tennantite and enargite are also present in the upper levels of these deposits (Pinchiera et al., 1998). The El Indio deposit lists enargite and tennantite as major minerals, chalcopyrite, arsenopyrite and tetrahedrite are among the minor minerals. Chalcopyrite is mainly associated with enargite and gold associations are also reported with these minerals (Smith, 1986).

The Cananea copper deposit in Mexico contains a stockwork and breccia pipe system of Cu–Mo sulphide mineralisation. The most important copper mineral is chalcopyrite, enargite is present and there are traces of stibioluzonite–luzonite ( $\text{Cu}_3\text{SbS}_4\text{–Cu}_3\text{AsS}_4$ ). Tennantite and tetrahedrite have also been reported. The arsenic content is variable and decreases with depth. The highest arsenic content is contained within the breccia pipes. Enargite accounts for 80% of the arsenic in the concentrate; other arsenic bearing sulphides contribute the other 20% (Perez-Segura and Zendejas-Mendivil, 1991).

Arsenic is present in the majority of the copper mineralisation at the Chelopech mine, Bulgaria, principally as the copper–arsenic sulphosalts. The flotation process recovers nearly all of the arsenic into the copper–gold concentrate, with the copper–arsenic

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sulphosalts recovery of 93% (Baltov et al., 2008). At Northparkes, chalcopyrite and bornite are the major copper minerals. Parts of the orebody are high in arsenic with the arsenic mainly occurring as tennantite (Smith and Bruckard, 2007). Development of a flowsheet to treat the Tampakan deposit in the Philippines has had to consider rejection of arsenic present as enargite (Senior et al., 2006). The Gortdrum deposit (Republic of Ireland) contained tetrahedrite and tennantite; these minerals also contained significant amounts of mercury in their lattice (Stuart and Down, 1973).

The Iberian Pyrite Belt runs in an east–west arc through southern Portugal and Spain, and contains the Aljustrel and Neves-Corvo deposits. These deposits are mined for copper, lead, zinc and tin. Arsenopyrite, tennantite and tetrahedrite have been identified in both deposits (Gaspar, 1994). Tetrahedrite and tennantite exist as a solid solution series, with zinc and mercury also present. Chalcopyrite is the main mineral of economic interest, but payments are received for silver. Tetrahedrite and tennantite depression was desired to reduce penalty payments, but any reduction in silver content has the potential to reduce total income (Byrne et al., 1995). Arsenopyrite and tetrahedrite were present in the Hellyer deposit, Australia. Tetrahedrite, although a trace constituent, accounted for about 75% of silver in the ore (Holder, 1994). Arsenopyrite was found in the McCoy/Cove gold mine in Nevada, USA, along with trace amounts of tennantite. There was an association of silver with the tennantite (Kimbal, 1993). Tennantite was present with a variety of copper sulphide minerals in both primary and transition copper/gold ore at Phu Kham, Laos (Glatthaar et al., 2007).

The majority of arsenic in copper concentrates tends to exit as either enargite or tennantite. Tennantite further co-exists, in varying proportions, in solid solution with tetrahedrite ( $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ ) at the opposite end of the series. These minerals are chemically similar to the copper minerals, so they follow the copper minerals into the saleable product. This association is found in many of the major copper deposits around the world. Arsenic and antimony are not the only elements substituting for each other, and interstitial zinc and mercury have also been reported as well as the precious metals, gold and silver. The presence of mercury compounds the environmental issues already caused by arsenic and antimony. Having gold and silver present causes an entirely different problem as the loss of these elements can reduce payments received by concentrate producers.

### 3. Removal options

#### 3.1. Magnetic separation

Tennantite and tetrahedrite belong to a group of minerals that are paramagnetic, but magnetic susceptibility can vary from particle to particle, even within the same ore. This effect may be due to the presence of surface films, or differing ratios of tetrahedrite and tennantite within an ore (Gaudin and Spedden, 1943). Magnetic separation of copper and lead minerals from tailings was attempted at the Tsumeb mine, South West Africa. The magnetic susceptibilities of the relevant minerals, bornite and tennantite, were low and there were no arsenic assay results quoted. It was however noted that recoveries to the magnetic concentrate were 70% for copper and 80% for arsenic, indicating that selectivity was poor (Svoboda et al., 1988).

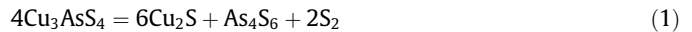
Magnetic separation of copper and copper–arsenic sulphides present a low chance of separation, so little work to progress this treatment option appears to have been conducted.

#### 3.2. Roasting

Arsenic volatilises direct to a gas. Under oxidising conditions, arsenic trioxide will form. The Gortdrum copper mine at the

Republic of Ireland produced a copper concentrate containing tennantite and tetrahedrite that assayed up to 4.7% arsenic and 5% mercury. The amount of mercury, arsenic and antimony made the concentrate unsaleable. A reduced oxygen content roasting step was incorporated, initially to reduce the mercury content, but as a secondary effect the arsenic content was also reduced (Stuart and Down, 1973).

Roasting was also used to reduce the arsenic content of copper concentrates at the El Indio mine, Chile. A high arsenic–copper flotation concentrate was produced that contained 10.5% arsenic, contained within enargite and tennantite. Roasting under oxygen deficient conditions produced a virtually arsenic free copper sulphide and an arsenic sulphide by-product:



In the post roasting step, oxygen was expected to oxidize the arsenic sulphide to arsenic trioxide and the  $\text{S}_2$  gas to  $\text{SO}_2$  (Smith, 1986). Approximately 60% of the concentrates were treated this way (Malhotra and Harris, 1999).

Incorporation of a roasting stage to the post production stream has some advantages in that an existing process will remain largely unchanged; flowsheet changes are add-ons to the back end of an existing process. However, due to the increasing environmental awareness within the industry, incorporation of roasting stages presents a serious business risk should either arsenic trioxide or sulphur dioxide be released to the atmosphere. It also fails to remove the toxic emissions problem as it merely moves it.

#### 3.3. Liberation

Kappes et al. (2007) investigated an unnamed gold–copper deposit that contained elevated levels of tennantite. Product specifications required a copper concentrate below 2000 ppm arsenic. They utilised a fine grind, approximately 20  $\mu\text{m}$ , to liberate tennantite and chalcopyrite. Flotation tests resulted in 62–80% of the arsenic reporting to cleaner tails, but so too did 7.4–14.1% of the liberated copper. They concluded that although a metallurgically successful separation of chalcopyrite and tennantite was achieved, there may be limitations to copper recovery when fine grinding was targeted as a means of liberating the arsenic-bearing minerals. Re-grinding of scavenger concentrate was however a success within a flowsheet developed for Neves-Corvo (Byrne et al., 1995). Liberation of tetrahedrite from chalcopyrite allowed for differential flotation of the two minerals in downstream stages.

The incorporation of a liberation stage into a flowsheet may be helpful in some circumstances, but it will require a thorough review of the mineralogical nature of a given orebody to determine if it has any potential uses. It will also require a differential flotation step to perform the actual separation of the liberated components.

### 4. Chemical depression

Various chemicals have been tested to depress arsenic bearing minerals. Some of the more common have been lime, cyanide and sulphide.

#### 4.1. Lime

At the Tsumeb concentrator in South West Africa, a bulk copper–lead–zinc concentrate containing tennantite was floated then sent to a 'High Lime' circuit. Copper minerals were differentially floated with only 20–30% of the tennantite reporting to the copper concentrate. Tennantite associations with sphalerite were reported, so sphalerite depression may have contributed to



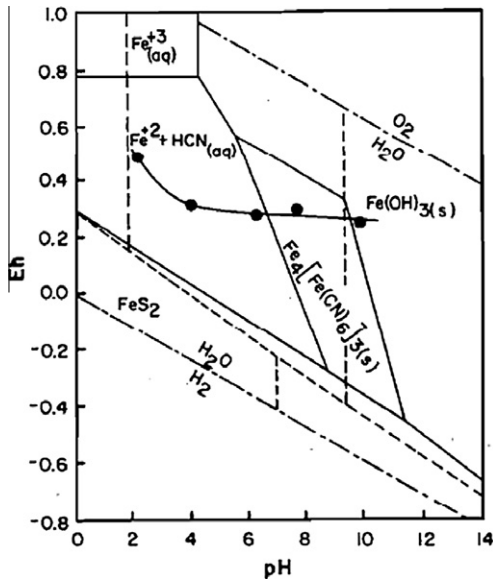
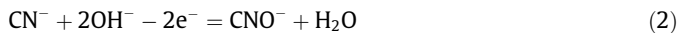


Fig. 1. Eh/pH diagram for the stability regions of various iron, sulphur, hydroxide and cyanide species in solution (from Fuerstenau and Han, 1993).

tennantite depression (Boyce et al., 1970). Lime was also used at Inco's Thompson mill to depress pentlandite and effect a copper/nickel separation (Farr, 1992). Lime reacts with the mineral to form metal hydroxides which act to prevent electron transfer on the mineral surface, thus preventing the anodic oxidation of collector anions (Fuerstenau and Han, 1993).

#### 4.2. Cyanide

Cyanide has been reported to reduce the self-induced floatability of chalcopyrite (Grano et al., 1991) and has reduced the collectorless flotation of chalcopyrite above an Eh of 0 mV SHE (Gebhardt and Richardson, 1987). Heyes and Trahar (1977) reported that the effect of cyanide was due to a reduction in the pulp potential. Guo and Yen (2003a) reported that cyanide acted by inhibiting the oxidation of xanthate ions due to the following competing reactions:



Chemical depressants were used to depress arsenopyrite from Broken Hill lead concentrates in a laboratory study. Potassium cyanide provided the best selectivity (David and Quast, 1991). Miller-

ite (NiS) was depressed from a chalcopyrite/bornite-pentlandite mix at Vale's Clarabelle mill by the use of sodium cyanide (Xu et al., 2011). Aeration conditioning increased nickel and iron recoveries over arsenic in an ore containing pentlandite, pyrrhotite and nickel-arsenides. Sodium cyanide additions and regrinding further increased nickel arsenide depression in this ore (Qun and Heiskanen, 1990).

Fuerstenau and Han (1993) reported that the depression of iron bearing minerals (such as chalcopyrite) with cyanide involves the formation of a surface ferric ferrocyanide species. The Eh/pH diagram in Fig. 1 indicates that the stability region of  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  is in the region pH 7–10, indicating a pH dependence.

