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de minerales"

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①

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☐ Patente de Modelo de Utilidad.

☐ Capítulo I.

☒ Capítulo II.

②

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DE MINERALES Y CONCENTRADOS DE MINERALES".**

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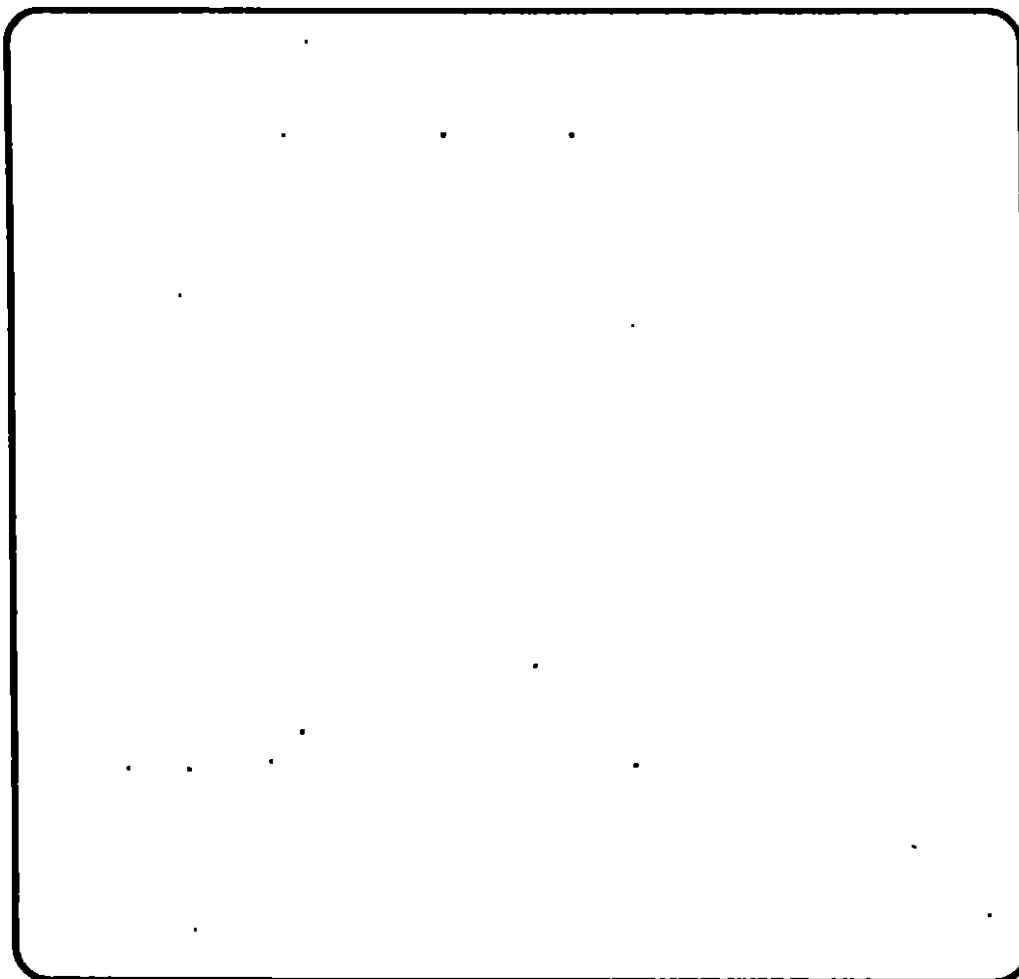
Instrucciones para el diligenciamiento del presente formulario, ver reverso de esta página.

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ANEXOS

- ☒ Comprobante de pago de la tasa de presentación de la solicitud.
- ☐ Documento que acredite la existencia y representación legal cuando el solicitante sea persona jurídica.
- ☐ Poderes, si fuere el caso.
- ☐ Documento de cesión del inventor al solicitante o a su causante.
- ☐ Declaraciones
- ☒ Copia de la solicitud internacional. (Resumen, descripción, reivindicaciones, dibujos)
- ☒ Traducción de la solicitud internacional al castellano. (Resumen, descripción, reivindicaciones, dibujos)
- ☒ Copia del examen preliminar internacional efectuado por la Autoridad Internacional de Examen Preliminar (IPEA).
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- ☐ De ser el caso, copia del contrato de acceso.
- ☐ De ser el caso, documento que acredite la licencia o autorización de uso de conocimientos tradicionales de las comunidades indígenas.
- ☐ De ser el caso, certificado de depósito del material biológico
- ☐ Arte final 12x12.
- ☐ De ser el caso, información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante, relacionadas parcial o totalmente con la invención de esta solicitud.
- ☐ De ser el caso, modificaciones efectuadas a la solicitud internacional.
- ☒ Otros Reporte de Búsqueda Internacional.

11 FIGURA CARACTERÍSTICA:



12 Solicito la concesión de la patente,

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Instrucciones para la presentación de los anexos, ver reverso de esta página.

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Otros anexos que se acompañan a la solicitud.

Forma PCT/IB/304 correspondientes a la notificación y transmisión del documento de prioridad.

Forma PCT/IB/301 correspondiente a la notificación de recibo de copia de registro.

Forma PCT/IB/332 referente a la información concerniente a las oficinas elegidas notificadas de su elección.

Forma PCT/IB/306 correspondiente a la notificación del registro de un cambio.

Una hoja con las Reivindicaciones modificadas con su correspondiente traducción.

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Zur Erklärung der Zweibuchstaben-Codes und der anderen
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WO 03/025234 A2

(54) Title: METHOD FOR OBTAINING COBALT AND NICKEL FROM ORES AND ORE CONCENTRATES

(54) Bezeichnung: VERFAHREN ZUR GEWINNUNG VON COBALT UND NICKEL AUS ERZEN UND ERZKONZENTRATEN

(57) Abstract: The invention relates to a method for obtaining metals from a cobalt and/or nickel arsenic sulfide ore or ore concentrate and/or a cobalt and/or nickel sulfide ore or ore concentrate, according to which the cobalt and/or nickel arsenic sulfide ore or ore concentrate and/or the cobalt and/or nickel sulfide ore or ore concentrate is reacted with sulfur or sulfur arsenic compounds to a reaction product, and dissolving and removing soluble metals and rare-earth metals.

(57) Zusammenfassung: Verfahren zur Gewinnung von Metallen aus einem arsenosulfidischen und/oder sulfidischen Cobalt- und/oder Nickelerz oder -erzkonzentrat, bei dem - das arsenosulfidische und/oder sulfidische Cobalt- und/oder Nickelerz oder -erzkonzentrat mit Schwefel oder schwefelhaltigen Arsenverbindungen zu einem Reaktionsprodukt umgesetzt wird, und - lösliche Metalle und seltene Erden aus dem Reaktionsprodukt gelöst werden.

Verfahren zur Gewinnung von Cobalt und Nickel aus Erzen und Erzkonzentraten

Die Erfindung betrifft ein Verfahren zur Gewinnung von Cobalt und Nickel aus arsenosulfidischen oder sulfidischen Erzen oder Erzkonzentraten.

Der weitaus größte Teil der weltweiten Nickel- und Cobaltproduktion wird aus arsenosulfidischen oder sulfidischen Mineralen gewonnen. Dabei treten Cobalt und Nickel häufig zusammen sowie vergesellschaftet mit weiteren Metallerzen auf.

Unter den cobalthaltigen Arsenosulfiden sind vor allem zu nennen Safflorit (CoAs_2), Skutterudit (CoAs_3), Arsenopyrit ($(\text{Fe,Co,Ni})\text{AsS}$), und Cobaltin (CoAsS). Bei den Sulfiden ist vor allem Linneit (Co_3S_4) zu nennen.

Unter den Arsenosulfiden sind vor allem zu nennen Rammelsbergit NiAs_2 , Arsenopyrit (FeAsS), Gersdorffit (NiAsS) und Nickellin (NiAs). Bei den Sulfiden ist vor allem Pentlandit ($\text{Fe,Ni}_9\text{S}_8$), Millerit (NiS) und Bravoit (Ni,FeS_2) zu nennen.

Der Cobaltin ist unter den Cobaltmineralen, der Pentlandit unter den Nickelmineralen das am stärksten verbreitete Mineral. Diese besitzen daher die

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größte wissenschaftliche und wirtschaftliche Bedeutung bei der Entwicklung neuer Gewinnungsverfahren.

Beide Mineralien zeichnen sich außerdem dadurch aus, dass in ihnen regelmäßig ein Gehalt an Gold, Platinmetallen und anderen seltenen Metallen sowie seltenen Erden angelagert oder gelöst ist.

Die arsenosulfidischen und/oder sulfidischen Cobaltminerale werden aus Erzeugnissen gewonnen, die in der Regel gemahlen und im Flotationsverfahren zu einem Erzkonzentrat aufkonzentriert werden, wobei insbesondere ein wesentlicher Teil der im Mahlgut enthaltenen Silikate abgetrennt werden.

Die Aufarbeitung der Erze oder Erzkonzentrate erfolgt klassischerweise durch Rösten der Erze, wobei das Sulfid bei hohen Temperaturen zu SO_2 oxidiert wird und Metalloxide zurückbleiben. Die so erhaltenen Erze können dann durch Zugabe von Kohlenstoff reduziert werden und die einzelnen Metalle werden durch spezielle Verfahren gegebenenfalls weiter aufgereinigt.

Mittlerweile gibt es neben den bekannten pyrometallurgischen und hydrometallurgischen Verfahren verschiedene Ansätze, Cobalt, Nickel und andere in den arsenosulfidischen und/oder sulfidischen Cobaltmineralen zu lösen.

Der Begriff "Laugung" umfasst sowohl chemische Laugung durch Fe^{III} als auch die biologische Laugung (Bio-Leaching) durch Mikroorganismen, die den Schwefel als Energiequelle nutzen können. Insbesondere bei der Verwendung

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von eisenhaltigen Kupfer- und Nickelerzen ist eine Laugung bisher nur unvollständig möglich.

Der Erfindung liegt die Aufgabe zugrunde, ein verbessertes Verfahren zur Gewinnung von Cobalt und Nickel und anderen Metallen aus arsenosulfidischen und/oder sulfidischen Erzen oder Erzkonzentration zur Verfügung zu stellen.

Diese Aufgabe wird mit einem Verfahren gelöst, bei dem

- das arsenosulfidische und/oder sulfidische Cobalt- und/oder Nickelerz oder -erzkonzentrat mit Schwefel oder schwefelhaltigen Arsenverbindungen zu einem Reaktionsprodukt umgesetzt wird, und
- lösliche Metalle und seltene Erden aus dem Reaktionsprodukt gelöst werden.

Diese Umsetzung wird durch die Formel



dargestellt.

Es hat sich gezeigt, dass sich der Cobaltin bei geeigneter Prozessführung nahezu vollständig in CoS und Realgar umsetzen lässt. Pentlandit lässt sich bei der Prozessführung hingegen nahezu vollständig in NIS und Pyrit umsetzen.

Bei dieser Umsetzung entsteht aus einem Cobaltinkorn des Mahlgutes ein Korn überwiegend mit einem Kern aus Realgar und einem Mantel aus CoS. Im Gegensatz zu Cobaltin lässt sich aus Cobaltsulfid Cobalt sowie übrige darin

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angereicherte Metalle problemlos mit herkömmlichen Oxidationsverfahren herauslösen. Im Falle des Nickels entsteht ebenfalls aus einem Pentlanditkorn des Mahlguts ein Korn mit einem Kern aus Pyrit und einem Mantel aus NIS. Dieses lässt sich problemlos durch herkömmliche Laugungsverfahren herauslösen. Besonders geeignet ist der Schwefel in einem flüssigen Aggregatzustand. Je nach Temperatur ist der Schwefel leichtflüssig gelb bis zähflüssig dunkelrot/braun. In der flüssigen Phase treten Umwandlungen zwischen λ -, π - und μ -Schwefel ein. Die unterschiedlichen Formen führen zu einer Absenkung des Erstarrungspunktes. Flüssig ist Schwefel daher im Allgemeinen im Bereich von 111-444 °C, wobei der Siedepunkt abhängig ist vom Druck. Dieser Temperaturbereich wird daher bevorzugt verwendet, wobei weniger vorteilhaft der Bereich um 187 °C ist, da der Schwefel dort eine besonders hohe Viskosität hat, die bei höheren Temperaturen wieder abnimmt. Bevorzugt sind zum einen Temperaturbereiche von 111-159 °C, alternativ 350-444 °C. Niedrige Temperaturen sind selbstverständlich vom notwendigen Energieeintrag her günstiger, höhere Temperaturen beschleunigen die Reaktion.

Diese Reaktionen sind exotherm, so dass ein vergleichsweise geringer Energieaufwand für die Umsetzung nötig ist.

Ein mögliches Verfahren zur Gewinnung von Cobalt bzw. Nickel aus CoS bzw. NIS wird mit den Formeln



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beschrieben. Das erzeugte Cobalt- bzw. Nickelsulfat ist ebenso wie das Eisensulfat säurelöslich, Cobalt, Nickel und Eisen gehen somit nacheinander in Lösung und können bei geeigneter Prozessführung separiert und abgetrennt werden.

Übrig bleibt ein im Mahlgut enthaltenes Gemisch aus Edel- und sonstigen Metallen und seltenen Erden, insbesondere aus Gold, Silber, Platin, PME's und Zink, das sich als Residuum am Boden des Tanks, in dem der Lösungsprozess abläuft, absetzt.