#### 4.3. Sulphide

Sodium sulphide has been shown to be a chalcopyrite depressant; MAA, a mixture of 5 mol of magnesium chloride, 2 mol of ammonium chloride and 1.5 mol of ammonium hydroxide an enargite depressant. Aeration further depressed the arsenic minerals (Tajadod and Yen, 1997). Luttrell and Yoon (1984) found that repeated washing with sodium sulphide could remove hydrophilic surface products and restore the flotation response of heavily oxidised chalcopyrite. They concluded that a combination of a relatively fresh surface and oxidising conditions are required for collectorless flotation. Guo and Yen (2003a) determined that the depression effect of sulphide on the surface of synthetic chalcopyrite was due to its reducing properties, and the prevention of the oxidation of xanthate to dixanthogen on the mineral surface.

Sodium sulphide was used in the Sarcheshmeh (Iran) copper circuit to depress chalcopyrite and bornite and selectively float molybdenite. From Fig. 2, a potential of  $-550$  mV SCE ( $-306$  mV SHE) was found to provide maximum selectivity between molybdenite flotation, copper sulphide depression and sodium sulphide consumption (Kolahdoozan and Noori, 2006). Sulphide acts by the creation of reducing conditions in the flotation system, with nitrogen gas used in place of air as a means of maintaining a reducing potential.

#### 4.4. Other depressants

Other chemical depressants have been used in sulphide flotation to effect separation. Sodium dichromate was added to the Black Mountain (South Africa) copper cleaners to depress lead. Hydrogen peroxide and sodium hypochlorite were added to the copper rougher conditioner to enhance oxidising conditions and rougher grade increased (Twidle and Engelbrecht, 1984). A lead depressant was used in a plant in Peru that was based on a dichromate complex with carboxy methylcellulose (CMC) and sodium

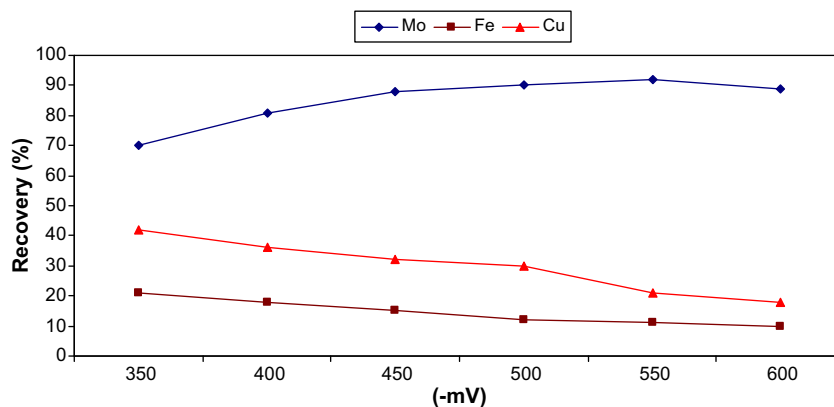


Fig. 2. Mo, Fe and Cu recovery using mineral  $\text{Na}_2\text{S}$  to control pulp potential (from Kolahdoozan and Noori, 2006).

phosphate (Bulatovic et al., 2001). Sodium hydrosulphide (NaHS) additions depressed both copper and zinc in an unnamed Turkish ore (Goktepe and Williams, 1995). In a report on the flotation of antimonial minerals, the flotation response of stibnite ( $\text{Sb}_2\text{S}_3$ ) and boulangerite ( $\text{Pb}_5\text{Sb}_4\text{S}_{11}$ ) showed a strong dependence on pH. The use of lime was more detrimental than caustic soda to the flotation response of both minerals. Bournonite ( $\text{CuPbSbS}_3$ ), however, showed flotation characteristics similar to chalcopyrite. This response was thought to be due to the presence of copper in the matrix (Lager and Forssberg, 1989).

## 5. Collector type

Goktepe and Williams (1995) determined that the highest copper recoveries were obtained in the order: potassium amyl xanthate > thionocarbamate > dithiophosphate. The dithiophosphate however was more selective, returning the highest copper concentrate grade. Hangone et al. (2005) found the order of hydrophobicity to be in the order: dithiophosphate > xanthate > dithiocarbamate. Byrne et al. (1995) found in developing a flow-sheet for Neves-Corvo that, for a given concentration, xanthate gave a higher recovery than dithiophosphate, but dithiophosphate improved selectivity between chalcopyrite and tetrahedrite. They also found that a staged collector addition improved chalcopyrite selectivity, but had to increase addition rates in the scavenger to restore copper recovery.

## 6. Pulp potential and oxidising conditions

### 6.1. Chalcopyrite

#### 6.1.1. Collectorless flotation

Chalcopyrite recovery, with and without collector, was shown to be dependent on pulp potential by Heyes and Trahar (1977), with oxidising conditions necessary for flotation. The effect was reversible when potential was cycled from oxidising to reducing, although there was some hysteresis in the potential at which flotation was initiated (Fig. 3). These results were confirmed by Gardner and Woods (1979), Trahar (1983) and Hayes and Ralston (1988). Chalcopyrite would not float in reducing conditions using a range of reducing agents. Sodium dithionite, ferrous sulphate and sodium sulphite were equally effective in reducing potential and floatability. Chalcopyrite floated with nitrogen gas in the presence of chemical oxidants, therefore the presence of oxygen gas was not considered to be a pre-requisite for chalcopyrite flotation. Gardner and Woods confirmed that the effect was due to pulp potential rather than oxygen by applying a potential directly to the pulp

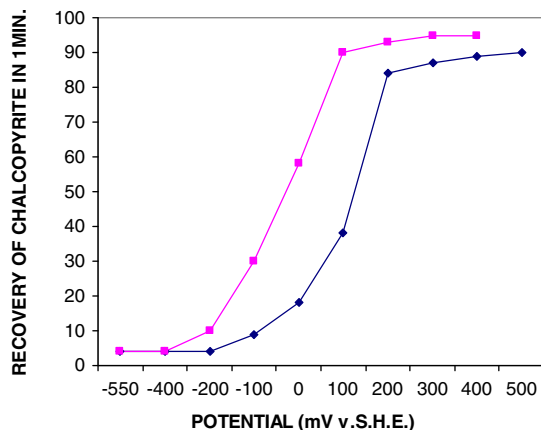
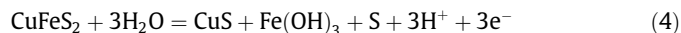


Fig. 3. Pulp potential versus recovery for collectorless chalcopyrite at pH 10 (from Heyes and Trahar, 1977).

then floating with nitrogen gas. The oxidation reaction in alkaline solutions was suggested to be:



Hayes and Ralston (1988) supported this reaction as the mechanism for chalcopyrite flotation, but noted that grinding under oxidising conditions would favour the formation of hydrophilic surface coatings; grinding under reducing conditions was necessary to produce surface hydrophobic products. Fairthorne et al. (1997) noted that the concentration of iron in solutions was higher than that of copper, and that the surface became sulphur rich although, unlike collectorless flotation, there was an absence of elemental sulphur. Hydrophobicity increases with metal dissolution, but this is offset by the formation of hydrophilic metal hydroxide species. The kinetics of formation and precipitation of the metal hydroxide species may control the hydrophobicity of the sulphide mineral surfaces.

#### 6.1.2. Flotation with collector

Guo and Yen (2003a) measured bubble contact angles in PAX solutions and confirmed that oxidising conditions were required for chalcopyrite to become hydrophobic; their work indicated a pulp potential of  $-0.2$  V SCE ( $+0.04$  V SHE) as the change from hydrophilic to hydrophobic. They also found that the contact angle decreased to a minimum around  $+0.2$  V SCE ( $+0.44$  V SHE) due to the formation of an oxide film, but increased thereafter due to an increased dixanthogen formation rate.

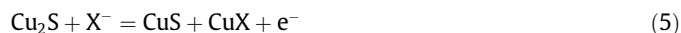
The Black Mountain concentrator, in South Africa, suffered poor copper recovery (<50%), caused by low dissolved oxygen levels following grinding. Tests determined that a combination of stainless steel grinding media and pre-aeration restored dissolved oxygen levels and pulp potential, and higher copper recoveries (above 75% as observed in the laboratory) were then achieved. It was also determined that, for this series of testwork, chemical oxidants were an unsuitable alternative to aeration (Graham and Heathcote, 1982).

A copper ore containing chalcopyrite from Cobar (Australia) demonstrated the same potential-recovery behaviour as the synthetic ore of Heyes and Trahar (1977). Flotation tests at  $+100$ ,  $+200$ ,  $+300$  and  $+400$  mV SHE demonstrated that sodium sulphite additions depressed chalcopyrite recovery at potentials greater than  $+300$  mV SHE without affecting galena, sphalerite or pyrite recoveries (Baker et al., 1991).

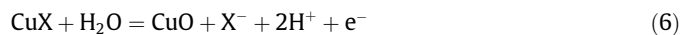
### 6.2. Chalcocite

Heyes and Trahar (1979) tested the flotation dependence of chalcocite on pulp potential. Tests using potassium ethyl xanthate showed that the lower limiting potential was between  $-200$  and  $-100$  mV SHE, similar to chalcopyrite, but there was an upper limiting potential at pH 11 in the range  $+200$  to  $+300$  mV SHE.

The exact shape of the pH 11 curve was unknown due to poor reproducibility of results in this range (see Fig. 4). The reaction product responsible for chalcocite flotation was assumed to be cuprous xanthate, formed according to the reaction:



At pH 11, cuprous xanthate decomposed to an oxide according to the reaction:



At pH 11, the upper limiting potential was determined to be  $+231$  mV SHE for  $4.7 \times 10^{-5}$  M xanthate solutions. Chalcocite also exhibited a similar hysteresis to chalcopyrite, providing the potential did not exceed the upper limiting value.

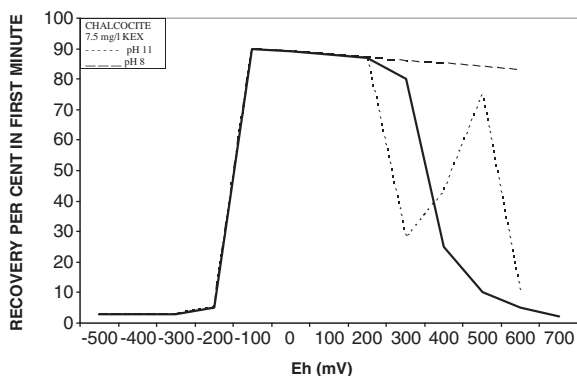


Fig. 4. Pulp potential versus recovery for chalcocite at pH 8 and 11 (from Hayes and Trahar, 1979).

In order to determine the effect of oxygen, samples were prepared in conditions designed to remove exposure to oxygen and surface oxidation products. Strong flotation was possible from a pulp in which the dissolved oxygen content was below the detection limit providing the potential was high enough. This confirmed the results obtained using chalcopyrite. If xanthate can be reduced at the surface of the mineral, the role of oxygen may be limited to that of setting pulp potential.