Mit neuartigen Bioleaching-Verfahren kann das Cobalt oder Nickel besonders umweltfreundlich unter vergleichsweise geringer Erzeugung von Schwefelsäure herausgelöst werden. Dabei wird das Cobaltsulfid gemäß



bzw.



bei Anwesenheit spezieller Bakterien oxidiert und in wässriger Lösung abgetrennt und elektrolysiert.

Die Umsetzung der Erze oder Erzkonzentrate sollte bevorzugt in einer inerten Atmosphäre ablaufen, beispielsweise unter Stickstoff oder Argon.

Als bevorzugter Temperaturbereich für die Umsetzung hat sich der Bereich zwischen 50°C und 550°C -herausgestellt, insbesondere zwischen 350°C und

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450°C kann die Umsetzung vergleichsweise schnell erfolgen. Die Dauer der Umsetzung hängt von der Größe der Mahlkörner und der Temperatur ab und kann vom Fachmann durch einfache Versuche optimiert werden.

Der Umsetzungsprozess der Erze oder Erzkonzentrate kann durch eine Mikrowellenbestrahlung unterstützt werden. Da durch die Mikrowellen die einzelnen Körner des Mahlgutes gleichermaßen Innen wie Außen aufgeheizt werden, können hierdurch die bei der Umsetzung ablaufenden Diffusionsprozesse beschleunigt werden. Durch diese Verbesserung der Reaktionskinetik kann der Prozess beschleunigt werden.

Je nach Umsetzungstemperatur und gegebenenfalls Intensität der Mikrowellenbestrahlung kann die Umsetzung während einer Dauer von 0,5 h bis 10 h, Insbesondere von 2 h bis 5 h erfolgen.

Der Schwefel sollte dem Cobaltin stöchiometrisch zugeführt werden. Dies bedeutet, dass im Regelfall vor der Umsetzung eine Analyse durchgeführt werden sollte, um festzustellen, welche Mengen an Schwefel benötigt werden, um in Abhängigkeit vom eingesetzten Erz zur Umsetzung gemäß Formel (1), (2), (3) oder vergleichbaren Umsetzungen zu gelangen. Ein Überschuss an Schwefel sollte vermieden werden, da dieser beim Abkühlen meist eine klebrige Masse ergibt. Stöchiometrisch bedeutet also in diesem Fall, dass bezogen auf den Metallgehalt der Erze oder Erzkonzentrat nach Ablauf der Reaktion praktisch kein freier Schwefel verbleiben sollte.

Dabei kann der Schwefel dem Mahlgut in festem Zustand zugeführt werden, wobei die Umsetzung des Erzes oder Erzkonzentrates bei Umgebungsdruck erfolgen sollte, jedoch auch mit einem Überdruck von bis zu 10 bar

durchgeführt werden kann. Um zu vermeiden, dass bei den Temperaturen für die Umsetzung zu viel Schwefel verdampft, kann es von Vorteil sein, wenn die Umsetzung in einer Schwefeldampf gesättigten Atmosphäre abläuft.

Andererseits kann die Umsetzung auch ohne Zugabe festen Schwefels in einer gasförmigen Schwefel enthaltenden Atmosphäre bei Unterdruck erfolgen.

Auch ist die Umsetzung unter Zugabe eines Schwefelplasmas möglich.

Möglich ist auch die Umsetzung von flüssigem Schwefel mit entsprechend vorgewärmtem Erz oder Erzkonzentrat, da dies die Reaktion stark beschleunigt und die Bildung von Nebenprodukten verringert.

Das Verfahren kann z. B. in einem Dreikammer-Tunnelofen realisiert werden. Der Dreikammer-Tunnelofen weist eine erste und eine dritte Kammer auf, die als Schleusen für die zweite Kammer dienen. Die zweite Kammer des Ofens ist mit elektrischen Heizwendeln versehen und weist einen Einlass für Stickstoff bzw. Argon auf, das als Spülgas verwendet wird. Darüber hinaus kann die zweite Kammer mit Quarzglasfenstern zum Einbringen von Mikrowellen versehen sein.

Versuche haben gezeigt, dass die Umsetzung insbesondere bei einer Bestrahlung des Gemisches aus Mahlgut und Schwefel mit Mikrowellen mit einer auf die Menge des Mahlguts bezogenen spezifischen Energiedichte von 8-35 kWh/t optimiert ist. Es können sowohl Mikrowellen mit 815 MHz als auch mit 2,45 GHz verwendet werden.

Auch kann die Umsetzung in einem Wirbelschichtreaktor erfolgen.

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Überraschenderweise werden durch das erfindungsgemäße Verfahren rieselfähige Produkte erhalten, d.h. der zugesetzte Schwefel führt nicht zu einer Verklebung der Reaktionsprodukte, sondern wird für die Umsetzung benötigt. Eventuell vorhandene Verklebungen lassen sich leicht aufbrechen. Das Produkt weist durch die entstandene Porosität, auch bedingt durch die exotherme Reaktion, eine mindestens 50-fache Oberflächenvergrößerung auf, bezogen auf das Ausgangsmaterial. Dies erlaubt einen erheblich besseren Angriff von biologischen und/oder chemischen Laugungsmitteln.

Patentansprüche

1. Verfahren zur Gewinnung von Metallen aus einem arsenosulfidischen und/oder sulfidischen Cobalt- und/oder Nickelerz oder -erzkonzentrat, bei dem
 - das arsenosulfidische und/oder sulfidische Cobalt- und/oder Nickelerz oder -erzkonzentrat mit Schwefel oder schwefelhaltigen Arsenverbindungen zu einem Reaktionsprodukt umgesetzt wird, und
 - lösliche Metalle und seltene Erden aus dem Reaktionsprodukt gelöst werden.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass Arsen aus dem Reaktionsprodukt gelöst wird und die am Reaktionsprodukt angelagerten Metalle und seltene Erden, insbesondere Gold, Silber, Platin, PME, Nickel, Cobalt und Zink abgetrennt werden.
3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, dass die Metalle mit einem Bioleaching-Verfahren aus dem Reaktionsprodukt herausgelöst werden.
4. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass die Umsetzung in inerter Atmosphäre durchgeführt wird.
5. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass die Umsetzung bei einer Temperatur zwischen 50°C und 550°C, insbesondere zwischen 350°C und 450°C erfolgt.
6. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass die Umsetzung durch Mikrowellenbestrahlung unterstützt wird.

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7. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass die Umsetzung während einer Dauer von 0,5 bis 10 h, insbesondere von 2 h bis 5 h erfolgt.
8. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass der Schwefel zugeführt wird.
9. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass der Schwefel in festem Zustand zugeführt wird und die Umsetzung bei einem Druck von 1 bis 10 bar durchgeführt wird.
10. Verfahren nach Anspruch 8, dadurch gekennzeichnet, dass die Umsetzung in einer mit Schwefeldampf gesättigten Atmosphäre abläuft.
11. Verfahren nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, dass Schwefel in gasförmigen Zustand zugeführt wird und die Umsetzung bei einem Unterdruck erfolgt.
12. Verfahren nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, dass die Umsetzung mit einem Schwefelplasma erfolgt.

Procedimiento para la extracción de cobalto y níquel a partir de minerales y concentrados de minerales

La invención se refiere a un procedimiento para la extracción de cobalto y níquel a partir de minerales o concentrados de minerales arsenosulfurosos o sulfurosos.

Por lejos, la mayor parte de la producción de cobalto y níquel se obtiene a partir de minerales arsenosulfurosos o sulfurosos. Aquí, el cobalto y el níquel se presentan juntos o acompañados por otros minerales metálicos.

Entre los arsenosulfuros que contienen cobalto se pueden mencionar, sobre todo, la saflorita (CoAs_2), la esku-
terudita (CoAs_3), la arsenopirita ($(\text{Fe}, \text{Co}, \text{Ni})\text{AsS}$) y la cobaltina (CoAsS). Entre los sulfuros se puede mencionar, sobre todo, la lineita (Co_3S_4).

Entre los arsenosulfuros se pueden mencionar, sobre todo, la ramelsbergita ((NiAs_2)), la arsenopirita (FeAsS), la gersdorffita (NiAsS) y la niquelita (NiAs). Entre los sulfuros se pueden mencionar, sobre todo, la pentlandita ($(\text{Fe}, \text{Ni})_9\text{S}_8$), la millerita (NiS) y la bravoita ($(\text{Ni}, \text{Fe})\text{S}_2$).

El mineral más ampliamente difundido entre los de cobalto es la cobaltina y entre los de níquel la pentlandita. A raíz de ello, los mismos poseen la mayor importancia científica y económica en el desarrollo de nuevos \pros de extracción.

Ambos minerales se destacan, además, porque con-

tienen regularmente, depositados o disueltos, oro y platino metálicos, otros metales raros, así como tierras raras.

Los minerales de cobalto arsenosulfurosos y/o sulfurosos son extraídos de minerales usualmente molidos y concentrados mediante un \pro de flotación para obtener un concentrado de minerales, donde es separada, \enp, una parte considerable de los silicatos contenidos en el material molido.

El procesamiento de los minerales o de los concentrados de minerales se lleva a cabo, convencionalmente, mediante la calcinación de los minerales, donde los sulfuros son oxidados a alta temperatura a SO_2 , quedando un residuo de óxidos metálicos. Los minerales obtenidos de esta manera pueden ser reducidos entonces mediante el agregado de carbono, siendo opcionalmente purificados los metales individuales mediante \pros especiales.

En la actualidad, junto a los conocidos \pros pirometalúrgicos e hidrometalúrgicos hay varios \pros para separar cobalto, níquel y otros metales de los minerales o concentrados de minerales arsenosulfurosos o sulfurosos.

La expresión "lixiviación" comprende tanto la lixiviación química por medio de Fe^{III} como también la lixiviación biológica (Bio-Leaching) mediante microorganismos que pueden utilizar el azufre como fuente energética. Hasta ahora , especialmente al emplear minerales que contienen

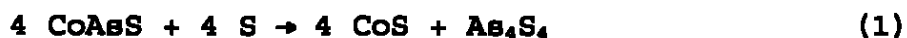
hierro y cobre, una lixiviación es posible solo en forma incompleta.

El objetivo de la invención es dar a conocer un \pro mejorado para la extracción de cobalto, níquel y otros metales a partir de minerales y concentrados de minerales arsenosulfurosos y/o sulfurosos.

Este objetivo se resuelve mediante un \pro en el cual

- se hace reaccionar el mineral y/o concentrado de mineral arsenosulfuroso y/o sulfuroso de cobalto y/o de níquel con azufre o compuestos azufrados de arsénico para obtener un producto de la reacción, y
- se lixivian metales solubles y tierras raras del producto de reacción.

Esta reacción está representada por las siguientes ecuaciones:



Se comprobó que la cobaltina, con una conducción adecuada del proceso, se puede convertir en forma casi completa en CoS y rejalgar (sulfuro de arsénico rojo). Por el contrario, la pentlandita se puede convertir casi completamente en NiS y pirita. En esta reacción se forma, a partir de un grano de cobaltina del material molido, un grano cons-

tituido preponderantemente por un núcleo de rejalgar y una camisa de CoS. Contrariamente a la cobaltina, a partir de sulfuro de cobalto se puede lixiviar sin dificultades, mediante procesos de oxidación convencionales, cobalto, así como otros metales enriquecidos en el mismo. En el caso del níquel se forma asimismo, a partir de un grano de pentlandita del material molido, un grano con un núcleo de pirita y una camisa de NiS. El mismo puede ser lixiviado sin dificultades utilizando procesos de lixiviado convencionales. Particularmente adecuado es el azufre en estado de agregación líquido. De acuerdo a la temperatura, el azufre es líquido y amarillo o viscoso y rojo oscuro/pardo. En la fase líquida se presentan transformaciones entre azufre λ , π y μ . Las distintas formas conducen a una disminución del punto de solidificación. Por ello, el azufre es en general líquido en el rango de 111 °C - 444 °C, donde el punto de ebullición es función de la presión. Por ello se emplea con preferencia este rango de temperaturas, donde es menos conveniente el rango de aproximadamente 187 °C, dado que allí el azufre posee una viscosidad particularmente elevada, la que disminuye nuevamente a mayores temperaturas. Se prefieren, por un lado, temperaturas de 111 °C - 159 °C o, alternativamente, de 350 °C - 444 °C. Por supuesto que más convenientes son las temperaturas bajas como consecuencia del menor aporte energético a incorporar, en tanto que las temperaturas mayores

aceleran el proceso.

Estas reacciones son exotérmicas, de manera de requerir un aporte energético comparativamente más reducido para la reacción.

Un posible proceso para la extracción de cobalto o níquel se describe mediante las siguientes reacciones



El sulfato de cobalto o de níquel producido, al igual que el sulfato de hierro, son solubles en ácidos, por lo que se solubilizan sucesivamente, pudiendo ser separados entre sí y de la solución con una conducción adecuada del proceso.

En el material molido queda como residuo una mezcla de metales preciosos, otros metales y tierras raras, en particular, oro, plata, platino, metales de platino y zinc. lo que se deposita como residuo en el fondo del tanque en el cual se desarrolla el proceso de lixiviación.

Mediante el nuevo \pro de biolixiviación, el cobalto y el níquel puede ser extraído en forma particularmente amigable con el medio ambiente y con una formación comparativamente reducida de ácido sulfúrico. En tal \pro, el sulfuro de cobalto es oxidado en presencia de bacterias especiales de acuerdo con las reacciones



o



separado en solución acuosa y sometido a electrólisis.