Differential flotation of chalcocite and molybdenite was performed in the laboratory at pH 9.3 using potassium diethyldithiophosphate. Molybdenite floated under reducing conditions and chalcocite floated under oxidising conditions (Chander and Fuerstenau, 1983). Earlier work had shown that molybdenite surfaces showed an anisotropic response to bubble contact angle as measured on the faces and edges. Crystal faces were hydrophobic, yet the edges were hydrophilic (Chander and Fuerstenau, 1972).

### 6.3. Grinding conditions

In flotation tests with galena, grinding in a stainless steel or ceramic mill allowed flotation at even the lowest potential tested. When a mild steel mill was used, flotation did not occur below 0 mV. The difference was in the redox potential within the mills. In the ceramic and stainless steel mills, the mineral was free to oxidise by the reaction with atmospheric oxygen, but the mild steel would provide cathodic protection and keep the mineral at a low potential. The use of sodium sulphide in the mill would produce a similar result (Woods, 2010).

Galena and chalcopyrite can be selectively floated without collector using Eh control providing they are ground under reducing conditions. Elemental sulphur on the surface was thought to be responsible for the hydrophobicity of both minerals. Selective sphalerite flotation was also possible providing conditions were made oxidising enough, but a metal-deficient, sulphur rich surface was thought to be responsible for sphalerite flotation rather than elemental sulphur (Hayes and Ralston, 1988). They also reported that grinding in reducing conditions reduced galvanic interactions between minerals. Gebhardt and Richardson (1987) had shown that there was a difference in the flotation rates of natural and synthetic chalcopyrite ores caused by interactions with other minerals in the natural ore. These interactions were minimised when the mineral bed was conditioned in a reducing state. Oxygen level in pulp affected chalcopyrite recovery rate from two Swedish chalcopyrite containing ores (from the Langsele and Aitik mines), but there was an optimum recovery for both when using a gas containing 50% oxygen by volume. Selectivity against both non-sulphide gangue and pyrite also increased when the environment became more oxidising (Berglund, 1991). Hintikka and Leppinen (1995)

tested a copper-lead-zinc ore and reported that optimum flotation of copper from this ore was at about 0 mV SHE. Tests on a copper-gold ore containing arsenopyrite indicated arsenic recovery reached a maximum at +150 mV SHE and dropped off over +200 mV SHE. Copper recovery remained high, indicating a selective flotation was possible.

Grinding in reducing conditions followed by an air oxidation step has been reported to decrease mineral interactions, and improve selectivity in subsequent flotation steps. Grano et al. (1990) in a study on the electrochemical effects of Mount Isa ore concluded that the critical factor appeared to be the control of addition of complexing/depressing reagents at low Eh followed by adequate conditioning to achieve an oxidising potential prior to flotation. The addition of reagents at a low enough potential may prevent, or at least minimise, these interactions. Since potentials are low during grinding in iron mills, it may be beneficial to add complexing agents, such as cyanide, during grinding to have a beneficial effect on selectivity.

### 6.4. Arsenic mineral surface oxidation

There is a limited amount of literature on the surface behaviour of the copper sulphosalts (tetrahedrite, tennantite and enargite), but what there is provides a comparison to the copper sulphides. Mielczarski et al. (1995) identified a multi-layered structure on the surface of chalcopyrite, tennantite and tetrahedrite. The outermost layer containing hydrophilic species, (mainly ferric or cupric oxides and adsorbed water), a second, sulphur rich layer exhibited hydrophobic properties and the innermost layers transitioned into the bulk mineral. The outer layer of tennantite and tetrahedrite were found to be copper rich, despite the presence of other elements in the minerals. The oxidation products in the outer layers were thinner for tennantite and tetrahedrite than for chalcopyrite due to a slower oxidation rate. Fullston et al. (1999a) later reported the rate of oxidation of various copper containing minerals followed the order: chalcocite > tennantite > enargite > covellite > chalcopyrite. Fullston et al. (1999b) found that in alkaline conditions, natural samples of tennantite and enargite oxidise more than the synthetic samples and tennantite oxidises more extensively than enargite. They also determined that there was more copper than arsenic in solution at pH 5 during dissolution tests on tennantite and enargite. The presence of copper hydroxide may have presented a barrier for the diffusion of arsenic away from the surface and confirmed that surface oxidation products on tennantite are mainly thin copper hydroxide layers. Mineral impurities and different crystal structures may be at the origin of the difference in oxidation rate observed between the natural and synthetic mineral samples, and between enargite and tennantite (Fullston et al., 1999c).

Oxidation can promote the adsorption of collectors at low to moderate levels of oxidation or prevent their adsorption by creating a physical barrier of oxidation products for their diffusion to the mineral surface at high levels of oxidation. Mineral systems of copper sulphides and copper-arsenic sulphides were tested, including a 1:1 mix of tennantite and chalcopyrite. The copper minerals could be separated from the copper-arsenic minerals due to more collector adsorption and less oxide/hydroxide species on the surface of the copper only minerals. It was likely that the surface oxide layer inhibited collector adsorption on the tennantite surfaces. There was a good separation of tennantite from chalcopyrite at pH 5.0, or at pH 11.0 after oxidation with hydrogen peroxide followed by EDTA addition to remove surface oxidation products (Fornasiero et al., 2000). pH was shown to have an effect on enargite oxidation, with a higher potential being required for oxidation as the pH was lowered. Copper hydroxide was the major oxidation

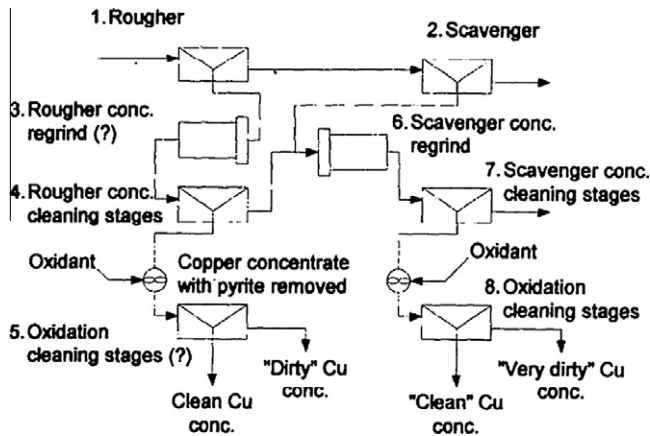


Fig. 5. Conceptual Neves-Corvo flowsheet (from Byrne et al., 1995).

product on the surface of enargite in alkaline solutions (Guo and Yen, 2008).

### 6.5. Arsenic mineral surface products

Mielczarski et al. (1995, 1996a,b) investigated the surface products of chalcopyrite, tetrahedrite and tennantite in amyl xanthate solutions at pH 10. All three minerals had a two product surface structure, with a surface, generally thin, layer of cuprous amyl xanthate, and an outer layer of dixanthogen. The inner layer was constant once formed, but the amount of dixanthogen increased with an increase in potential. The cuprous amyl xanthate layer was more stable than the dixanthogen; the dixanthogen easily washed off with ethanol. Xanthate adsorption was by electrochemical means, which involved the formation of hydrophobic cuprous amyl xanthate and hydrophilic metal (iron, antimony and arsenic) oxides and hydroxides. Of the three minerals, only tetrahedrite formed hydrophobic products on the surface at the open circuit potential (OCP). Amyl xanthate was not adsorbed at OCP on chalcopyrite, and in order to produce a hydrophobic layer relatively quickly, an increase in potential of 50 mV was required. For tennantite, an extended adsorption time was required for the formation of the xanthate two-product adsorption layer, but this may have been due to the presence of sphalerite in the mineral.

The surface products of chalcopyrite, tetrahedrite and tennantite in xanthate solutions in pH 10 solutions are similar, so their flotation response would be thought to be similar. However, chalcopyrite required a 50 mV increase in pulp potential for the hydrophobic products to form, and formation on tennantite was the slowest. Maintenance of the pulp potential at the OCP is a possible means of preferentially floating tetrahedrite and tennantite over chalcopyrite.

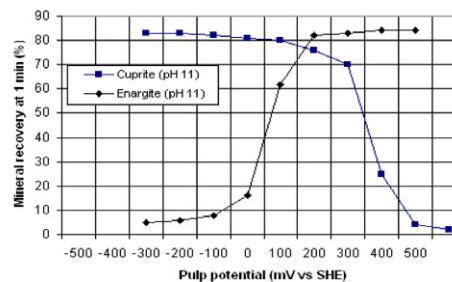
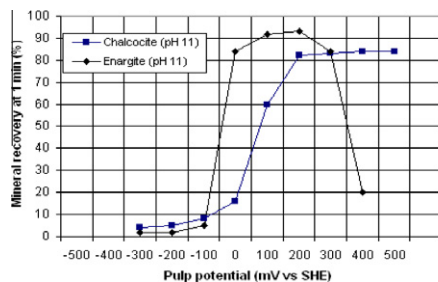


Fig. 6. Potential versus recovery curves for chalcocite and cuprite against enargite demonstrating the small window available for selective flotation (from Senior et al., 2006).

## 7. Methods of potential control

There are two main methods used to control potential in the laboratory, chemical addition or externally applied potentials. Hydrogen peroxide or sodium hypochlorite are common oxidising agents, sodium sulphide or sodium dithionite common reductants. By setting the potential externally, the chemical effect of the above reagents is removed as a variable from the flotation results. The application of an external potential is not however as effective in controlling Eh as chemical adjustments. The electrode configuration had an effect on the efficiency of the external potential for controlling the chalcopyrite flotation. This was due to the electronic charge staying on the surface of the bed and not penetrating into the bed (Guo and Yen, 2003b). A technique for Eh control using flotation gases was presented by Hintikka and Leppinen (1995). Air or nitrogen would be fed automatically as required to maintain the pulp potential to a set level.

## 8. Flowsheets

There have been four flowsheets developed to separate copper-arsenic minerals from copper minerals.

### 8.1. Neves-Corvo, Portugal

The Neves-Corvo deposit, located in southern Portugal, is part of the Iberian Pyrite Belt that runs through the southern part of Portugal and Spain. Copper, as chalcopyrite, was the main metal recovered, with credits obtained for silver. Impurity elements in the copper concentrate included arsenic, antimony and mercury, contained in a tetrahedrite-tennantite series of minerals. These minerals also host some of the silver. A process was sought that would remove the penalty elements while retaining the silver. Staged collector addition was employed to selectively float chalcopyrite and produce a rougher concentrate low in antimony. Further collector additions produced a scavenger concentrate high in antimony. Scavenger concentrate was re-ground to liberate tetrahedrite from chalcopyrite. Hydrogen peroxide was added to the late stages of the cleaning circuit (where pyrite content was low) to reject tetrahedrite. The cleaner circuit tails would contain high levels of arsenic, and silver, which would require further treatment to eliminate antimony. Fig. 5 contains a diagrammatical representation of the flowsheet. (Byrne et al., 1995).

### 8.2. Tampakan

The Tampakan copper-gold deposit is located on the SE part of Mindanao in the Philippines. The resource is currently estimated to be 1340 million tonnes at 0.66% copper and 0.27 g/t gold. The deposit also contains enargite. A conceptual flowsheet was developed to separate the minerals as follows (with reference to Figs. 6 and 7):

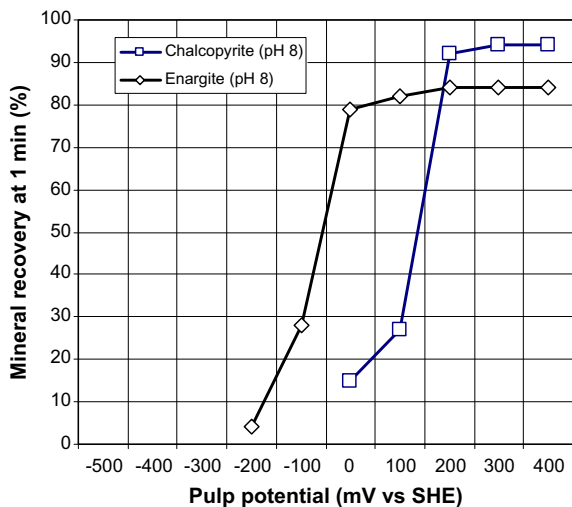


Fig. 7. Potential versus recovery curve for chalcopyrite and enargite (from Senior et al., 2006).

1. Flotation at under a reducing condition ( $-125$  mV SHE) at pH 11 to float off chalcocite and cuprite.
2. Raise the potential to 0 mV SHE at pH 11, to float off the enargite and any remaining chalcocite. The tails will be rich in chalcopyrite.
3. Combine the froth products from stage 1 and stage 2 and raise the potential above +290 mV (SHE). The enargite will float and leave a chalcocite-cuprite rich tails.

Potential changes were logical and reagent dosages should be minimal by keeping relevant flows low. Nitrogen was proposed as the flotation gas in stages 1 and 2; potential changes can be made through aeration where possible, but some chemical additions may be required. The enargite rich product from stage 3 would pass to an arsenic removal stage (Senior et al., 2006). In the Northparkes study, Smith and Bruckard (2007) reported that the technique was successfully tested on a sample of Tampakan drill core, enabling the production of high-arsenic and low-arsenic concentrates.

### 8.3. Northparkes

The Northparkes orebody contains chalcopyrite-bornite with tennantite the main arsenic bearing mineral. Conventional flotation testwork had indicated concentrates containing up to 5000–7000 ppm arsenic, the target being 2000 ppm. Selective oxidation or the exploitation of pulp potential effects was deemed the most

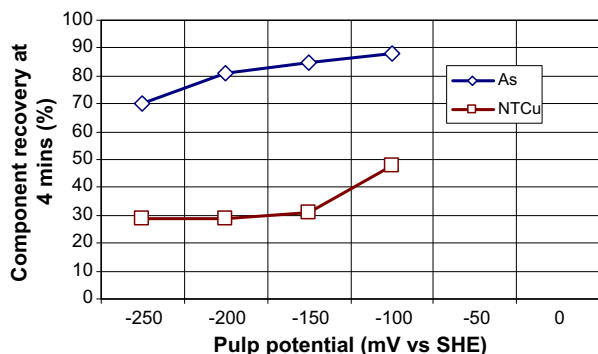


Fig. 8. Potential versus recovery for arsenic bearing copper minerals and non-tennantite copper minerals (from Smith and Bruckard, 2007).

likely approach if a successful separation of tennantite from the copper sulphide minerals was to be effective. Between  $-200$  and  $-130$  mV (SHE) there was a window of opportunity identified where tennantite could be floated from other non-tennantite copper minerals from a bulk rougher concentrate (see Fig. 8). Recovery of arsenic in this region was 80–90% while recovery of non-tennantite copper was about 30%. After the tennantite was removed, air was used instead of nitrogen and a low arsenic concentrate was floated.

A conceptual flowsheet was devised:

1. A bulk copper–arsenic concentrate is produced using standard flotation conditions.
2. The bulk concentrate is reground and fed to an arsenic rejection step (the benefits of liberation were unknown at the time of reporting, but it helped to produce the reducing conditions necessary for the next stage).
3. The pH is raised to 12 and the pulp potential set to about  $-150$  mV SHE with nitrogen being used as the carrier gas. The resultant froth concentrate is high in arsenic and needs to be treated to remove the arsenic and recover the copper.
4. Tails from stage 3 are floated at the air-set potential using air and chalcopyrite-bornite is floated off.

The bulk copper–arsenic product from stage 2 has low volume, so pulp potential should be easier to control in the subsequent stages (Smith and Bruckard, 2007).

### 8.4. Commonwealth Scientific and Industrial Research Organisation (CSIRO)

The Australian CSIRO has developed a flowsheet that combines selective flotation, roasting and safe disposal of arsenic bearing residues. Small scale flotation, roasting and stabilization tests were conducted using a high arsenic bearing ore as the primary feed to validate the process. The flowsheet involved a bulk rougher flotation stage to produce a combined arsenic–copper concentrate. This was treated in a controlled potential flotation stage to separate a high arsenic product which was roasted to remove the arsenic. The roast is conducted at low temperature, 700 °C, as per Gortdrum and El Indio. The arsenic reports to a fume which is stabilized in a ceramic matrix which can be stored underground (Bruckard et al., 2010).

## 9. Summary

The formation of copper oxide on the surface on chalcocite at pH 11 was reported by Heyes and Trahar (1979) to stop chalcocite flotation above a pulp potential of +231 mV SHE. Fullston et al. (1999c) have also shown that oxidised layers formed on each of chalcopyrite, tetrahedrite and tennantite, and the depth varied according to the oxidation rate. Fornasiero et al. (2000) determined an inverse relationship between the amount of oxidation and the level of xanthate adsorption, hence floatability. Surface oxidation products are similar for chalcopyrite and copper-sulphosalts, hence flotation response is similar.

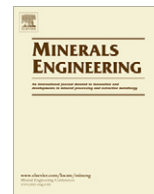
The formation of cuprous xanthate on the mineral surface was determined to be a requirement for copper mineral flotation by Heyes and Trahar (1979) and Mielczarski et al. (1995). There was a minimum potential above which cuprous xanthate would form, but further increases in potential could result in the decomposition of cuprous xanthate to an oxide, preventing flotation.

Dithiophosphate collectors provide lower copper recoveries but better selectivities than xanthates, so may be preferred for a given mineral.

Differential flotation with control of pulp potential represents an option for reducing the arsenic content of copper concentrates.

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## Selective leaching of arsenic and antimony from a tetrahedrite rich complex sulphide concentrate using alkaline sulphide solution

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### ABSTRACT

Removal of impurity elements in copper metallurgy is one of the major problems encountered today since pure copper ore reserves are becoming exhausted and the resources of unexploited ores often contain relatively high amounts of impurity elements like antimony, arsenic, mercury and bismuth, which need to be eliminated. The present work is aimed at pre-treating a tetrahedrite rich complex sulphide concentrate by selective dissolution of the impurities, therefore, upgrading it for pyrometallurgical processing. To accomplish this, dissolution of antimony and arsenic by an alkaline sulphide lixiviant from the concentrate were investigated. The lixiviant proved selective and effective to dissolve these impurity elements from the concentrate with good recoveries. Further investigations on the factors influencing the leaching efficiency of the lixiviant were studied. The parameters considered were sulphide ion and hydroxide ion concentrations, mineral particle size, reaction temperature and leaching time. Analysis of the leach residue indicates that copper content of tetrahedrite has transformed into copper sulphides with the average chemical formula  $\text{Cu}_{1.64}\text{S}$ . The grade and economic value of the concentrate were improved greatly after sulphide treatment, and therefore, suitable as a feedstock for smelting. The impurities have been reduced to low levels which are tolerable in the smelting furnace and consequently reduce both the treatment and environmental problem encountered when such concentrate is processed pyrometallurgically.

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### 1. Introduction

Copper extraction through pyrometallurgical processing of concentrate relies heavily on copper sulphides; and to a lesser degree on copper oxides, which are processed hydrometallurgically. The majority of copper sulphide mineral deposits mined today are complex in nature. These minerals are often found in association with tetrahedrite ( $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ ), enargite ( $\text{Cu}_3\text{AsS}_4$ ) and tennantite ( $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ ) minerals (Riveros and Dutrizac, 2008), which render them less appropriate as a feed material for smelting due to their antimony, arsenic and mercury contents that can create serious processing and environmental problems (Curreli et al., 2009; Filippou et al., 2007; Lattanzi et al., 2008). These minerals are economically attractive due to their substantial contents of silver and copper (Baláz et al., 1998; Havlik et al., 1999); however, the content of antimony and arsenic effectively reduces their economic value due to requirements for further treatment options for the containment of hazardous emissions from pyrometallurgical processing. Also, the presence of these noxious elements will signifi-

cantly affect both the quality and the physical properties of the copper product (Filippou et al., 2007; Mihajlovic et al., 2007; Tong-amp et al., 2009; Viñals et al., 2003; Wang, 2004). Besides, arsenic and antimony have been considered as undesirable elements that cause serious toxicological and environmental problems (Filippou et al., 2007) which have forced the smelters to be selective of the type of concentrate to process due to the stringent environmental laws. Wang (2004) explained further that during copper smelting, most of the undesirable impurities such as antimony, arsenic, bismuth and lead are only partially removed by oxidation. When white metal and blister copper are in equilibrium, these impurities are partly distributed into the copper phase, from which their removal is difficult. Furthermore, Navarro and Alguacil (2002) explained that during electro-refining of impure copper, the impurity elements would gradually increase in concentration to their solubility limits if no electrolyte was eliminated from the electro-refining circuit. However, they would passivate the anodes and also contaminate the cathodes which cause a decrease in the efficiency of the electro-refining plant. Consequently, the electrolyte is usually treated conventionally by withdrawing a bleed from the stream to recover its copper content and isolate, and recover the impurities afterwards. But, this conventional method of treatment has some disadvantages which include; difficult materials

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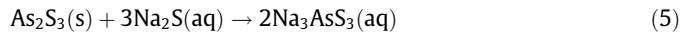
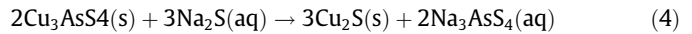
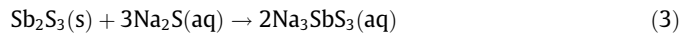
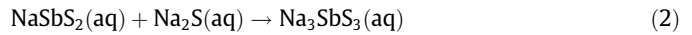
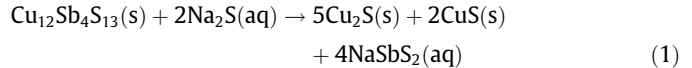
handling, energy consumption, possibility of toxic arsine gas formation, and loss of high copper in a low value recycle product (Navarro and Alguacil, 2002).