La reacción de los minerales o concentrados de minerales se debería llevar a cabo, con preferencia, en atmósfera inerte, por ejemplo, bajo nitrógeno o argón.

Como rango de temperatura preferido para la reacción se ha comprobado el de 50 °C a 550 °C, en particular, entre 350 °C y 450 °C puede proceder comparativamente rápido. La duración de la reacción es función del tamaño de los granos y de la temperatura, pudiendo ser optimizada por un especialista por medio de ensayos sencillos.

El proceso de reacción de los minerales o concentrados de minerales puede ser apoyado con una irradiación de microondas. Dado que los granos de material molido individuales son calentados en igual medida tanto interior como exteriormente debido a las microondas, se pueden acelerar los procesos de difusión que se llevan a cabo durante la reacción. El \pro se puede acelerar mediante este mejoramiento de la cinética de la reacción.

De acuerdo con la temperatura de la reacción y, en casos dados, la intensidad de la irradiación de microondas, la reacción se puede llevar a cabo en un tiempo de 0,5 h a 10 h, en particular, de 2 h a 5 h.

El azufre debe ser agregado a la cobaltina en for-

ma estequiométrica. Esto significa que se debe realizar usualmente un análisis antes de la reacción, a los fines de determinar las cantidades de azufre que son requeridas para acceder, en función del mineral incorporado, a la reacción de acuerdo con la fórmula (1), (2), (3) o similares. Se debe evitar un exceso de azufre, dado que el mismo, al enfriarse, produce usualmente una masa pegajosa. En este caso, estequiométricamente significa que, referido al contenido de metales del mineral o de los concentrados de mineral, prácticamente no debe quedar azufre libre luego de la reacción.

El azufre puede ser agregado al material molido en estado sólido, con lo que la reacción del mineral o de los concentrados de mineral puede ser llevada a cabo a temperatura ambiente y con una sobrepresión de hasta 10 bar. A los fines de impedir que se evapore demasiado azufre a la temperatura de reacción puede ser conveniente que la misma proceda en una atmósfera saturada de vapor de azufre.

Por otro lado, la reacción también puede proceder, sin agregado de azufre sólido y a presión reducida, en una atmósfera que contiene azufre gaseoso.

También es posible la reacción con el agregado de plasma de azufre.

También es posible la reacción de azufre líquido con mineral o concentrado de mineral previamente calentado, dado que esto acelera fuertemente la reacción y disminuye la

formación de subproductos.

El proceso puede ser llevado a cabo en un horno túnel con tres cámaras. El horno túnel con tres cámaras presenta una primera y una tercera cámara que actúan a modo de esclusas para la segunda cámara. La segunda cámara del horno está provista de espirales calefactoras eléctricas y presenta una entrada para nitrógeno o argón, los que son empleados como gases de lavado. Además, la segunda cámara puede estar dotada de ventanas de cuarzo fundido, a los fines de introducir microondas.

Experimentos han mostrado que la reacción se optimiza, en particular, mediante la irradiación de una mezcla de material molido y azufre con microondas que poseen una densidad energética específica de 8 kWh/t - 35 kWh/t con respecto a la cantidad de material molido. Se pueden utilizar microondas tanto de 815 MHz como también de 2,45 MHz.

La reacción también puede proceder en un reactor de lecho fluido.

Sorprendentemente, mediante el \pro de acuerdo con la invención se pueden obtener productos escurribles, es decir, el azufre agregado no conduce a una aglutinación de los productos de reacción, sino que es requerido para la reacción. Las aglutinaciones eventualmente producidas se pueden quebrar fácilmente. Como consecuencia de la porosidad generada, el producto presenta, también condicionado por la re-

acción exotérmica, una ampliación de a lo menos 50 veces su superficie con respecto al material de partida. Esto permite un ataque significativamente más fuerte de los medios de lixiviación biológicos o químicos.

REIVINDICACIONES

1- Procedimiento para la extracción de metales a partir de minerales o concentrados de minerales de cobalto y/o níquel arsenosulfurosos o sulfurosos, en el que

- se hace reaccionar el mineral y/o concentrado de mineral arsenosulfuroso y/o sulfuroso de cobalto y/o de níquel con azufre o compuestos azufrados de arsénico para obtener un producto de la reacción, y
- se lixivian metales solubles y tierras raras del producto de reacción.

2- Procedimiento de acuerdo con la reivindicación 1, caracterizado porque se lixivian arsénico del producto de la reacción y se separan los metales y tierras raras depositadas en el producto de la reacción, en particular, oro, plata, platino, metales de platino, níquel, cobalto y zinc.

3- Procedimiento de acuerdo con la reivindicación 1 o 2, caracterizado porque los metales son lixiviados del producto de la reacción utilizando un proceso de bio-lixivado.

4- Procedimiento de acuerdo con una de las reivindicaciones precedentes, caracterizado porque la reacción se lleva a cabo en una atmósfera inerte.

5- Procedimiento de acuerdo con una de las reivindicaciones precedentes, caracterizado porque la reacción

procede se lleva a cabo a una temperatura que se encuentra entre 50 °C y 550 °C, en particular, entre 350 °C y 450 °C.

6- Procedimiento de acuerdo con una de las reivindicaciones precedentes, **caracterizado** porque la reacción es apoyada por irradiación de microondas.

7- Procedimiento de acuerdo con una de las reivindicaciones precedentes, **caracterizado** porque la reacción procede durante un tiempo de 0,5 h a 10 h, en particular, de 2 h a 5 h.

8- Procedimiento de acuerdo con una de las reivindicaciones precedentes, **caracterizado** porque se agrega azufre.

9- Procedimiento de acuerdo con una de las reivindicaciones precedentes, **caracterizado** porque el azufre se agrega en estado sólido y la reacción se lleva a cabo a una presión de 1 bar a 10 bar.

10- Procedimiento de acuerdo con la reivindicación 8, **caracterizado** porque la reacción procede en una atmósfera saturada de vapor de azufre.

11- Procedimiento de acuerdo con una de las reivindicaciones 1 a 7, **caracterizado** porque el azufre se agrega en estado gaseoso y la reacción se lleva a cabo a presión reducida.

12- Procedimiento de acuerdo con una de las reivindicaciones 1 a 7, **caracterizado** porque la reacción se

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lleva a cabo con un plasma de suero.

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(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES
PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

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02000758.9 12. Januar 2002 (12.01.2002) EP

(71) Anmelder und

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ichmannhaus am Dom, P.O. Box 10 22 41, D-50462 Köln
(DE).

(81) Bestimmungsstaaten (national): AE, AG, AL, AM, AT,
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GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR,
KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK,
MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU,
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(84) Bestimmungsstaaten (regional): ARIPO-Patent (GH,
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TM), europäisches Patent (AT, BE, BG, CH, CY, CZ, DE,
DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT,
SE, SK, TR), OAPI-Patent (BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Veröffentlicht:

- mit internationalem Recherchenbericht
- vor Ablauf der für Änderungen der Ansprüche geltenden
Frist; Veröffentlichung wird wiederholt, falls Änderungen
eintreffen

(88) Veröffentlichungsdatum des internationalen
Recherchenberichts: 19. Juni 2003

Zur Erklärung der Zweibuchstaben-Codes und der anderen
Abkürzungen wird auf die Erklärungen ("Guidance Notes on
Codes and Abbreviations") am Anfang jeder regulären Ausgabe
der PCT-Gazette verwiesen.

(54) Title: METHOD FOR OBTAINING COBALT AND NICKEL FROM ORES AND ORE CONCENTRATES

(54) Bezeichnung: VERFAHREN ZUR GEWINNUNG VON COBALT UND NICKEL AUS ERZEN UND ERZKONZENTRA-
TEN

(57) Abstract: The invention relates to a method for obtaining metals from a cobalt and/or nickel arsenic sulfide ore or ore concen-
trate and/or a cobalt and/or nickel sulfide ore or ore concentrate, according to which the cobalt and/or nickel arsenic sulfide ore or
ore concentrate and/or the cobalt and/or nickel sulfide ore or ore concentrate is reacted with sulfur or sulfur arsenic compounds to a
reaction product, and dissolving and removing soluble metals and rare-earth metals.

(57) Zusammenfassung: Verfahren zur Gewinnung von Metallen aus einem arsenosulfidischen und/oder sulfidischen Cobalt-
und/oder Nickelerz oder -erzkonzentrat, bei dem - das arsenosulfidische und/oder sulfidische Cobalt- und/oder Nickelerz oder -
erzkonzentrat mit Schwefel oder schwefelhaltigen Arsenverbindungen zu einem Reaktionsprodukt umgesetzt wird, und - lösliche
Metalle und seltene Erden aus dem Reaktionsprodukt gelöst werden.

WO 03/025234 A3

28. x

International	Application No
PCT/DE	02/03394

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C22B23/00 C22B1/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 43 29 417 C (METALLGESELLSCHAFT AG) 18 August 1994 (1994-08-18)	1,2,4,5, 8,9
Y	* Anspruch 1; Seite 2, Zeilen 6 und 11-12 *	3,4,6-12
X	US 4 585 477 A (MIOEEN THOMAS K) 29 April 1986 (1986-04-29)	1,2,11
Y	* Ansprüche 1 und 4; Spalte 1, Zeile 22 *	3,4, 6-10,12
Y	US 5 626 648 A (DUYVESTEYN WILLEM P C ET AL) 6 May 1997 (1997-05-06) abstract	3
	-/-	

X

Further documents are listed in the continuation of box C.

☒

Patent family members are listed in annex.

* Special categories of cited documents :

- "A"** document defining the general state of the art which is not considered to be of particular relevance
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- "L"** document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O"** document referring to an oral disclosure, use, exhibition or other means
- "P"** document published prior to the international filing date but later than the priority date claimed

- "1" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "2" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "3" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "4" document member of the same patent family

Date of the actual completion of the international search

15 Apr 11 2003

Date of mailing of the international research report

07/05/2003

Next: How training works at the NSA

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Authorized officer

Bjoerk, P

INTERNATIONAL SEARCH REPORT

Internat Application No
PCT/DE 02/03394

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DATABASE WPI Section Ch, Week 199701 Derwent Publications Ltd., London, GB; Class M25, AN 1997-000006 XP002201989 & AU 17751 95 A (COMMONWEALTH SCI & IND RES ORG), 7 November 1996 (1996-11-07) abstract	4
Y	EP 0 041 841 A (CATO RESEARCH CORP) 16 December 1981 (1981-12-16) abstract	6
Y	US 4 328 192 A (TOLLEY WILLIAM K ET AL) 4 May 1982 (1982-05-04) * Ansprüche 1 und 4; Spalte 4, Zeilen 51-55 *	7-12
A	US 3 451 804 A (MALMSTROM ROLF EINAR ET AL) 24 June 1969 (1969-06-24) the whole document	1-12
A	US 4 888 207 A (FLYNN JR CHARLES M ET AL) 19 December 1989 (1989-12-19) the whole document	1,2
A	US 4 110 106 A (FRANKIEWICZ THEODORE C) 29 August 1978 (1978-08-29) abstract	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internal Application No

PCT/DE 02/03394

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 4329417 C	18-08-1994	DE 4329417 C1	18-08-1994
		AU 672715 B2	10-10-1996
		AU 7158394 A	16-03-1995
		DE 59405354 D1	09-04-1998
		EP 0641864 A1	08-03-1995
		ES 2113050 T3	16-04-1998
		ZA 9406709 A	21-04-1995
US 4585477 A	29-04-1986	SE 446276 B	25-08-1986
		AU 543453 B2	18-04-1985
		AU 7804181 A	07-06-1982
		CA 1183689 A1	12-03-1985
		DE 3166362 D1	31-10-1984
		EP 0052595 A1	26-05-1982
		FI 822337 A ,B,	30-06-1982
		GR 76324 A1	04-08-1984
		JP 57501735 T	24-09-1982
		PH 16991 A	04-05-1984
		SE 8008053 A	18-05-1982
		WO 8201725 A1	27-05-1982
		ZW 26181 A1	20-01-1982
US 5626648 A	06-05-1997	WO 9826100 A1	18-06-1998
		AU 720713 B2	08-06-2000
		AU 1288697 A	03-07-1998
		BR 9612802 A	28-03-2000
		EP 0948655 A1	13-10-1999
AU 1775195 A	07-11-1996	NONE	
EP 0041841 A	16-12-1981	US 4324582 A	13-04-1982
		US 4321089 A	23-03-1982
		CA 1175240 A1	02-10-1984
		DE 3166290 D1	31-10-1984
		EP 0041841 A1	16-12-1981
		JP 1011696 B	27-02-1989
		JP 1526652 C	30-10-1989
		JP 57067138 A	23-04-1982
US 4328192 A	04-05-1982	NONE	
US 3451804 A	24-06-1969	FI 43499 B	31-12-1970
		DE 1558427 A1	24-09-1970
		SE 324244 B	25-05-1970
US 4888207 A	19-12-1989	NONE	
US 4110106 A	29-08-1978	AU 512385 B2	09-10-1980
		AU 2200377 A	17-08-1978
		CA 1098713 A1	07-04-1981