As a result of the global increase in demand for base metals, mining companies are now paying more attention to the low grade and complex sulphide ore deposits to economically process them. However, this necessitates pre-treatment operations to be conducted to selectively remove the impurities prior to the smelting of the copper concentrates. Therefore, this paper reports and discusses the studies carried out on the selective leaching of antimony and arsenic under various experimental conditions from a tetrahedrite rich complex sulphide concentrate in alkaline sulphide media.

## 2. Methods of pre-treating As/Sb rich sulphide ores/concentrates

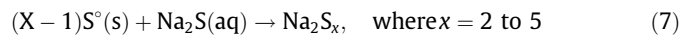
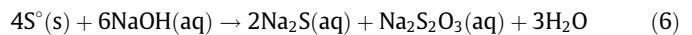
In an attempt to upgrade sulphide concentrates rich in arsenic and antimony for pyrometallurgical processing, selective flotation of enargite, tetrahedrite and tennantite from other copper sulphides such as covelite (CuS), chalcopyrite (CuFeS<sub>2</sub>), chalcocite (Cu<sub>2</sub>S) and bornite (Cu<sub>5</sub>FeS<sub>4</sub>) has been studied (Curreli et al., 2005; Filippou et al., 2007). The outcome showed that these minerals are difficult to separate from other sulphide minerals (Filippou et al., 2007) because they exhibit similar flotation properties as copper sulphides and therefore report to copper concentrates.

Apart from this, a more cost effective and environmentally friendly process for the removal of antimony and arsenic from the so called “dirty concentrates” prior to pyrometallurgical processing has been considered to be achieved through hydrometallurgical process (Baláz and Achimovičová, 2006b; Baláz et al., 1998; Nadkarni et al., 1975). The discussions about the possibility of leaching antimony–arsenic bearing minerals in copper resources are available in literature. It is reported that the amphoteric nature of antimony allows the use of both acidic and basic media for its solubilization (Anderson, 2001; Baláz et al., 2001). In reality, only two lixiviant systems are utilized in antimony hydrometallurgy: acidic chloride (Correia et al., 2001; Correia et al., 2000; Guy et al., 1983; Havlik et al., 1999; Havlik and Kammel, 2000; Padilla et al., 2005) and alkaline sulphide (Awe, 2008; Baláz and Achimovičová, 2006a; Baláz and Achimovičová, 2006b; Baláz et al., 2001; Frohlich and Miklos, 2001). Previous studies have shown that arsenic and antimony containing minerals dissolve slowly in acidic media below 100 °C (Correia et al., 2001; Padilla et al., 2005). Significantly faster leaching rates have been obtained in alkaline media containing sulphide (Awe et al., 2010; Awe and Sandström, 2010; Baláz et al., 2000; Baláz et al., 2001) or sodium hypochlorite (Viñals et al., 2003) as well as in acid media at elevated temperatures (Neiva Correia et al., 1993; Riveros and Dutrizac, 2008). Due to the refractoriness of tetrahedrite, enargite and tennantite to most lixiviant; concentrated leaching agents, high reaction temperatures and long leaching times are required to efficiently dissolve antimony and arsenic (Baláz, 2000). In a recent study conducted by the authors, it was shown that the rate of leaching tetrahedrite in alkaline sulphide lixiviant was chemically controlled through the particle surface reaction (Awe et al., 2010). Filippou et al. (2007) reported that alkaline sulphide solution is selective in dissolving antimony and arsenic; and the copper product obtained after sulphide leaching may be chalcocite or covelite, while arsenic and antimony are dissolved as thioanions: thioarsenite (AsS<sub>3</sub><sup>3-</sup>), thioarsenate (AsS<sub>4</sub><sup>3-</sup>), thioantimonite (SbS<sub>3</sub><sup>3-</sup>), thioantimonate (SbS<sub>4</sub><sup>3-</sup>), etc. depending on the feed composition and the reaction conditions. The chemical reactions occurring during sulphide leaching are briefly described as follow (Filippou et al., 2007):



Baláz et al. (1998) disclosed that sulphide lixiviant reacts with mercury to form a soluble salt complex which could easily be hydrolyzed if the alkali concentration is very low.

Furthermore, alkaline sulphide leaching processes have been utilized industrially at operations in Russia, China, the Sunshine antimony refinery, Idaho, USA (Anderson and Krysz, 1993), and also at Equity Silver Mines Ltd., British Columbia, Canada (Dayton, 1982; Filippou et al., 2007). At Sunshine, the lixiviant was produced on site by dissolving elemental sulphur, a major product of the silver refinery, in sodium hydroxide and the resulting solution contains the following chemical species; sodium sulphide, thiosulphate and polysulphides according to reactions (6) and (7) (Ackerman et al., 1993).



In addition, the leach processes at Sunshine Mining and Equity Silver Mines are somehow similar while the solution purification processes are different. Antimony was electrowon from the leach solution at Sunshine Mining (Nordwick and Anderson, 1993) whereas Equity Silver Mines entirely recovered antimony in autoclaves as sodium hydroxyl antimonate and arsenic was converted to calcium arsenate to be impounded at a site far from the mine (Dayton, 1982; Filippou et al., 2007).

Due to the widespread occurrence of antimony and arsenic containing minerals in copper concentrates, a suitable pre-treatment process to selectively remove antimony and arsenic from such concentrates is a necessity. If the impurity content is reduced to an acceptable limit the penalties charged by the smelters would be alleviated. Thus, antimony can be recovered as marketable products while arsenic can be precipitated as a stable material (e.g. ferric arsenate) suitable for landfills. By so doing, pyrometallurgical treatment of the so called “dirty ore/concentrate” will be made possible with more economical viability and environmental friendliness.

## 3. Materials and methods

### 3.1. Material characterization

The antimony-bearing sulphide material used in this investigation was bought from Gregory, Bottley & Llooyd Company, United Kingdom and originated from Casapalca, Departamento Lima, Peru. The coarse material was first crushed and part of its associated quartz was removed by handpicking prior to grinding. The ground sample was sieved into the following size fractions: –106 + 75, –75 + 53, –53 + 38 and –38 + 20 μm, which were used in the study. The concentrate contains 5.43–5.78% Sb and 1.77–1.87% As and other elements as shown in Table 1.

X-ray powder diffraction (XRD) patterns were collected from pulverised solid samples using a Siemens D5000 Automated Powder Diffractometer equipped with a continuous scanning device. Patterns were collected between 2θ angles of 5–90° (at Cu Kα radiation of 40 kV, 30 mA). Mineral phases were identified using the



**Table 1**  
Chemical analysis of a tetrahedrite rich sulphide concentrate.

Size fraction (%)	−106 + 75 μm	−75 + 53 μm	−53 + 38 μm
Cu	15.6	15.2	15.7
Fe	11.1	14.2	13.3
Zn	16.1	16.8	16.9
Sb	5.78	5.43	5.71
As	1.87	1.86	1.77

Joint Committee for Powder Diffraction Standards (JCPDS) file of the instrument.

A representative sample was taken from the antimony-bearing sulphide concentrate and also from the leach residue, at which the highest recovery of antimony was obtained, for QEMSCAN (a scanning electron microscope with four energy dispersive X-ray detectors and a microanalyser) analysis. The samples were mounted in epoxy and a diamond cutting wheel was used to cut the hardened blocks to size and expose the sample grains. The samples were polished and carbon coated prior to QEMSCAN analysis. The mineralogy of particles was inferred from data obtained using the QEMSCAN<sup>®</sup> advanced mineral analysis system. The particles were examined using the Field Scan method, involving spot analyses over the surface of the block, collection of the resultant X-ray spectra and comparison with a spectral data base.

### 3.2. Leaching

Antimony and arsenic selective removal tests were performed by dissolving the antimony-bearing sulphide concentrate in alkaline sulphide solutions, to determine the effect of the following parameters: sodium sulphide ( $\text{Na}_2\text{S}\cdot 3\text{H}_2\text{O}$ ) concentration (0.76 M, 1.14 M and 1.89 M), sodium hydroxide (NaOH) concentration (0.75 M and 1.5 M), leaching temperature (357 K, 364 K, 371 K and 378 K) and mineral particle size (−53 + 38 μm, −75 + 53 μm and −106 + 75 μm). All experiments, each lasting 6 h, were carried out with 0.5% solids, −75 + 53 μm particle size and 378 K reaction temperature (except where otherwise stated) in 500 mL leach

solution containing 1.14 M  $\text{Na}_2\text{S}\cdot 3\text{H}_2\text{O}$  + 1.5 M NaOH. A 500 mL four-necked round bottomed glass reactor was used which was stirred mechanically with a paddle stirrer at a constant stirring rate of 600 rpm and heated in an auto-regulated system. The lixiviant was first added to the reactor and when the desired temperature was reached, the solid sample was added. At predetermined time intervals, 5 mL sample solution was taken from the reactor for the analysis of dissolved metals. All reagents used for leaching and chemical analysis were of analytical grade and used without further purification. The influence of each variable was determined by keeping all other variables constant. Leaching results were evaluated by means of chemical determinations on the leach products using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)/Sector Field Mass Spectrometry (ICP-SFMS).

## 4. Results and discussion

### 4.1. Mineralogical composition

The mineralogical composition of the antimony-bearing sulphide concentrate was investigated using XRD and QEMSCAN methods of analysis. Fig. 1 shows the result obtained from XRD analysis performed on the concentrate. The major mineralogical phases identified in the diffractogram were tetrahedrite, sphalerite, galena, chalcopyrite, pyrite and iron sulphide.