C. (Fortsetzung) ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
Y	DATABASE WPI Section Ch, Week 199701 Derwent Publications Ltd., London, GB; Class M25, AN 1997-000006 XP002201989 & AU 17751 95 A (COMMONWEALTH SCI & IND RES ORG), 7. November 1996 (1996-11-07) Zusammenfassung	4
Y	EP 0 041 841 A (CATO RESEARCH CORP) 16. Dezember 1981 (1981-12-16) Zusammenfassung	6
Y	US 4 328 192 A (TOLLEY WILLIAM K ET AL) 4. Mai 1982 (1982-05-04) * Ansprüche 1 und 4; Spalte 4, Zeilen 51-55 *	7-12
A	US 3 451 804 A (MALMSTROM ROLF EINAR ET AL) 24. Juni 1969 (1969-06-24) das ganze Dokument	1-12
A	US 4 888 207 A (FLYNN JR CHARLES M ET AL) 19. Dezember 1989 (1989-12-19) das ganze Dokument	1,2
A	US 4 110 106 A (FRANKIEWICZ THEODORE C) 29. August 1978 (1978-08-29) Zusammenfassung	1

INTERNATIONALER RECHERCHENBERICHT

Angaben zu Veröffentlichungen, die zur selben Patentfamilie gehören

Internat. Abkürzungen
PCT/DE 02/03394

Im Recherchenbericht angeführtes Patentedokument	Datum der Veröffentlichung	Mitglied(er) der Patentfamilie	Datum der Veröffentlichung
DE 4329417 C	18-08-1994	DE 4329417 C1 AU 672715 B2 AU 7158394 A DE 59405354 D1 EP 0641864 A1 ES 2113050 T3 ZA 9406709 A	18-08-1994 10-10-1996 16-03-1995 09-04-1998 08-03-1995 16-04-1998 21-04-1995
US 4585477 A	29-04-1986	SE 446276 B AU 543453 B2 AU 7804181 A CA 1183689 A1 DE 3166362 D1 EP 0052595 A1 FI 822337 A ,B, GR 76324 A1 JP 57501735 T PH 16991 A SE 8008053 A WO 8201725 A1 ZW 26181 A1	25-08-1986 18-04-1985 07-06-1982 12-03-1985 31-10-1984 26-05-1982 30-06-1982 04-08-1984 24-09-1982 04-05-1984 18-05-1982 27-05-1982 20-01-1982
US 5626648 A	06-05-1997	WO 9826100 A1 AU 720713 B2 AU 1288697 A BR 9612802 A EP 0948655 A1	18-06-1998 08-06-2000 03-07-1998 28-03-2000 13-10-1999
AU 1775195 A	07-11-1996	KEINE	
EP 0041841 A	16-12-1981	US 4324582 A US 4321089 A CA 1175240 A1 DE 3166290 D1 EP 0041841 A1 JP 1011696 B JP 1526652 C JP 57067138 A	13-04-1982 23-03-1982 02-10-1984 31-10-1984 16-12-1981 27-02-1989 30-10-1989 23-04-1982
US 4328192 A	04-05-1982	KEINE	
US 3451804 A	24-06-1969	FI 43499 B DE 1558427 A1 SE 324244 B	31-12-1970 24-09-1970 25-05-1970
US 4888207 A	19-12-1989	KEINE	
US 4110106 A	29-08-1978	AU 512385 B2 AU 2200377 A CA 1098713 A1	09-10-1980 17-08-1978 07-04-1981

VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS

32
31

Absender: DIE MIT DER INTERNATIONALEN VORLÄUFIGEN
PRÜFUNG BEAUFTRAGTE BEHÖRDE

PCT

An SCHEIRBER Christoph et al. VON KREISLER SELTING WERNER Deichmannhaus am Dom P.O. Box 10 22 41 D-50462 Köln ALLEMAGNE		AW Sg W Da Hi HP ME TW JH KB 20.AUG 2003 CS K 7-11	SCHRIFTLICHER BESCHIED L. (Regel 66 PCT)
Aktenzeichen des Anmelders oder Anwalts 022392wo CS/gn		ABSENDUNGSDATUM (Tag/Monat/Jahr) 19/08/2003	
Internationales Aktenzeichen PCT/DE 02/ 03394	Internationales Anmeldedatum (Tag/Monat/Jahr) 14/09/2002	ANTWORT FÄLLIG innerhalb von 2 / 00 Monaten/Tagen ab obigem Absenddatum Prioritätsdatum (Tag/Monat/Jahr) 14/09/2001	
Internationale Patentklassifikation (IPK) oder nationale Klassifikation und IPK C22B1/00			
Anmelder BECKMANN, Alexander			

1. Dieser Bescheid ist der erste schriftliche Bescheid der mit der internationalen vorläufigen Prüfung beauftragten Behörde.

2. Dieser Bescheid enthält Angaben zu folgenden Punkten:

I ☒ Grundlage des Bescheids

II ☐ Priorität

III ☐ Keine Erstellung eines Gutachtens über Neuheit, erfinderische Tätigkeit und gewerbliche Anwendbarkeit

IV ☐ Mangelnde Einheitlichkeit der Erfindung

V ☒ Begründete Feststellung nach Regel 66.2 a)ii) hinsichtlich der Neuheit, der erfinderischen Tätigkeit und der gewerblichen Anwendbarkeit; Unterlagen und Erklärungen zur Stützung dieser Feststellung

VI ☐ Bestimmte angeführte Unterlagen

VII ☐ Bestimmte Mängel der internationalen Anmeldung

VIII ☐ Bestimmte Bemerkungen zur internationalen Anmeldung

3. Der Anmelder wird aufgefordert, zu diesem Bescheid Stellung zu nehmen.

Wenn? Siehe oben genannte Frist. Der Anmelder kann vor Ablauf dieser Frist bei der Behörde eine Verlängerung beantragen, siehe Regel 66.2 d).

Wie? Durch Einreichung einer schriftlichen Stellungnahme und gegebenenfalls von Änderungen nach Regel 66.3. Zu Form und Sprache der Änderungen siehe Regeln 66.8 und 66.9.

Dane: Hinsichtlich einer zusätzlichen Möglichkeit zur Einreichung von Änderungen siehe Regel 66.4.
Hinsichtlich der Verpflichtung des Prüfers, Änderungen und/oder Gegenvorstellungen zu berücksichtigen, siehe Regel 66.4 btr.
Hinsichtlich einer formlosen Erörterung mit dem Prüfer siehe Regel 66.6.

Wird keine Stellungnahme eingereicht, so wird der internationale vorläufige Prüfungsbericht auf der Grundlage dieses Bescheids erstellt.

4. Der Tag, an dem der internationale vorläufige Prüfungsbericht gemäß Regel 69.2 spätestens erstellt sein muß, ist der 14/01/2004

Name und Postanschrift der mit der internationalen vorläufigen Prüfung beauftragten Behörde  Europäisches Patentamt D-80298 München Tel. (+49-89) 2399-0, Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Revollmächtigter Bediensteter Prüfer Formalsachbearbeiter (einschl. Fristverlängerung) Tel. (+49-89) 2399 2828
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Formblatt PCT/IPEA/408 (Deckblatt) (march 2002)



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SCHRIFTLICHER BESCHEID

Internationales Aktenzeichen PCT/DE 02/ 03394

I. Grundlage des Bescheids

1. Grundlage dieses schriftlichen Bescheids sind die Anmeldungsunterlagen in der ursprünglich eingereichten Fassung.

V. Begründete Feststellung nach Regel 66.2(a)(ii) hinsichtlich der Neuheit, der erfinderischen Tätigkeit und der gewerblichen Anwendbarkeit

1. In Anbetracht der im internationalen Recherchenbericht angeführten Unterlagen wird festgestellt, daß die Erfindung, wie sie in mindestens einigen von den Ansprüchen gekennzeichnet ist, die in Artikel 33(1) PCT aufgeführten Kriterien allem Anschein nach nicht erfüllt, d.h. nicht als neu und/oder auf erfinderischer Tätigkeit beruhend anzusehen ist (siehe internationaler Recherchenbericht, insbesondere die mit X und/oder Y angeführten Unterlagen und die entsprechenden Anspruchsnummern).
2. Reicht der Anmelder Änderungen ein, so sind die Erfordernisse der Regel 66.8 PCT zu erfüllen und es sind die Stellen in den ursprünglich eingereichten Anmeldungsunterlagen anzugeben, die die Änderungen stützen (Artikel 34 (2) (b) PCT), andernfalls könnten diese Änderungen bei der internationalen vorläufigen Prüfung nicht berücksichtigt werden. Der Anmelder wird darauf hingewiesen, daß keiner der Ansprüche geprüft wird, falls die Anmeldung eine unnötig große Anzahl unabhängiger Ansprüche enthält.

NB: Sollte der Anmelder sich für eine eingehende Sachprüfung entscheiden, dann wird normalerweise direkt der Internationale Vorläufige Prüfungsbericht erstellt. Ausnahmsweise kann ein zweiter Bescheid erstellt werden, wenn dies ausdrücklich beantragt wurde.

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Patentanwalt Patent Anwälte
VON KREISLER SELTING WERNER

Deichmannhaus am Dom
D-50667 KÖLN

von Kreisler Selting Werner · Postfach 102241 · D-50462 Köln
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Dipl.-Chem. Dr. Thomas Weber

Dipl.-Chem. Dr. Jörg Heibing

Dipl.-Ing. Alexander von Kirschbaum

Dipl.-Chem. Dr. Christoph Schreiber

Our Ref.:
022392wo/CS/tg

September 09, 2003

PCT-Application PCT/DE02/03394
Alexander Beckmann

Hiermit wird um eine sog. **detaillierte** Prüfung gebeten.

Es wird weiterhin gebeten, einen 2. schriftlichen Bescheid auf der Grundlage der detaillierten Prüfung zu erlassen.

Der Patentanwalt


(Dr. Meyers)

VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS

Absender: MIT DER INTERNATIONALEN VORLÄUFIGEN PRÜFUNG BEAUFTRAGTE BEHÖRDE

An:

SCHEIRBER Christoph et al.
VON KREISLER SELTING WERNER
Deichmannhaus am Dom
P.O. Box 10 22 41
D-50462 Köln
ALLEMAGNE

Ar	K	Sg	W	Da	Hi	IP	ME	TW	JH	KB
01. OKT. 2003										
CS	K	Absenddatum (Tag/Monat/Jahr)								

PCT

SCHRIFTLICHER BESCHEID
(Regel 66 PCT)

30.09.2003

Aktenzeichen des Anmelders oder Anwalts
022392wo CS/gn

ANTWORT FÄLLIG innerhalb von 2 Monat(en)
ab obigem Absenddatum

Internationales Aktenzeichen
PCT/DE02/03394

Internationales Anmeldedatum (Tag/Monat/Jahr)
14.09.2002

Prioritätsdatum (Tag/Monat/Jahr)
14.09.2001

Internationale Patentklassifikation (IPK) oder nationale Klassifikation und IPK
C22B1/00

Anmelder
BECKMANN, Alexander

- Dieser Bescheid ist der zweite schriftliche Bescheid der mit der internationalen vorläufigen Prüfung beauftragten Behörde.
- Dieser Bescheid enthält Angaben zu folgenden Punkten:
 - ☒ Grundlage des Bescheids
 - ☐ Priorität
 - ☐ Keine Erstellung eines Gutachtens über Neuheit, erfinderische Tätigkeit und gewerbliche Anwendbarkeit
 - ☐ Mangelnde Einheitlichkeit der Erfindung
 - ☒ Begründete Feststellung nach Regel 66.2 a)ii) hinsichtlich der Neuheit, der erfinderischen Tätigkeit und der gewerblichen Anwendbarkeit; Unterlagen und Erklärungen zur Stützung dieser Feststellung
 - ☐ Bestimmte angeführte Unterlagen
 - ☐ Bestimmte Mängel der Internationalen Anmeldung
 - ☐ Bestimmte Bemerkungen zur Internationalen Anmeldung
- Der Anmelder wird aufgefordert, zu diesem Bescheid Stellung zu nehmen.

Wann? Siehe oben genannte Frist. Der Anmelder kann vor Ablauf dieser Frist bei der Behörde eine Verlängerung beantragen, siehe Regel 66.2 d).

Wie? Durch Einreichung einer schriftlichen Stellungnahme und gegebenenfalls von Änderungen nach Regel 66.3. Zu Form und Sprache der Änderungen, siehe Regeln 66.8 und 66.9.

Dazu: Hinsichtlich einer zusätzlichen Möglichkeit zur Einreichung von Änderungen, siehe Regel 66.4. Hinsichtlich der Verpflichtung des Prüfers, Änderungen und/oder Gegenvorstellungen zu berücksichtigen, siehe Regel 66.4 bis. Hinsichtlich einer formlosen Erörterung mit dem Prüfer, siehe Regel 66.6.

Wird keine Stellungnahme eingereicht, so wird der internationale vorläufige Prüfungsbericht auf der Grundlage dieses Bescheides erstellt.
- Der Tag, an dem der internationale vorläufige Prüfungsbericht gemäß Regel 69.2 spätestens erstellt sein muß, ist der: 14.01.2004

Name und Postanschrift der mit der Internationalen Prüfung beauftragten Behörde



Europäisches Patentamt
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Tel. +49 89 2399 - 0 Tx: 523856 epmu d
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Bevollmächtigter Bediensteter

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Formalsachbearbeiter (einschl. Fristverlängerung)
Novoa, C
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SCHRIFTLICHER BESCHEID

Internationales Aktenzeichen PCT/DE02/03394

I. Grundlage des Bescheids

1. Hinsichtlich der Bestandteile der internationalen Anmeldung (*Ersatzblätter, die dem Anmeldeamt auf eine Aufforderung nach Artikel 14 hin vorgelegt wurden, gelten im Rahmen dieses Bescheids als "ursprünglich eingereicht"*):

Beschreibung, Seiten

1-8 in der ursprünglich eingereichten Fassung

Ansprüche, Nr.

1-12 in der ursprünglich eingereichten Fassung

2. Hinsichtlich der Sprache: Alle vorstehend genannten Bestandteile standen der Behörde in der Sprache, in der die internationale Anmeldung eingereicht worden ist, zur Verfügung oder wurden in dieser eingereicht, sofern unter diesem Punkt nichts anderes angegeben ist.

Die Bestandteile standen der Behörde in der Sprache: zur Verfügung bzw. wurden in dieser Sprache eingereicht; dabei handelt es sich um

- ☐ die Sprache der Übersetzung, die für die Zwecke der internationalen Recherche eingereicht worden ist (nach Regel 23.1(b)).
- ☐ die Veröffentlichungssprache der internationalen Anmeldung (nach Regel 48.3(b)).
- ☐ die Sprache der Übersetzung, die für die Zwecke der internationalen vorläufigen Prüfung eingereicht worden ist (nach Regel 55.2 und/oder 55.3).

3. Hinsichtlich der in der internationalen Anmeldung offenbarten Nucleotid- und/oder Aminosäuresequenz ist die internationale vorläufige Prüfung auf der Grundlage des Sequenzprotokolls durchgeführt worden, das:

- ☐ in der internationalen Anmeldung in schriftlicher Form enthalten ist.
- ☐ zusammen mit der internationalen Anmeldung in computerlesbarer Form eingereicht worden ist.
- ☐ bei der Behörde nachträglich in schriftlicher Form eingereicht worden ist.
- ☐ bei der Behörde nachträglich in computerlesbarer Form eingereicht worden ist.
- ☐ Die Erklärung, daß das nachträglich eingereichte schriftliche Sequenzprotokoll nicht über den Offenbarungsgehalt der internationalen Anmeldung im Anmeldezeitpunkt hinausgeht, wurde vorgelegt.
- ☐ Die Erklärung, daß die in computerlesbarer Form erfassten Informationen dem schriftlichen Sequenzprotokoll entsprechen, wurde vorgelegt.

4. Aufgrund der Änderungen sind folgende Unterlagen fortgefallen:

- ☐ Beschreibung, Seiten:
- ☐ Ansprüche, Nr.:
- ☐ Zeichnungen, Blatt:

5. ☐ Dieser Bescheid ist ohne Berücksichtigung (von einigen) der Änderungen erstellt worden, da diese aus den angegebenen Gründen nach Auffassung der Behörde über den Offenbarungsgehalt in der ursprünglich eingereichten Fassung hinausgehen (Regel 70.2(c)).

(Auf Ersatzblätter, die solche Änderungen enthalten, ist unter Punkt 1 hinzuweisen; sie sind diesem Bescheid beizufügen.)

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6. Etwaige zusätzliche Bemerkungen:

V. Begründete Feststellung nach Regel 66.2(a)(ii) hinsichtlich der Neuheit, der erfinderischen Tätigkeit und der gewerblichen Anwendbarkeit; Unterlagen und Erklärungen zur Stützung dieser Feststellung

1. Feststellung	
Neuheit (N)	Ansprüche Nein: 1,2,4,5,8,9,11 Ja: 3,6,7,10,12
Erfinderische Tätigkeit (IS)	Ansprüche Nein: 1-12
Gewerbliche Anwendbarkeit (IA)	Ansprüche Ja: 1-12

2. Unterlagen und Erklärungen:

siehe Beiblatt

1. Die Anmeldung bezieht sich auf der Gewinnung von Cobalt und Nickel aus arsenosulfidischen oder sulfidischen Erzen.

2. Es wird auf die folgenden Dokumente verwiesen:

D1 = US-A-4 585 477

D2 = DE-C-43 29 417

D3 = DATABASE WPI Section Ch, Week 199701 Derwent Publications Ltd., London, GB; Class M25, AN 1997-000006 & AU 17751 95 A (COMMONWEALTH SCI & IND RES ORG), 7. November 1996 (1996-11-07)

D4 = US-A-5 626 648

D5 = EP-A-0 041 841

D6 = US-A-4 328 192

D1 beschreibt ein Verfahren zur Gewinnung von Kupfer und Nickel aus sulfidischen Erze wie Pentlandit (Sp.1, Z.22) bei dem das Erz durch Sulfatierung mit z.B. Schwefeldioxid (Anspruch 4) zu einem Reaktionsprodukt umgesetzt wird und lösliche Metalle wie Kupfer und Nickel aus dem Reaktionsprodukt gelöst werden (Anspruch 1).

D2 beschreibt ein Verfahren zum Rösten refraktärer Golderze wie Arsenopyrite (S.2, Z.6) bei dem das Erz mit Schwefel in oxidierender Atmosphäre bei einer Temperatur von 450 bis 650°C geröstet wird (Anspruch 1). Nach der Röstung folgt eine Laugung, um das Gold auszubringen (S.2, Z.11-12).

D3 lehrt, daß beim Rösten von sulfidischen Erzen wird die oxidierende Atmosphäre inert durch Reaktion mit dem Schwefel (Zusammenfassung).

D4 beschreibt ein Bioleaching-Verfahren zur Gewinnung von Nickel aus sulfidischen Erzen oder -erzkonzentraten (Zusammenfassung).

D5 beschreibt eine selektive Heizung durch Mikrowellenenergie von sulfidischen Erzen, die zu einer Verbesserung der Gewinnung von Metallen beiträgt (Zusammenfassung).

D6 beschreibt ein Verfahren zur Gewinnung von Nickel aus Laterit-erzen bei dem

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TRATADO DE COOPERACIÓN INTERNACIONAL
EN MATERIA DE PATENTES

Remitente: EL ORGANISMO ENCARGADO DEL EXAMEN PRELIMINAR INTERNACIONAL

A		PCT	
SCHREIBER Christoph et al. VON KREISLER SELTING WERNER Deichmannhaus am Dom P.O. Box 10 22 41 D-50462 Colonia ALEMANIA		INFORME ESCRITO (regla PCT Nº 66)	
		Fecha de envío (día/mes/año) 19/08/2003	
Referencia del Solicitante o Agente 022392wo GS/gn		Vencimiento de contestación dentro de los 2/00 meses/días a partir de la fecha de envío indicada arriba	
Referencia Internacional PCT/DE 02/03394	Fecha de Presentación Internacional (día/mes/año) 14/09/2002	Fecha de Prioridad (día/mes/año) 14/09/2001	
Clasificación Internacional de Patente (CIP) o Clasificación Nacional y CIP C22B1/00			
Solicitante: Beckmann, Alexander			

1.	Este informe es el primer informe escrito del organismo encargado del Examen Preliminar.
2.	Este informe contiene indicaciones acerca de los siguientes puntos: I ☒ Fundamentos del informe II Prioridad III Ninguna elaboración de un dictamen sobre novedad, actividad inventiva y aplicabilidad industrial. IV Uniformidad insatisfactoria de la invención. V ☒ Determinación fundada según la regla 66.2 a)ii), desde el punto de vista de la novedad, de la actividad inventiva y de la aplicabilidad industrial; antecedentes y aclaraciones para apoyar esta determinación. VI Antecedentes definidos citados. VII Palencias definidas de la Solicitud Internacional. VIII Observaciones definidas a la solicitud Internacional.
3.	El solicitante es llamado a tomar posición con respecto a este informe. ¿Cuándo? Ver el plazo mencionado arriba. El solicitante puede gestionar, antes del vencimiento de este plazo, una postergación ante la autoridad. ¿Cómo? Mediante la presentación por escrito de una posición y, en casos dados, de modificaciones según la regla 66.3. Acerca de la forma e idioma de las modificaciones, ver reglas 66.8 y 66.9. Para ello: Desde el punto de vista de una posibilidad adicional para la presentación de modificaciones, ver regla 66.4. Desde el punto de vista de la obligación del examinador de tomar en consideración modificaciones y/u objeciones, ver regla 66.4 bis. Desde el punto de vista de una conversación informal con el examinador, ver regla 66.6. Si no se presenta una posición, el informe del Examen Preliminar Internacional será confeccionado fundado en este informe.
4.	El día en el cual debe estar a más tardar confeccionado el informe de Examen Preliminar Internacional, según regla 69.2, es el 14/01/2004.

Nombre y Dirección Postal del Organismo encargado del Examen Preliminar Internacional Europatentes Patentamt D-80298 Munich Tel. (+49-89) 2399-0, Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Funcionario Apoderado Examinador Encargado formal (incl. prolongación de plazo) Tel: (+49-89) 2399-2828
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INFORME ESCRITO

Referencia Internacional: PCT/DE 02/ 03394

I. Fundamentos del Informe

1. Fundamento de este Informe escrito es la documentación de la solicitud en su presentación original.

V. Determinación fundada según la regla 66.2 a)ii), desde el punto de vista de la novedad, de la actividad inventiva y de la aplicabilidad Industrial; documentación y aclaraciones para apoyar esta determinación.

1. Se comprobó, teniendo en cuenta la documentación incorporada por medio del Informe de Búsqueda Internacional, que la Invención, tal como está caracterizada en a lo menos algunas de las reivindicaciones, aparentemente no cumple con criterios indicados en el artículo PCT 33(1), es decir, no se puede considerar basada en una novedad y/o en una actividad inventiva (ver Informe de Búsqueda Internacional, en particular, la documentación indicada X y/o y los correspondientes números de reivindicación).
2. Si el solicitante presenta modificaciones se deben cumplir los requisitos de la regla PCT 66.8, debiéndose indicar sus posiciones en la documentación de la solicitud presentada originalmente y que apoyan las modificaciones (artículo PCT 34 (2) (b)); en caso contrario, estas modificaciones no pueden ser tomadas en cuenta en el Informe del Examen Preliminar Internacional. Se hace saber al solicitante que no se examina ninguna de las reivindicaciones en caso de que la solicitud contenga una cantidad innecesariamente grande de reivindicaciones independientes.

Obs.: En el caso de que el solicitante se decida por un examen técnico detallado, usualmente se elabora directamente el Informe de Examen Preliminar Internacional. En casos excepcionales se puede elaborar un segundo informe si es solicitado expresamente.

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9 de septiembre de 2003

Solicitud de PCT PCT/DE02/03394

Alexander Beckmann

Por medio de la presente se solicita un denominado Examen Detallado.

Asimismo se solicita elaborar un segundo informe escrito basado sobre el Examen Detallado.

El Agente de Patentes

(Fdo.)

TRATADO DE COOPERACIÓN INTERNACIONAL EN MATERIA DE PATENTES

Remitente: EL ORGANISMO ENCARGADO DEL EXAMEN PRELIMINAR INTERNACIONAL

A
SCHREIBER Christoph et al.
VON KREISLER SELTING WERNER
Deichmannhaus am Dom
P.O. Box 10 22 41
D-50462 Colonia
ALEMANIA

PCT

INFORME ESCRITO

(regla PCT N° 66)

Referencia del Solicitante o Agente 022392wo CS/gn		Fecha de envío (día/mes/año) 30/09/2003
Referencia Internacional PCT/DE 02/03394		Vencimiento de contestación dentro de los 2 meses/días a partir de la fecha de envío indicada arriba
Fecha de Presentación Internacional (día/mes/año) 14/09/2002	Fecha de Prioridad (día/mes/año) 14/09/2001	
Clasificación Internacional de Patente (CIP) o Clasificación Nacional y CIP C22B1/00		
Solicitante Beckmann, Alexander		

1. Este informe es el segundo informe escrito del organismo encargado del Examen Preliminar.	
2. Este informe contiene indicaciones acerca de los siguientes puntos:	
I	☒ Fundamentos del informe
II	Prioridad
III	Ninguna elaboración de un dictamen sobre novedad, actividad inventiva y aplicabilidad industrial.
IV	Uniformidad insatisfactoria de la invención.
V	☒ Determinación fundada según la regla 66.2 a)ii), desde el punto de vista de la novedad, de la actividad inventiva y de la aplicabilidad industrial; documentación y aclaraciones para apoyar esta determinación.
VI	Documentación definida citada.
VII	Falencias definidas de la Solicitud Internacional.
VIII	Observaciones definidas a la solicitud Internacional.
3. El solicitante es intimado a tomar posición con respecto a este informe.	
¿Cuándo?	Ver el plazo mencionado arriba. El solicitante puede gestionar, antes del vencimiento de este plazo, una extensión ante la autoridad.
¿Cómo?	Mediante la presentación por escrito de una posición y, en casos dados, de modificaciones según la regla 66.3. Acerca de la forma e idioma de las modificaciones, ver reglas 66.8 y 66.9.
Para ello:	Desde el punto de vista de una posibilidad adicional para la presentación de modificaciones, ver regla 66.4. Desde el punto de vista de la obligación del examinador de tomar en consideración modificaciones y/u objeciones, ver regla 66.4 bis. Desde el punto de vista de una conversación informal con el examinador, ver regla 66.6.
Si no se presenta una posición, el informe del Examen Preliminar Internacional será elaborado fundado en este informe.	
4. El día en el cual debe estar a más tardar elaborado el informe de Examen Preliminar Internacional, según regla 69.2, es el 14/01/2004	

Nombre y Dirección Postal del Organismo encargado del Examen Preliminar Internacional Europäisches Patentamt D-80298 Munich Tel. (+49-89) 2399-0, Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Funcionario Apoderado Bjoerk, P. Encargado formal (incl. extensión de plazo) Krova, C. Tel: (+49-89) 2399-2828
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Formulario PCT/IPEA/408 (carátula)(marzo 2002)

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INFORME ESCRITO

Referencia Internacional: PCT/DE 02/ 03394

I. Fundamentos del informe

1. Desde el punto de vista de los componentes de la Solicitud Internacional (*las hojas de reemplazo que fueron presentadas al organismo como requisito según el artículo 14 son válidas como "presentadas originalmente" en el marco de este informe*).