QEMSCAN analysis was conducted on the concentrate sample to confirm the mineralogy previously determined by the XRD technique. The result from this method is shown in Fig. 2 and Table 2. This result compares well with the XRD identification of the major phases present in the concentrate, but the method identifies a much wider range of minor minerals (Table 2) that were below the detection limit for XRD. This confirms that QEMSCAN analysis can provide much more mineralogical information than the XRD method for trace mineralogy (Goodall et al., 2005). No arsenic mineral was detected by the two techniques meaning that the arsenic in the mineral is hosted in the tetrahedrite structure. Also, QEMSCAN result shows that the concentrate is rich in tetrahedrite (Table 2) and silver is found bonded in the tetrahedrite

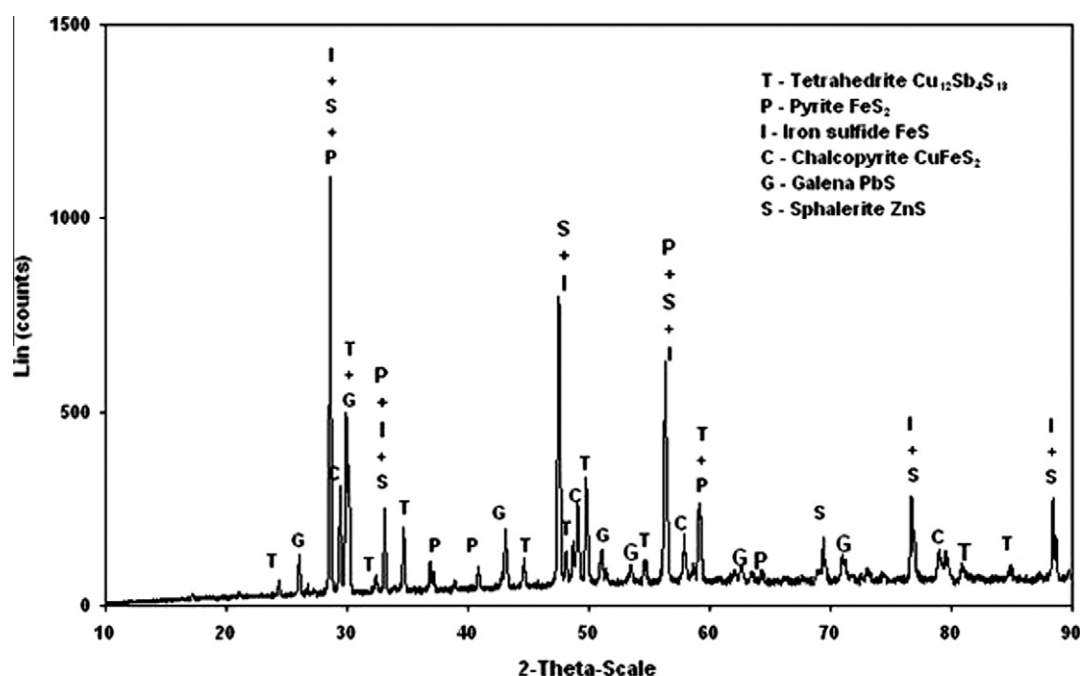


Fig. 1. XRD diffractogram of antimony-bearing sulphide concentrate.

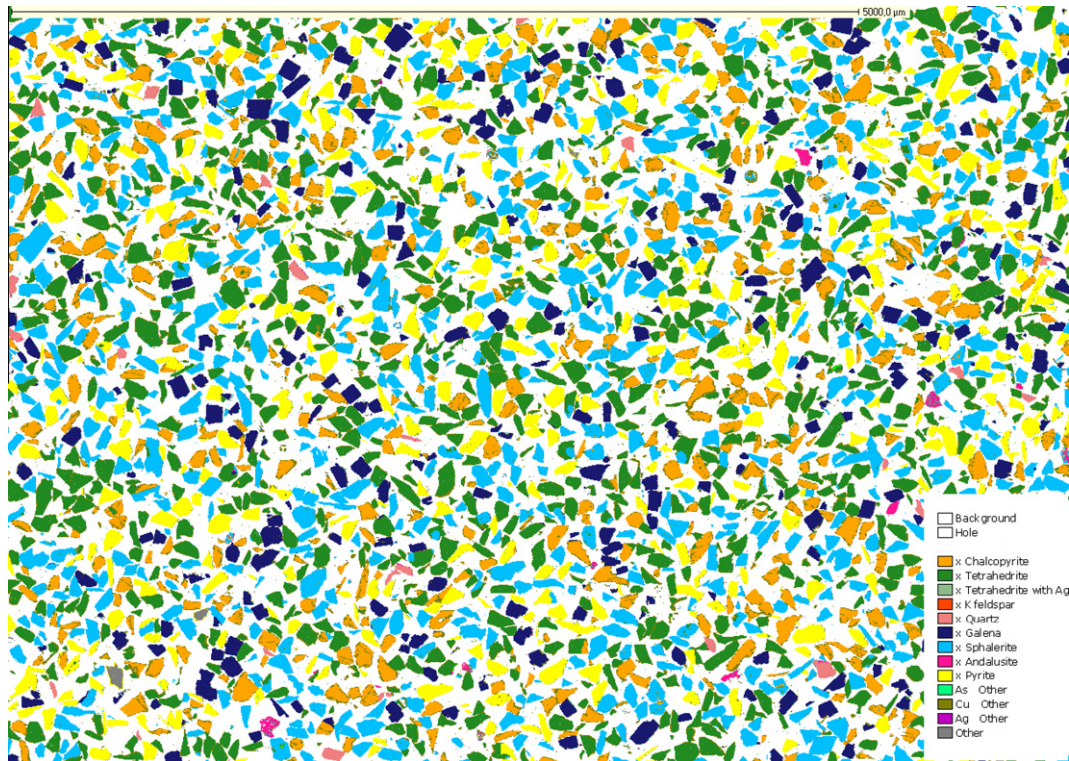


Fig. 2. QEMSCAN micrograph of Sb-bearing sulphide concentrate.

**Table 2**  
Material mineralogy defined by QEMSCAN.

Mineral	Mass fraction (% w/w)
Tetrahedrite	30.2
Sphalerite	20.6
Galena	19.0
Pyrite	15.7
Chalcopyrite	13.4
Quartz	0.4
Tetrahedrite with Ag	0.1
Andalusite ( $\text{Al}_2\text{SiO}_5$ )	0.1
Total	99.5

(Fig. 2). This confirms the presence of silver and arsenic as a solid solution in the tetrahedrite crystal structure as widely reported in the literature (Filippou et al., 2007).

#### 4.2. $E_h$ -pH and speciation diagrams

In order to study the behaviour of sulphide ions during leaching in relation to the solution pH, an equilibrium  $E_h$ -pH diagram for S- $\text{H}_2\text{O}$  system was constructed using FactSage 6.1 computer software at the temperatures of 298 K and 378 K (Fig. 3a and b), respectively. The equilibrium diagram (Fig. 3) obtained shows that at lower redox potential,  $\text{S}^{2-}$  ion is the dominant ion in the solution at  $\text{pH} \geq 13$  at 298 K (Fig. 3a) and at  $\text{pH} \geq 11$  at 378 K (Fig. 3b). This implies that higher concentration of sodium hydroxide will be required at 298 K than at 378 K in order to prevent the protonation of  $\text{S}^{2-}$  to  $\text{HS}^-$  in the solution and therefore, making it available to solubilize antimony by forming soluble sulphide complexes. During sulphide leaching of tetrahedrite, sodium sulphide dissociates according to reaction (8) and antimony forms the complexes thioantimonite and thioantimonate (Filippou et al., 2007) with sulphide ions as shown in reactions (1) and (2). Many other species

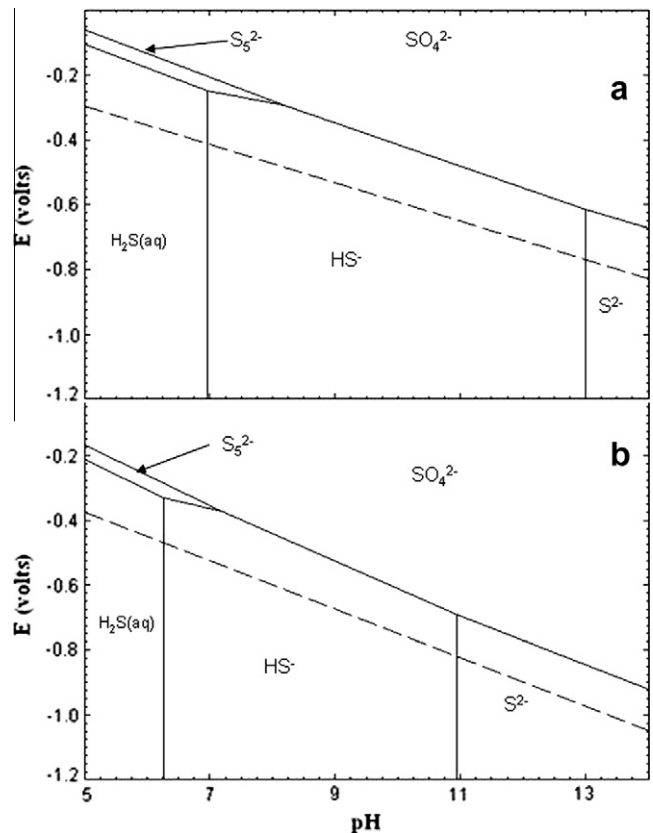


Fig. 3.  $E_h$ -pH diagram of the S- $\text{H}_2\text{O}$  system at (a) 298 K and (b) 378 K. The dashed line represents  $\text{H}_2(\text{g})/\text{H}_2\text{O}$ .

such as polysulphides, thiosulphates and sulphates (Fig. 3) may form if the leaching is performed under an oxidising environment.

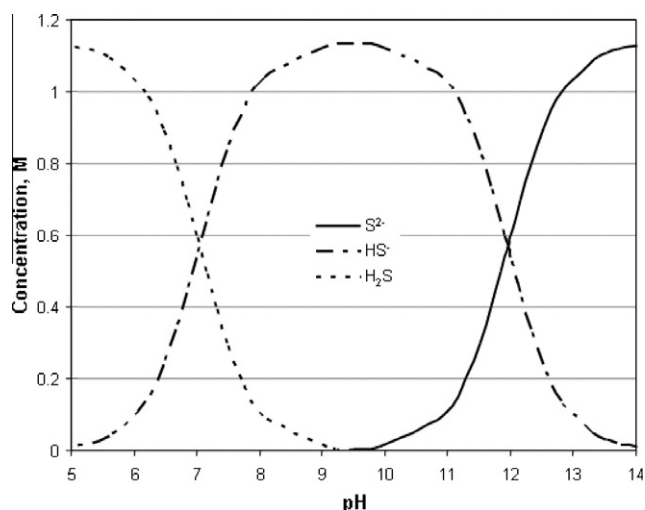


Fig. 4. Equilibrium diagram of sulphide species as a function of pH at a total sulphide ion concentration of 1.14 M at 298 K.

Protonation of sulphide ions occur according to the equilibria (9) and (10) (Delfini et al., 2003) which take place simultaneously during the leaching process.

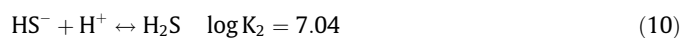
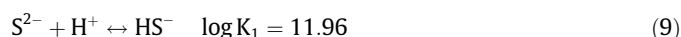
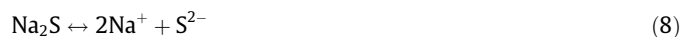


Fig. 4 shows a plot of the molar concentrations of  $\text{S}^{2-}$ ,  $\text{HS}^-$  and  $\text{H}_2\text{S}$  in the leach liquor as a function of the solution pH at a total sulphide concentration of 1.14 M. It can be seen from Fig. 4 that sulphide ion concentration increases rapidly when pH is increased from 10 and upwards, therefore, pH is an important factor. This is because, at a  $\text{pH} > 12$ , the protonation of sulphide ions will be prevented and therefore available to solubilize antimony according to reactions (1) and (2). Also, a strong alkaline environment is needed to reduce the consumption of more expensive sodium sulphide due to the hydrolysis of sulphide ions (Eq. (11)).