Descripción, páginas

1-8 en el texto presentado originalmente.

Reivindicaciones, N°

1-12 en el texto presentado originalmente.

2. Desde el punto de vista del idioma: todos los componentes mencionados anteriormente estaban a disposición del organismo en el idioma en el cual fue presentada la solicitud internacional o fueron presentados en la misma en tanto bajo este punto no se indique otra cosa.

Los componentes estaban disponibles para el organismo en el idioma: o fueron presentados en este idioma; aquí se trata de:

el idioma de la traducción que fue presentada a los efectos de la búsqueda internacional (según regla 23.1 b)).

el idioma de la publicación de la solicitud internacional (según regla 48.3 b)).

el idioma de la traducción presentada a los efectos del Examen Preliminar Internacional (según regla 55.2 y/o 55.3).

3. Desde el punto de vista de la secuencia de nucleótidos y/o de aminoácidos revelada en la solicitud internacional, el Examen Preliminar Internacional fue llevado a cabo basado sobre el protocolo de secuencias, el que:

está contenido por escrito en la solicitud internacional.

fue presentado en forma legible por computadora junto con la solicitud internacional.

fue presentado posteriormente en forma escrita ante el organismo.

fue presentado posteriormente en forma legible por computadora ante el organismo.

se presentó la declaración de que el protocolo de secuencias presentado posteriormente por escrito no excede el contenido revelado en la solicitud internacional en el momento de la presentación.

la declaración de que las informaciones vertidas en forma legible por computación se corresponden con el protocolo de secuencias escrito.

4. Como consecuencia de las modificaciones caducó la siguiente documentación:

Descripción, páginas:

Reivindicaciones: N°:

Ilustraciones, páginas:

5. Este informe fue elaborado sin tomar en cuenta (algunas de) las modificaciones, dado que las mismas, según opinión del organismo y por los motivos indicados, exceden el contenido revelado en el texto presentado originalmente (regla 70.2(c)).

(Con respecto de las hojas de reemplazo que, según el punto 1, contienen tales modificaciones, deben ser indicadas; deben ser adjuntadas a este informe).

6. Otras observaciones adicionales:

V. **Determinación fundada según la regla 68.2 (a) II), desde el punto de vista de la novedad, de la actividad inventiva y de la aplicabilidad Industrial; documentación y aclaraciones que apoyan esta determinación.**

- | | |
|---------------------------------|--|
| 1. Determinación | |
| Novedad (N) | Reivindicaciones No: 1, 2, 4, 5, 8, 9, 11; SI: 3, 6, 7, 9, 12. |
| Actividad inventiva | Reivindicaciones No: 1 – 12. |
| Aplicabilidad Industrial | Reivindicaciones SI: 1 – 12. |

2. **Documentación y aclaraciones**

Ver Anexo

INFORME ESCRITO
Anexo

Referencia Internacional: PCT/DE 02/ 03394

1. La solicitud se refiere a la extracción de cobalto y níquel a partir de minerales arsenosulfurosos o sulfurosos.
2. Se hace referencia a los siguientes documentos:

D1 = US-A-4 585 477
D2 = DE-C-43 29 417
D3 = DATABASE WPI Section Ch, Week 199701 Derwent Publications Ltd., London, GB, Class M25, AN 1997-000006 & AU 17751 95 A (COMMONWEALTH SCI & IND RES ORG) 7 November 1996 (1996-11-07)
D4 = US-A-5 626 848
D5 = EP-A-0 041 841
D6 = US-A-4 328 192

D1 describe un procedimiento para la extracción de cobre y níquel a partir de minerales sulfurosos como la pentlandita (pág. 1, renglón 22) en el cual se sulfata el mineral con, por ejemplo, dióxido de azufre (reivindicación 4) y se lixivian los metales solubles como el cobre y el níquel del producto de la reacción (reivindicación 1)..

D2 describe un procedimiento para la calcinación de minerales refractarios de oro como la arsenopirita (pág. 2; renglón 6) en el cual el mineral es calcinado con azufre en una atmósfera oxidante a una temperatura de 450 °C a 650 °C (reivindicación 1). Luego de la calcinación se lleva a cabo una lixiviación, para extraer el oro (pág. 2, renglones 11-12).

D3 enseña que, en la calcinación de minerales sulfurosos, la atmósfera oxidante se convierte en inerte por la reacción con el azufre (resumen).

D4 describe un procedimiento de biolixiviación para extraer níquel a partir de minerales o concentrados de minerales sulfurosos (resumen).

D5 describe un calentamiento selectivo de minerales sulfurosos mediante energía de microondas, lo que aporta a un mejoramiento de la extracción de metales (resumen).

D6 describe un procedimiento para la extracción de níquel a partir de minerales de lauterita en el cual se trata con azufre elemental en estado sólido, líquido o gaseoso a 360 °C – 900 °C durante a lo menos 20 minutos. continuación se lixivian los metales solubles del producto de la reacción (reivindicaciones 1, 4; pág. 4, renglones 51-55).

3. Novedad

Los atributos de las reivindicaciones 1, 2 y 11 se pueden tomar directamente de D1.

Los atributos de las reivindicaciones 1, 2, 5, 8 y 9 son conocidos por medio de D2.

La atmósfera inerte reivindicada en la reivindicación 4 existe automáticamente en D2 por la presencia de oxígeno y azufre. Esta enseñanza también se puede tomar claramente de D3.

De esta manera, de acuerdo con el artículo 33 (2), las reivindicaciones 1, 2, 4, 5, 8, 9 y 11 no son novedosas.

4. Actividad Inventiva

Los atributos de las reivindicaciones secundarias 3 y 6 a 12 pertenecen a pasos de proceso conocidos en la extracción de metales a partir de minerales sulfurosos.

Así, es evidente para el especialista un procedimiento de biolixiviación tal como el conocido por medio de D4 utilizado como método para la lixiviación de metales en el producto de reacción de D1, dado que ambas publicaciones se refieren a minerales sulfurosos de níquel.

De manera similar, el apoyo de la calcinación de minerales sulfurosos por medio de microondas es conocido a través de D5 y evidente para el especialista cuando desea mejorar la extracción de metales.

La duración de la reacción con azufre no está expresamente descrita en D1 y D2. No obstante, una duración de 0,5 h a 10 h es una duración usual en un paso de proceso de tal tipo. Esto también se puede apreciar en D6, el que trata de minerales no sulfurosos (laterita) pero comprende los mismos pasos que la presente solicitud.

D6 describe también el agregado de azufre en diversos estados. Dado que D6 se puede combinar muy bien con D1 y D2, puesto que todos se refieren al agregado de azufre para mejorar la extracción de metales, no se puede apreciar una actividad inventiva en los atributos de las reivindicaciones secundarias 8 a 12.

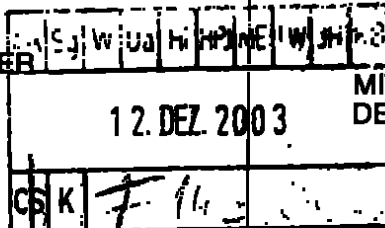
Así, los objetos de las reivindicaciones 3 y 6 a 12 no son inventivos según el artículo PCT 33 (3).

VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS

Absender: MIT DER INTERNATIONALEN VORLÄUFIGEN PRÜFUNG BEAUFTRAGTE BEHÖRDE

An:

SCHEIRBER Christoph et al.
VON KREISLER SELTING WERNER
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ALLEMAGNE



PCT

MITTEILUNG ÜBER DIE ÜBERSENDUNG
DES INTERNATIONALEN VORLÄUFIGEN
PRÜFUNGSBERICHTS

(Regel 71.1 PCT)

Absendedatum
(Tag/Monat/Jahr)

11.12.2003

Aktenzeichen des Anmelders oder Anwalts
022392wo CS/gn

WICHTIGE MITTEILUNG

Internationales Aktenzeichen
PCT/DE02/03394

Internationales Anmeldedatum (Tag/Monat/Jahr)
14.09.2002

Prioritätsdatum (Tag/Monat/Jahr)
14.09.2001

Anmelder
BECKMANN, Alexander

1. Dem Anmelder wird mitgeteilt, daß ihm die mit der internationalen vorläufigen Prüfung beauftragte Behörde hiermit den zu der internationalen Anmeldung erstellten internationalen vorläufigen Prüfungsbericht, gegebenenfalls mit den dazugehörigen Anlagen, übermittelt.
2. Eine Kopie des Berichts wird - gegebenenfalls mit den dazugehörigen Anlagen - dem Internationalen Büro zur Weiterleitung an alle ausgewählten Ämter übermittelt.
3. Auf Wunsch eines ausgewählten Amtes wird das Internationale Büro eine Übersetzung des Berichts (jedoch nicht der Anlagen) ins Englische anfertigen und diesem Amt übermitteln.

4. ERINNERUNG

Zum Eintritt in die nationale Phase hat der Anmelder vor jedem ausgewählten Amt innerhalb von 30 Monaten ab dem Prioritätsdatum (oder in manchen Ämtern noch später) bestimmte Handlungen (Einreichung von Übersetzungen und Entrichtung nationaler Gebühren) vorzunehmen (Artikel 39 (1)) (siehe auch die durch das Internationale Büro im Formblatt PCT/IB/301 übermittelte Information).

Ist einem ausgewählten Amt eine Übersetzung der internationalen Anmeldung zu übermitteln, so muß diese Übersetzung auch Übersetzungen aller Anlagen zum internationalen vorläufigen Prüfungsbericht enthalten. Es ist Aufgabe des Anmelders, solche Übersetzungen anzufertigen und den betroffenen ausgewählten Ämtern direkt zuzuleiten.

Weitere Einzelheiten zu den maßgebenden Fristen und Erfordernissen der ausgewählten Ämter sind Band II des PCT-Leitfadens für Anmelder zu entnehmen.

Der Anmelder wird auf Artikel 33(5) hingewiesen, in welchem erklärt wird, daß die Kriterien für Neuheit, erfinderische Tätigkeit und gewerbliche Anwendbarkeit, die im Artikel 33(2) bis (4) beschrieben werden, nur für die internationale vorläufige Prüfung Bedeutung haben, und daß "jeder Vertragsstaat (...) für die Entscheidung über die Patentfähigkeit der beanspruchten Erfindung in diesem Staat zusätzliche oder abweichende Merkmale aufstellen" kann (siehe auch Artikel 27(5)). Solche zusätzlichen Merkmale können z.B. Ausnahmen von der Patentierbarkeit, Erfordernisse für die Offenbarung der Erfindung sowie Klarheit und Stützung der Ansprüche betreffen.

Name und Postanschrift der mit der internationalen Prüfung beauftragten Behörde



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**VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM
GEBIET DES PATENTWESENS**

PCT
INTERNATIONALER VORLÄUFIGER PRÜFUNGSBERICHT
(Artikel 36 und Regel 70 PCT)

Aktenzeichen des Anmelders oder Anwalts 022392wo CS/gn	WEITERES VORGEHEN siehe Mitteilung über die Übersendung des internationalen vorläufigen Prüfungsberichts (Formblatt PCT/PEA/416)	
Internationales Aktenzeichen PCT/DE02/03394	Internationales Anmeldedatum (Tag/Monat/Jahr) 14.09.2002	Prioritätsdatum (Tag/Monat/Jahr) 14.09.2001
Internationale Patentklassifikation (IPK) oder nationale Klassifikation und IPK C22B1/00		
Anmelder BECKMANN, Alexander		

1. Dieser Internationale vorläufige Prüfungsbericht wurde von der mit der Internationalen vorläufigen Prüfung beauftragten Behörde erstellt und wird dem Anmelder gemäß Artikel 36 übermittelt.
2. Dieser BERICHT umfaßt insgesamt 4 Blätter einschließlich dieses Deckblatts.
- ☒ Außerdem liegen dem Bericht ANLAGEN bei; dabei handelt es sich um Blätter mit Beschreibungen, Ansprüchen und/oder Zeichnungen, die geändert wurden und diesem Bericht zugrunde liegen, und/oder Blätter mit vor dieser Behörde vorgenommenen Berichtigungen (siehe Regel 70.16 und Abschnitt 607 der Verwaltungsrichtlinien zum PCT).
- Diese Anlagen umfassen insgesamt 1 Blätter.

3. Dieser Bericht enthält Angaben zu folgenden Punkten:

- I ☒ Grundlage des Bescheids
- II ☐ Priorität
- III ☐ Keine Erstellung eines Gutachtens über Neuheit, erfinderische Tätigkeit und gewerbliche Anwendbarkeit
- IV ☐ Mangelnde Einheitlichkeit der Erfindung
- V ☒ Begründete Feststellung nach Regel 66.2 a)ii) hinsichtlich der Neuheit, der erfinderischen Tätigkeit und der gewerblichen Anwendbarkeit; Unterlagen und Erklärungen zur Stützung dieser Feststellung
- VI ☐ Bestimmte angeführte Unterlagen
- VII ☐ Bestimmte Mängel der Internationalen Anmeldung
- VIII ☐ Bestimmte Bemerkungen zur Internationalen Anmeldung

Datum der Einreichung des Antrags 10.04.2003	Datum der Fertigstellung dieses Berichts 11.12.2003
Name und Postanschrift der mit der Internationalen Prüfung beauftragten Behörde  Europäisches Patentamt D-80298 München Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Bevollmächtigter Bediensteter Bjoerk, P Tel. +49 89 2399-8452 

INTERNATIONALER VORLÄUFIGER PRÜFUNGSBERICHT

Internationales Aktenzeichen PCT/DE02/03394

I. Grundlage des Berichts

1. Hinsichtlich der Bestandteile der internationalen Anmeldung (Ersatzblätter, die dem Anmeldeamt auf eine Aufforderung nach Artikel 14 hin vorgelegt wurden, gelten im Rahmen dieses Berichts als "ursprünglich eingereicht" und sind ihm nicht beigelegt, weil sie keine Änderungen enthalten (Regeln 70.16 und 70.17)):

Beschreibung, Seiten

1-8 in der ursprünglich eingereichten Fassung

Ansprüche, Nr.