#### 4.3. Influence of temperature on antimony and arsenic dissolution

The plot shown in Fig. 5 describes the dependency of antimony and arsenic extraction from a tetrahedrite rich sulphide concentrate on the reaction temperature which was varied in the range between 357 K and 378 K. It is evident from Fig. 5 that, after 6 h, the extraction of antimony and arsenic from the mineral is highly influenced by the reaction temperature. At 357 K, 15% and 16% of antimony and arsenic were extracted respectively, and when the reaction temperature was increased to 378 K, about 57% and 60% of antimony and arsenic were extracted, respectively. This observation supports the conclusion made by (Baláž and Achimovičová, 2006a) that temperature accelerates and enhances the extraction of metals into the leach liquor.

#### 4.4. Effect of leaching time on extraction

The effect of leaching time on antimony and arsenic dissolution from the complex sulphide concentrate were investigated and the experimental results are presented in Fig. 6. Increasing the leaching time resulted in increased antimony and arsenic extraction. Due to the narrow size fraction used in this investigation, the metal extraction by the lixiviant is linearly dependent on the leaching time. After 1 h of leaching, approximately 13% of both antimony and arsenic was extracted, and when the leaching time was increased to 6 h, antimony and arsenic extraction was 57% and 60%, respectively. Examination of metal extraction trend shown in Fig. 6 reveals that higher extraction could be achieved if the leaching time was extended beyond 6 h.

#### 4.5. Influence of sulphide ion and hydroxide ion concentrations

In the experiments to study the influence of  $\text{Na}_2\text{S}$  concentration on antimony and arsenic dissolution,  $\text{Na}_2\text{S}$  concentration was varied in the range of 0.76–1.89 M while the  $\text{NaOH}$  concentration was kept constant at 1.5 M. The result is described in Fig. 7. It is apparent from the figure that  $\text{Na}_2\text{S}$  concentration has a significant effect on the extraction of antimony and arsenic from the mineral. After 6 h leaching, approximately 21% of antimony and arsenic was extracted at a concentration of 0.76 M  $\text{Na}_2\text{S}$  and when the  $\text{Na}_2\text{S}$  concentration was increased to 1.14 M, the extraction increased with almost a factor of 3. Further increase in the concentration to 1.89 M  $\text{Na}_2\text{S}$  resulted in an extraction of antimony and arsenic of 87% and 92%, respectively (Fig. 7).

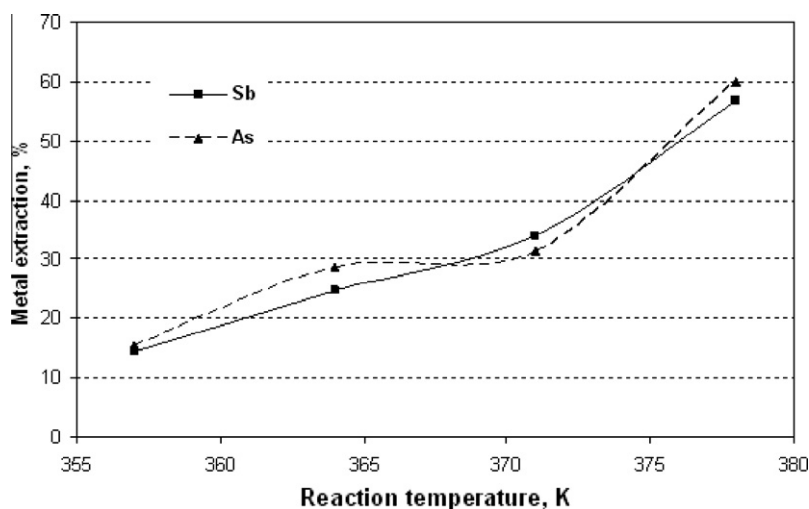


Fig. 5. Influence of reaction temperature on As/Sb leaching.

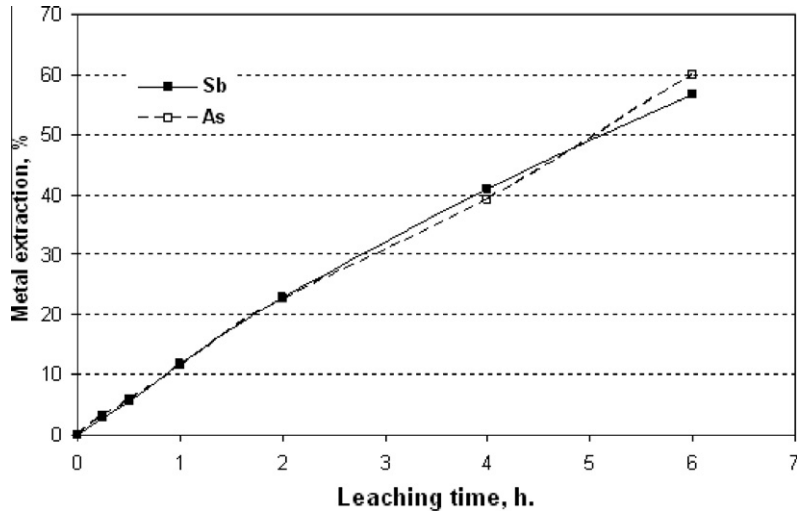


Fig. 6. Effect of leaching time on As/Sb leaching.

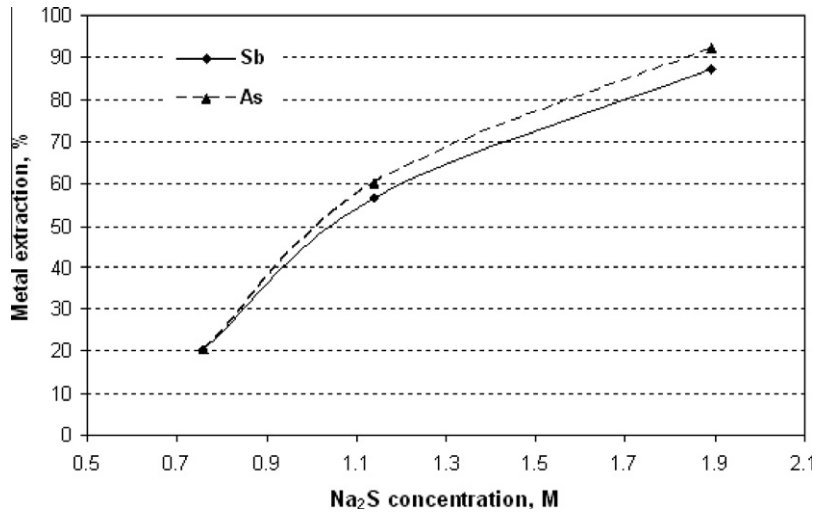


Fig. 7. Effect of sodium sulphide concentration on As/Sb leaching.

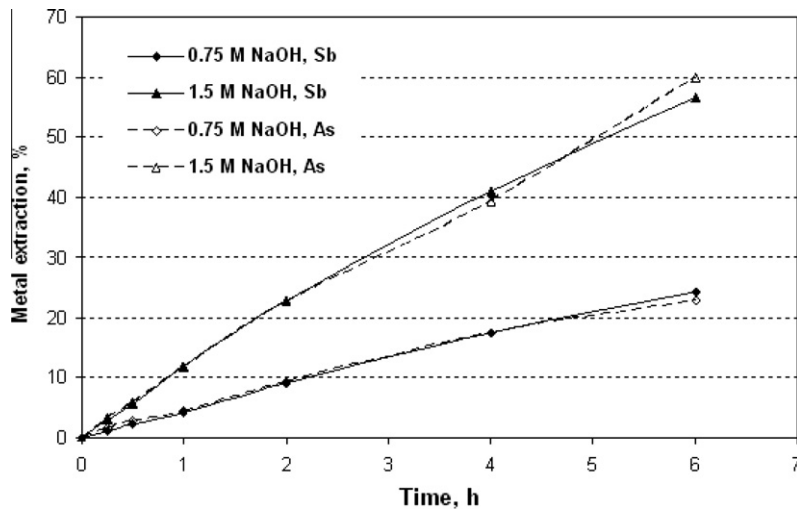


Fig. 8. Effect of sodium hydroxide concentration on As/Sb leaching.

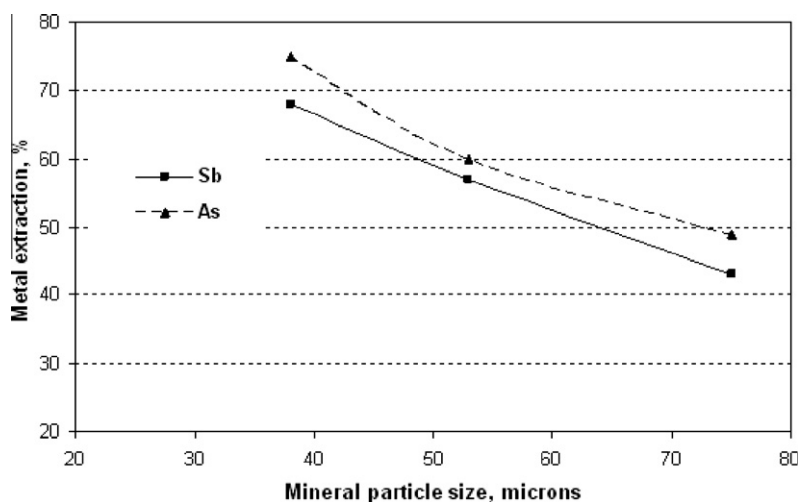


Fig. 9. Effect of particle size on As/Sb leaching.

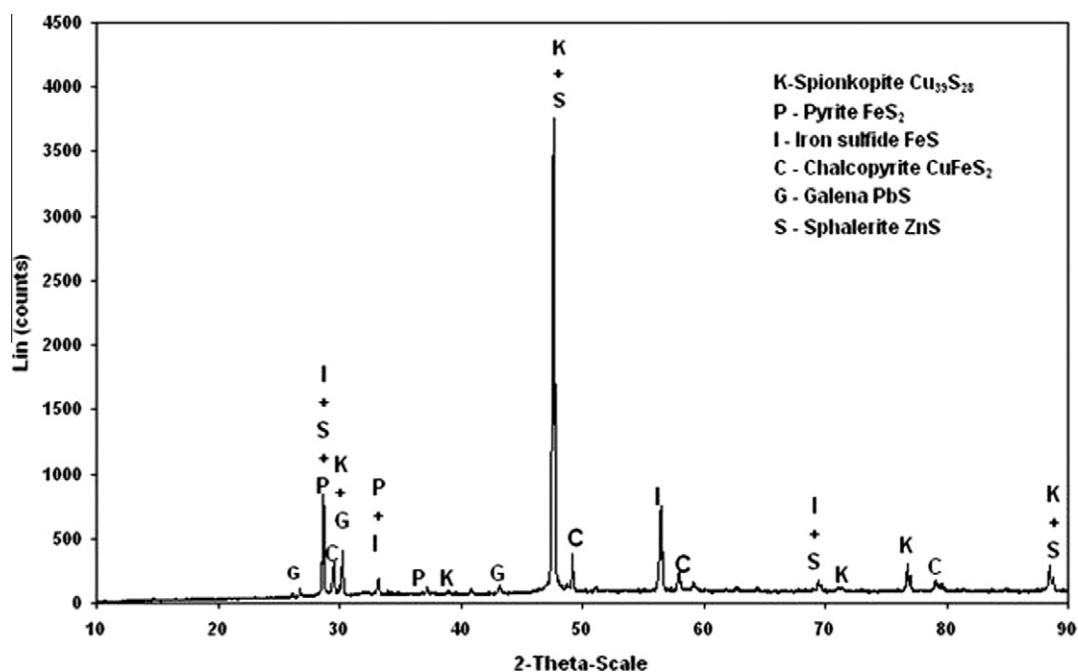


Fig. 10. XRD diffractogram of the residue after alkaline sulphide leaching.

In order to study the effect of hydroxide ion concentration on the extraction, the leaching conditions were maintained the same as described above except that the concentration of  $\text{Na}_2\text{S}$  was constant at 1.14 M while the concentration of  $\text{NaOH}$  were 0.75 M and 1.5 M.

Fig. 8 illustrates that when a low concentration (0.75 M) of  $\text{NaOH}$  was used, the rate of extracting antimony and arsenic was slower and about 25% and 24% of antimony and arsenic were dissolved respectively. As the concentration of  $\text{NaOH}$  increased to 1.5 M, the metal extraction rate is accelerated and the percentage of metal extracted was enhanced. About 57% antimony and 60% arsenic was leached by the lixiviant after 6 h. The observed increase in metal extraction at high concentration of  $\text{NaOH}$  is due to the higher availability of  $\text{S}^{2-}$  ion for dissolution reaction (as described in Section 4.2 above), which is promoted by the increase in the pH of the leach liquor and consequently, prevents the hydrolysis

of sulphide ion which otherwise would reduce its leaching efficiency.

#### 4.6. Particle size dependence on antimony and arsenic dissolution

The influence of particle size on the extraction of antimony and arsenic from the complex sulphide concentrate was examined for three different size fractions ( $-106 + 75$ ,  $-75 + 53$  and  $-53 + 38 \mu\text{m}$ ) at 378 K using solutions containing 1.14 M  $\text{Na}_2\text{S}$  and 1.5 M  $\text{NaOH}$ . It is illustrated in Fig. 9 that extraction of both metals increases with decreasing particle size. After 6 h leaching of the  $-106 + 75 \mu\text{m}$  particle size fraction, about 43% and 49% of antimony and arsenic were extracted, respectively. When the same leaching conditions were applied to the size fraction  $-53 + 38 \mu\text{m}$ , antimony and arsenic extraction were 68% and 75%, respectively. Since the leaching kinetics of tetrahedrite is relatively slow

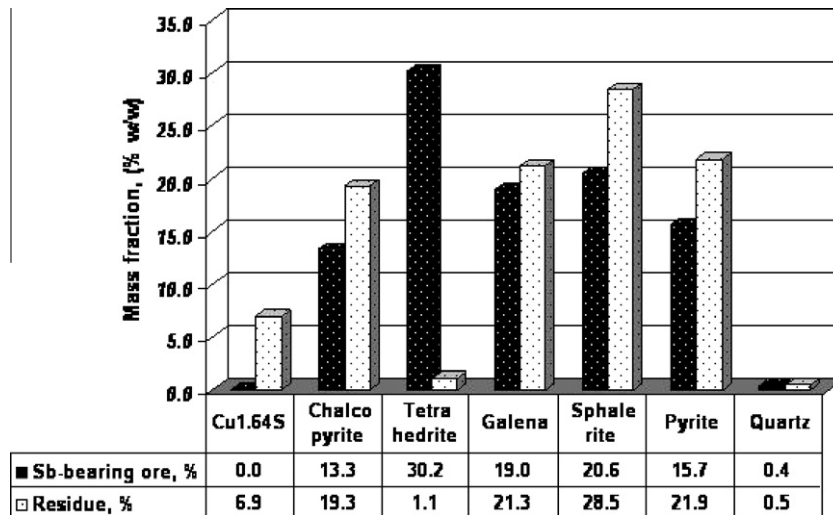


Fig. 11. Mineralogical study of Sb-bearing concentrate and leach residue based on QEMSCAN analysis.



Fig. 12. QEMSCAN micrograph of leach residue.

there is much to gain by grinding the material thereby creating a larger surface area which is advantageous for the leaching efficiency.

#### 4.7. Selective removal of the impurity elements

In order to identify the mineralogical changes brought about by leaching, solid residue from the leaching test at which the highest antimony extraction was obtained, was characterized by XRD and QEMSCAN analyses. The results were compared with the mineralogy of the original concentrate. The residue used was obtained under the following leaching conditions: 1.89 M  $\text{Na}_2\text{S}$  + 1.5 M

NaOH, 0.5% solids, 378 K reaction temperature and 6 h leach time where antimony recovery of 87% was obtained. The XRD pattern shown in Fig. 10 indicates that a new mineralogical phase, spinokopite ( $\text{Cu}_{39}\text{S}_{28}$ ) is observed together with other major phases identified in the original concentrate (Fig. 1). Similarly, a non-stoichiometric copper sulphide ( $\text{Cu}_{3.9}\text{S}_{2.8}$ ) phase was observed when the residues from enargite leached in alkaline sulphide solutions were analyzed (Filippou et al., 2007). The XRD pattern in Fig. 10 shows that the tetrahedrite peaks found in the concentrate (Fig. 1) have disappeared completely meaning that copper content of the tetrahedrite had been transformed to the new copper sulphide phase observed in the residue.

The results of the QEMSCAN analysis on the leach residue are presented in Figs. 11 and 12. The major mineral phases observed in the residue were sphalerite, galena, pyrite and chalcopyrite, with the newly formed copper sulphide phase. In particular, observation of the polished sections of the leach residue (Fig. 12) showed a micro-porous structure of the new solid phase often enclosing a nucleus of untransformed tetrahedrite. The average crystal chemical formulae of the solid residue determined by QEMSCAN analysis on the transformed phase proves the conversion of tetrahedrite into a copper sulphide having stoichiometry of  $\text{Cu}_{1.64}\text{S}$ , which is close to the stoichiometry of the spionkopite observed by XRD but can also be a mixture of chalcocite and covellite. This observation confirms the expectation that tetrahedrite would decompose to either covellite or chalcocite in alkaline sulphide solution (Filippou et al., 2007). However, if the leaching time had been prolonged further, the untransformed tetrahedrite would have been converted completely into the new copper sulphide phase observed in the residue. Additionally, QEMSCAN analysis provides more interesting information about the selectivity of the lixiviant to solubilize the impurity elements from the concentrate. Comparing the information given in Fig. 11 concerning the concentrate and the residue, one can see that the major phases found in the concentrate were upgraded and not leached (Fig. 12) with the only exception of the tetrahedrite phase which was reduced from 30.2% to 1.1% in the residue. This result confirms that other metal sulphides in the concentrate remains insoluble in the sulphide solution with the exception of antimony and arsenic sulphides which form soluble complexes in sulphide media. This analysis shows that the  $\text{Na}_2\text{S}/\text{NaOH}$  lixiviant is suitable for pre-treating, difficult to treat, complex antimony–arsenic-containing sulphide ores/concentrates prior to their smelting and thereby avoiding the difficulty experienced when such ores/concentrates are directly treated in smelting plant.

## 5. Conclusions

The mineralogical investigation of the complex sulphide concentrate reveals that the concentrate is rich in tetrahedrite. Antimony, arsenic and silver form a solid solution in the tetrahedrite crystal structure and other major minerals identified were sphalerite, galena, chalcopyrite and pyrite. Alkaline sulphide leaching of the concentrate shows that antimony and arsenic extraction from tetrahedrite strongly depends on the concentration of sulphide and hydroxide ions, reaction temperature and the leaching time. Due to the relative slow leaching kinetics of tetrahedrite, fine mineral particles are required in order to significantly improve antimony and arsenic extraction. Analysis of the leach residue indicates that the lixiviant is strongly selective to remove the impurity metals As and Sb. Tetrahedrite in the concentrate was found to be converted into a new species having the average chemical formula  $\text{Cu}_{1.64}\text{S}$  which could be a mixture of chalcocite, covellite or spionkopite. The study shows that alkaline sulphide leaching can be a suitable hydrometallurgical pre-treatment process from technological and environmental point of view, to selectively and effectively reduce antimony and arsenic content from difficult to treat complex sulphide concentrates, and therefore, upgrading it for further pyrometallurgical treatment.

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#### ***Metalurgista I***

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- Supervisión de las pruebas metalúrgicas de lixiviación (ácida, cianurada y alcalina), concentración gramática (Mesa, Falcon), separación por medios densos, separación magnética, flotación, etc. Personal a cargo 18 personas.
- Asistente de la jefatura de Metalurgia. Control y seguimiento del sistema de Gestión de la Calidad.
- Responsable de elaboración de propuestas técnicas en coordinación directa con Jefatura.
- Desarrollo y elaboración de los Informes metalúrgicos.
- Control y seguimiento de los planes de Mantenimiento preventivo y calibraciones de los equipos.
- Proceso de variabilidad para fosfatos (disgregado, restregado, tamizado húmedo, atrición y flotación).

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Empresa minera peruana que desarrolla proyectos auríferos en el departamento de la libertad. La Unidad de Marañon y Unidad de Santa María producen un total de 100 000 onzas de oro anual.

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Supervisión de las operaciones en la Planta de Procesos.

- Responsable por la seguridad industrial y medio ambiente. A cargo de 15 operadores.
- Organizar, ejecutar y supervisar el cumplimiento del programa de producción de Lixiviación
- Coordinar con el Departamento de Mantenimiento Planta para trabajos de reparación, mantenimiento y calibración de equipos
- Supervisar los subprocesos de chancado, molienda, concentración, precipitación, sedimentación y agitación, y disposición de relaves
- Realizar mejoras en el proceso de Lixiviación, capacitar constantemente a sus colaboradores en aspectos de seguridad, salud ocupacional, medio ambiente y calidad.

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- Control de la operación del circuito de Chancado Secundario y Ore Bin, sistemas totalmente automatizados.
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