7-12 in der ursprünglich eingereichten Fassung

1-6 eingegangen am 02.12.2003 mit Schreiben vom 01.12.2003

2. Hinsichtlich der Sprache: Alle vorstehend genannten Bestandteile standen der Behörde in der Sprache, in der die internationale Anmeldung eingereicht worden ist, zur Verfügung oder wurden in dieser eingereicht, sofern unter diesem Punkt nichts anderes angegeben ist.

Die Bestandteile standen der Behörde in der Sprache: zur Verfügung bzw. wurden in dieser Sprache eingereicht; dabei handelt es sich um:

- ☐ die Sprache der Übersetzung, die für die Zwecke der internationalen Recherche eingereicht worden ist (nach Regel 23.1(b)).
- ☐ die Veröffentlichungssprache der internationalen Anmeldung (nach Regel 48.3(b)).
- ☐ die Sprache der Übersetzung, die für die Zwecke der internationalen vorläufigen Prüfung eingereicht worden ist (nach Regel 55.2 und/oder 55.3).

3. Hinsichtlich der in der internationalen Anmeldung offenbarten Nucleotid- und/oder Aminosäuresequenz ist die internationale vorläufige Prüfung auf der Grundlage des Sequenzprotokolls durchgeführt worden, das:

- ☐ in der internationalen Anmeldung in schriftlicher Form enthalten ist.
- ☐ zusammen mit der internationalen Anmeldung in computerlesbarer Form eingereicht worden ist.
- ☐ bei der Behörde nachträglich in schriftlicher Form eingereicht worden ist.
- ☐ bei der Behörde nachträglich in computerlesbarer Form eingereicht worden ist.
- ☐ Die Erklärung, daß das nachträglich eingereichte schriftliche Sequenzprotokoll nicht über den Offenbarungsgehalt der internationalen Anmeldung im Anmeldezeitpunkt hinausgeht, wurde vorgelegt.
- ☐ Die Erklärung, daß die in computerlesbarer Form erfassten Informationen dem schriftlichen Sequenzprotokoll entsprechen, wurde vorgelegt.

4. Aufgrund der Änderungen sind folgende Unterlagen fortgefallen:

- ☐ Beschreibung, Seiten:
- ☐ Ansprüche, Nr.:
- ☐ Zeichnungen, Blatt:

1. Die Anmeldung bezieht sich auf die Gewinnung von Cobalt und Nickel aus arsenosulfidischen oder sulfidischen Erzen, wobei das Erz oder Erzkonzentrat mit Schwefel oder schwefelhaltigen Arsenverbindungen zu einem Reaktionsprodukt, enthaltend CoS und/oder NiS, umgesetzt wird.

Das Verfahren gemäß Anspruch 1 führt zu rieselfähigen Produkten mit hoher Porosität, die sich gut für ein nachfolgendes Laugungsverfahren eignen.

Die weiteren Ansprüche beziehen sich auf bevorzugte Ausführungen des Verfahrens.

2. Das Verfahren unterscheidet sich von dem Verfahren aus US-A-4 585 477 dadurch, daß kein oxidierendes Röstverfahren von arsenosulfidischem oder sulfidischem Erz stattfindet.

DE-C-43 29 417 bezieht sich auch auf eine Röstung in oxidierender Atmosphäre.

Somit sind die Kriterien der Artikeln 33(2) und 33(3) PCT erfüllt.

TRATADO DE COOPERACIÓN INTERNACIONAL
EN MATERIA DE PATENTES

Remitente: EL ORGANISMO ENCARGADO DEL EXAMEN PRELIMINAR INTERNACIONAL

A
SCHREIBER Christoph et al.
VON KREISLER SELTING WERNER
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P.O. Box 10 22 41
D-50462 Colonia
ALEMANIA

PCT

NOTIFICACIÓN DE ENVÍO DEL INFORME DEL
EXAMEN PRELIMINAR INTERNACIONAL

(regla PCT N° 71.1)

Referencia del Solicitante o Agente		Fecha de envío (día/mes/año)
022392wo CS/gn		11/12/2003
Referencia Internacional		INFORME IMPORTANTE
PCT/DE 02/03394	Fecha de Presentación Internacional (día/mes/año)	Fecha de Prioridad (día/mes/año)
	14/09/2002	14/09/2001
Solicitante		
Beckmann, Alexander		

1. Se notifica al solicitante que el organismo encargado del Examen Preliminar Internacional envía mediante la presente el informe de Examen Preliminar Internacional elaborado para esta Solicitud Internacional, en casos dados, con los anexos correspondientes.
2. Una copia del informe— en casos dados, con los anexos correspondientes— es enviada a la Oficina Internacional por su derivación a todos los organismos seleccionados.
3. A petición de un organismo seleccionado, la Oficina Internacional traducirá el informe (con sus anexos) al inglés y lo enviará a tal organismo.
4. **RECORDATORIO**

Para el ingreso en la fase nacional, el solicitante debe proceder, dentro de los 30 meses de la fecha de prioridad (o más tarde en otros organismos), a llevar a cabo ciertos trámites (presentación de traducciones y pago de tasas nacionales) (artículo 39 (1)) (ver también la información brindada por la Oficina Internacional por medio del formulario PCT/IB/301).

Cuando se debe enviar a un organismo seleccionado una traducción de la solicitud internacional, esta traducción debe contener también las traducciones de todos los anexos del informe del Examen Preliminar Internacional. Es responsabilidad del solicitante elaborar tales traducciones y enviarlas directamente al organismo correspondiente seleccionado.

Otros detalles de los plazos y requisitos normativos de los organismos seleccionados se pueden tomar del Manual PCT para solicitantes.

El solicitante es advertido acerca del artículo 33 (5) en el cual se aclara que los criterios de novedad, actividad inventiva y aplicabilidad industrial descriptos en el artículo 33 (2) a (4) solo tiene significado para el Examen Preliminar Internacional, y que "cada estado adherido (...) puede disponer atributos adicionales o modificatorios en tal estado para la determinación de la patentabilidad de la invención reivindicada " (ver también artículo 27 (5)). Tales atributos adicionales se pueden referir, por ejemplo, a excepciones de patentabilidad, a requisitos para la revelación de la invención, así como a claridad y apoyo de las reivindicaciones.

Nombre y Dirección Postal del Organismo encargado del Examen Preliminar Internacional Europäisches Patentamt D-80298 Munich Tel. (+49-89) 2399-0, Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Funcionario Apoderado Novoa, C. Tel: (+49-89) 2399-2718
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Formulario PCT/PEA/416 (julio 1992)

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TRATADO DE COOPERACIÓN INTERNACIONAL
EN MATERIA DE PATENTES

PCT

INFORME DE EXAMEN PRELIMINAR INTERNACIONAL
(Artículo 36 y regla 70 PCT)

Referencia del Solicitante o Agente 022392wo GS/gn	Ver notificación sobre envío del informe de Examen Preliminar Internacional (formulario PCT/IPEA/416) PROCEDER	
Referencia Internacional PCT/DE 02/03394	Fecha de Presentación Internacional (día/mes/año) 14/09/2002	Fecha de Prioridad (día/mes/año) 14/09/2001
Clasificación Internacional de Patente (CIP) o Clasificación Nacional y CIP C22B1/00		
Solicitante Beckmann, Alexander		

1. Este informe de Examen Preliminar Internacional fue confeccionado por el organismo encargado del Examen Preliminar Internacional y, según el artículo 36, es enviado al solicitante.
2. Este INFORME comprende, en total, 4 hojas, incluida esta carátula.
- ☒ Además, este informe posee ANEXOS ; estos se tratan de hojas con descripciones, reivindicaciones y/o ilustraciones que fueron modificados y en los cuales se basa este informe, y/u hojas con correcciones llevadas a cabo por este organismo (ver regla 70.16 y sector 607 de los reglamentos administrativos de PCT).
- Estos anexos comprenden en total 1 hoja.

3. Este informe contiene indicaciones acerca de los siguientes puntos:
- I ☒ Fundamentos del informe
- II Prioridad
- III Ninguna elaboración de un dictamen sobre novedad, actividad inventiva y aplicabilidad industrial.
- IV Uniformidad insatisfactoria de la invención.
- V ☒ Determinación fundada según la regla 66.2 a) i), desde el punto de vista de la novedad, de la actividad inventiva y de la aplicabilidad industrial; antecedentes y aclaraciones para apoyar esta determinación.
- VI Antecedentes definidos citados.
- VII Falencias definidas de la Solicitud Internacional.
- VIII Observaciones definidas a la solicitud Internacional.

Fecha de presentación de la solicitud 10.04.2003	Fecha de confección de este informe 11.12.2003
Nombre y Dirección Postal del Organismo encargado del Examen Preliminar Internacional Europäisches Patentamt D-80298 Munich Tel. (+49-89) 2399-0, Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Funcionario Apoderado Bjoerk, P Tel: (+49-89) 2399-8452

Formulario PCT/IPEA/409 (carátula) (enero 1994)

I. Fundamentos del Informe

1. Desde el punto de vista de los componentes de la Solicitud Internacional (las hojas de reemplazo que fueron presentadas al organismo como requisito según el artículo 14 son válidas como "presentadas originalmente" en el marco de este informe y no se acompañan porque no contienen modificaciones (reglas 70.16 y 70.15)).

Descripción, páginas

1-8 en el texto presentado originalmente.

Reivindicaciones, N°

1-12 en el texto presentado originalmente.

1 - 6 ingresadas el 02.12.2003 con el escrito del 01.12.2003

2. Desde el punto de vista del idioma: todos los componentes mencionados anteriormente estaban a disposición del organismo en el idioma en el cual fue presentada la solicitud internacional o fueron presentados en la misma en tanto bajo este punto no se indique otra cosa.

Los componentes estaban disponibles para el organismo en el idioma: o fueron presentados en este idioma; aquí se trata de:

el idioma de la traducción que fue presentada a los efectos de la búsqueda internacional (según regla 23.1 b)).

el idioma de la publicación de la solicitud internacional (según regla 48.3 b)).

el idioma de la traducción presentada a los efectos del Examen Preliminar Internacional (según regla 55.2 y/o 55.3).

3. Desde el punto de vista de la secuencia de nucleótidos y/o de aminoácidos revelada en la solicitud internacional, el Examen Preliminar Internacional fue llevado a cabo basado sobre el protocolo de secuencias, el que:

está contenido por escrito en la solicitud internacional.

fue presentado en forma legible por computadora junto con la solicitud internacional.

fue presentado posteriormente en forma escrita ante el organismo.

fue presentado posteriormente en forma legible por computadora ante el organismo.

se presentó la declaración de que el protocolo de secuencias presentado posteriormente por escrito no excede el contenido revelado en la solicitud internacional en el momento de la presentación.

la declaración de que las informaciones vertidas en forma legible por computadora se corresponden con el protocolo de secuencias escrito.

4. Como consecuencia de las modificaciones caducó la siguiente documentación:

Descripción, páginas:

Reivindicaciones: N°:

ilustraciones, páginas:

1. La invención se refiere a la extracción de cobalto y níquel a partir de minerales o concentrados de minerales arsenosulfurosos o sulfurosos, donde el mineral o concentrado de mineral se hace reaccionar con azufre o compuestos de arsénico que contienen azufre para obtener un producto de reacción que contiene CoS y/o NiS.

De acuerdo con la reivindicación 1, el procedimiento conduce a productos escurribles con elevada porosidad, los que se adecuan para un procesamiento posterior de lixiviación.

Las demás reivindicaciones se refieren a realizaciones preferidas del procedimiento.

El procedimiento se diferencia del procedimiento de la US-A-4 585 477 en que no se lleva a cabo un proceso de calcinación oxidante de mineral arsenosulfuroso o sulfuroso.

La DE-C-43 29 417 se refiere también a una calcinación en atmósfera oxidante.

De esta manera se cumplen los criterios de los artículos PCT 33 (2) y 33 (3).

Patentansprüche

1. Verfahren zur Gewinnung von Metallen aus einem arsenosulfidischen und/oder sulfidischen Cobalt- und/oder Nickelerz oder -erzkonzentrat, bei dem
 - das arsenosulfidische und/oder sulfidische Cobalt- und/oder Nickelerz oder -erzkonzentrat mit Schwefel oder schwefelhaltigen Arsenverbindungen zu einem Reaktionsprodukt umgesetzt wird, und
 - lösliche Metalle und seltene Erden aus dem Reaktionsprodukt gelöst werden.

**enthaltend CoS und / oder NiS*
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass Arsen aus dem Reaktionsprodukt gelöst wird und die am Reaktionsprodukt angelagerten Metalle und seltene Erden, insbesondere Gold, Silber, Platin, PME, Nickel, Cobalt und Zink abgetrennt werden.
3. Verfahren nach Anspruch 1, oder 2, dadurch gekennzeichnet, dass die Metalle mit einem Bioleaching-Verfahren aus dem Reaktionsprodukt herausgelöst werden.
4. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass die Umsetzung in inerte Atmosphäre durchgeführt wird.
5. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass die Umsetzung bei einer Temperatur zwischen 50°C und 550°C, insbesondere zwischen 350°C und 450°C erfolgt.
6. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass die Umsetzung durch Mikrowellenbestrahlung unterstützt wird.

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REIVINDICACIONES

1- Procedimiento para la extracción de metales a partir de minerales o concentrados de minerales de cobalto y/o níquel arsenosulfurosos o sulfurosos, en el que

- se hace reaccionar el mineral y/o concentrado de mineral arsenosulfuroso y/o sulfuroso de cobalto y/o de níquel con azufre o compuestos azufrados de arsénico para obtener un producto de la reacción que contiene CoS y/o NiS , y
- se lixivian metales solubles y tierras raras del producto de reacción.

2- Procedimiento de acuerdo con la reivindicación 1, **caracterizado** porque se lixivia arsénico del producto de la reacción y se separan los metales y tierras raras depositadas en el producto de la reacción, en particular, oro, plata, platino, metales de platino, níquel, cobalto y zinc.

3- Procedimiento de acuerdo con la reivindicación 1 o 2, **caracterizado** porque los metales son lixiviados del producto de la reacción utilizando un proceso de biolixiviado.

4- Procedimiento de acuerdo con una de las reivindicaciones precedentes, **caracterizado** porque la reacción se lleva a cabo en una atmósfera inerte.

5- Procedimiento de acuerdo con una de las reivindicaciones precedentes, **caracterizado** porque la reacción procede se lleva a cabo a una temperatura que se encuentra entre $50\text{ }^{\circ}\text{C}$ y $550\text{ }^{\circ}\text{C}$, en particular, entre $350\text{ }^{\circ}\text{C}$ y $450\text{ }^{\circ}\text{C}$.

6- Procedimiento de acuerdo con una de las

reivindicaciones precedentes, **caracterizado** porque la
reacción es apoyada por irradiación de microondas.

CLAIMS:

(amended December 1, 2003)

1. A process for extracting metals from an arsenosulfidic and/or sulfidic cobalt and/or nickel ore or ore concentrate in which
 - the arsenosulfidic and/or sulfidic cobalt and/or nickel ore or ore concentrate is converted to a reaction product containing CoS and/or NiS by sulfur or sulfur-containing arsenic compounds; and
 - soluble metals and rare earth metals are leached from the reaction product.
2. The process according to claim 1, characterized in that arsenic is leached from the reaction product and that the metals and rare earth metals deposited on the reaction product, especially gold, silver, platinum, platinum metals, nickel, cobalt and zinc, are separated off.
3. The process according to claim 1 or 2, characterized in that the metals are leached out from the reaction product using a bioleaching process.
4. The process according to any of the preceding claims, characterized in that said conversion is performed in an inert atmosphere.
5. The process according to any of the preceding claims, characterized in that said conversion is performed at a temperature of between 50 °C and 550 °C, especially between 350 °C and 450 °C.
6. The process according to any of the preceding claims, characterized in that said conversion is promoted by microwave irradiation.
7. The process according to any of the preceding claims, characterized in that said conversion is effected for a period of from 0.5 h to 10 h, especially from 2 h to 5 h.

8. The process according to any of the preceding claims, characterized in that sulfur is added.
9. The process according to any of the preceding claims, characterized in that sulfur is added in a solid state and the conversion is effected under a pressure of from 1 to 10 bar.
10. The process according to claim 8, characterized in that said conversion proceeds in an atmosphere saturated with sulfur vapor.
11. The process according to any of claims 1 to 7, characterized in that sulfur is added in a gaseous state and the conversion is effected under reduced pressure.
12. The process according to any of claims 1 to 7, characterized in that the conversion is effected with a sulfur plasma.

PATENT COOPERATION TREATY

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PCT

From the INTERNATIONAL BUREAU

NOTIFICATION CONCERNING
SUBMISSION OR TRANSMITTAL
OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

To:

BECKMANN, Alexander
Haselnussweg 2
46487 Wesel
Germany

Date of mailing (day/month/year) 25 February 2003 (25.02.03)	
Applicant's or agent's file reference	IMPORTANT NOTIFICATION
International application No. PCT/DE02/03394	International filing date (day/month/year) 14 September 2002 (14.09.02)
International publication date (day/month/year) Not yet published	Priority date (day/month/year) 14 September 2001 (14.09.01)
Applicant BECKMANN, Alexander	

1. The applicant is hereby notified of the date of receipt (except where the letters "NR" appear in the right-hand column) by the International Bureau of the priority document(s) relating to the earlier application(s) indicated below. Unless otherwise indicated by an asterisk appearing next to a date of receipt, or by the letters "NR", in the right-hand column, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
2. This updates and replaces any previously issued notification concerning submission or transmittal of priority documents.
3. An asterisk(*) appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b). In such a case, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.
4. The letters "NR" appearing in the right-hand column denote a priority document which was not received by the International Bureau or which the applicant did not request the receiving Office to prepare and transmit to the International Bureau, as provided by Rule 17.1(a) or (b), respectively. In such a case, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

Priority date	Priority application No.	Country or regional Office or PCT receiving Office	Date of receipt of priority document
14 Sept 2001 (14.09.01)	101 45 419.8 ✓	DE	25 Febr 2003 (25.02.03)
12 Janu 2002 (12.01.02)	02000758.9 ✓	EP	06 Janu 2003 (06.01.03)

OK
12.02.03

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No. (41-22) 338.89.95	Authorized officer Céline Faust (Fax 338-8995) Telephone No. (41-22) 338 9728
--	---

Se WI Da hi PCT/DE02/03394

PATENT COOPERATION TREATY

19 MAY 2003

K F 71 : 1

PCT

From the INTERNATIONAL BUREAU

To:

SCHREIBER, Christoph
Postfach 10 22 41
50462 Köln
Germany

INFORMATION CONCERNING ELECTED
OFFICES NOTIFIED OF THEIR ELECTION

(PCT Rule 61.3)

Date of mailing (day/month/year) 02 May 2003 (02.05.03)		
Applicant's or agent's file reference		IMPORTANT INFORMATION
International application No. PCT/DE02/03394	International filing date (day/month/year) 14 September 2002 (14.09.02)	
Applicant BECKMANN, Alexander		Priority date (day/month/year) 14 September 2001 (14.09.01)

1. The applicant is hereby informed that the International Bureau has, according to Article 31(7), notified each of the following Offices of its election:

EP : AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR
National : AU, BG, CA, CN, DE, GB, IL, JP, KP, KR, MN, NO, PL, RO, RU, SK, US

2. The following Offices have waived the requirement for the notification of their election; the notification will be sent to them by the International Bureau only upon their request:

AP : GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW
EA : AM, AZ, BY, KG, KZ, MD, RU, TJ, TM
OA : BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG
National : AE, AG, AL, AM, AT, AZ, BA, BB, BR, BY, BZ, CH, CO, CR, CU, CZ, DK, DM, DZ, EC, EE, ES, FI, GD, GE, GH, GM, HR, HU, ID, IN, IS, KE, KG, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MW, MX, MZ, NZ, OM, PH, PT, SD, SE, SG, SI, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW

3. The applicant is reminded that he must enter the "national phase" before the expiration of 30 months from the priority date before each of the Offices listed above. This must be done by paying the national fee(s) and furnishing, if prescribed, a translation of the international application (Article 39(1)(a)), as well as, where applicable, by furnishing a translation of any annexes of the international preliminary examination report (Article 36(3)(b) and Rule 74.1).

Some offices have fixed time limits expiring later than the above-mentioned time limit. For detailed information about the applicable time limits and the acts to be performed upon entry into the national phase before a particular Office, see Volume II of the PCT Applicant's Guide.

The entry into the European regional phase is postponed until 31 months from the priority date for all States designated for the purposes of obtaining a European patent.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer: Odile ALIU (Fax 338-8995)
Facsimile No. (41-22) 338.88.85	Telephone No. (41-22) 338 8834

PATENT COOPERATION TREATY

Am	Sg	Da	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
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17. APR 2003

PCT

From the INTERNATIONAL BUREAU

To:

VON KREISLER SELTING WERNER
Deichmannhaus am Dom
P.O. Box 10 22 41
D-50462 Köln
Germany

NOTIFICATION OF THE RECORDING
OF A CHANGE

(PCT Rule 92bis.1 and
Administrative Instructions, Section 422)

Date of mailing (day/month/year) 02 April 2003 (02.04.03)	
Applicant's or agent's file reference	IMPORTANT NOTIFICATION
International application No. PCT/DE02/03394	International filing date (day/month/year) 14 September 2002 (14.09.02)

1. The following indications appeared on record concerning:

☐ the applicant ☐ the inventor ☒ the agent ☐ the common representative

Name and Address

State of Nationality

State of Residence

Telephone No.

Facsimile No.

Teleprinter No.

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☒ the person ☒ the name ☒ the address ☐ the nationality ☐ the residence

Name and Address

VON KREISLER SELTING WERNER
Deichmannhaus am Dom
P.O. Box 10 22 41
D-50462 Köln
Germany

State of Nationality

State of Residence

Telephone No.

49 221 91 65 20

Facsimile No.

49 221 13 42 97

Teleprinter No.

3. Further observations, if necessary:

Please note appointment of agent.

4. A copy of this notification has been sent to:

☒ the receiving Office ☒ the designated Offices concerned
☒ the International Searching Authority ☐ the elected Offices concerned
☐ the International Preliminary Examining Authority ☐ other:

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 338.89.85

Authorized officer

Céline Faust (Fax 338-8995)

Telephone No. (41-22) 338 9728

PATENT COOPERATION TREATY

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PCT

NOTIFICATION OF RECEIPT OF
RECORD COPY

(PCT Rule 24.2(a))

From the INTERNATIONAL BUREAU

To:

BECKMANN, Alexander
Haselnussweg 2
46487 Wesel
Germany

Date of mailing (day/month/year) 09 January 2003 (09.01.03)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference	International application No. PCT/DE02/03394

The applicant is hereby notified that the International Bureau has received the record copy of the international application as detailed below.

Name(s) of the applicant(s) and State(s) for which they are applicants:

BECKMANN, Alexander(all designated States)

International filing date : 14 September 2002 (14.09.02)

Priority date(s) claimed : 14 September 2001 (14.09.01)
12 January 2002 (12.01.02)

Date of receipt of the record copy
by the International Bureau : 04 December 2002 (04.12.02)

List of designated Offices :

AP : GH,GM,KE,LS,MW,MZ,SD,SL,SZ,TZ,UG,ZM,ZW

EA : AM,AZ,BY,KG,KZ,MD,RU,TJ,TM

EP : AT,BE,BG,CH,CY,CZ,DE,DK,EE,ES,FI,FR,GB,GR,IE,IT,LU,MC,NL,PT,SE,SK,TR

OA : BF,BJ,CF,CG,CI,CM,GA,GN,GQ,GW,ML,MR,NE,SN,TD,TG → nicht ankreuzt!

National : AE,AG,AL,AM,AT,AU,AZ,BA,BB,BG,BR,BY,BZ,CA,CH,CN,CO,CR,CU,CZ,DE,DK,DM,DZ,
EC,EE,ES,FI,GB,GD,GE,GH,GM,HR,HU,ID,IL,IN,IS,JP,KE,KG,KP,KR,KZ,LC,LK,LR,LS,LT,LU,
LV,MA,MD,MG,MK,MN,MW,MX,MZ,NO,NZ,OM,PH,PL,PT,RO,RU,SD,SE,SG,SI,SK,SL,TJ,TM,TN,TR,
TT,TZ,UA,UG,US,UZ,VN,YU,ZA,ZM,ZW

da in 1CS
13.03.03

ATTENTION

The applicant should carefully check the data appearing in this Notification. In case of any discrepancy between these data and the indications in the international application, the applicant should immediately inform the International Bureau.

In addition, the applicant's attention is drawn to the information contained in the Annex, relating to:

☒ time limits for entry into the national phase - see updated important information (as of April 2002)

☒ confirmation of precautionary designations (if applicable)

☒ requirements regarding priority documents (if applicable) → dies ist doch durch 304 art oder 2

A copy of this Notification is being sent to the receiving Office and to the International Searching Authority.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No. (41-22) 338.88.95	Authorized officer: N. Wagner (Fax 338-8995) Telephone No. (41-22) 338 8887
--	---

INFORMATION ON TIME LIMITS FOR ENTERING THE NATIONAL PHASE

The applicant is reminded that the "national phase" must be entered before each of the designated Offices indicated on the cover sheet of this Notification by paying national fees and furnishing translations, as prescribed by Articles 22 and 39 and the applicable national laws. In addition, the applicant may also have to comply with other special requirements applicable in certain Offices. It is the applicant's responsibility to ensure the necessary steps to enter the national phase are taken in a timely fashion. Most Offices do not issue reminders to applicants in connection with the entry into the national phase.

The applicable time limit for entering the national phase will, subject to what is said in the following paragraph, be **30 MONTHS** from the priority date, not only in respect of any elected Office where a demand for international preliminary examination is filed before the expiration of 18 months from the priority date (see Article 39(1)), but also in respect of any designated Office, in the absence of filing of such demand, where Article 22(1) as modified with effect from 1 April 2002 applies in respect of that designated Office. For further details, see PCT Gazette No. 44/2001 of 1 November 2001, pages 19928, 19932 and 19934, as well as the PCT Newsletter, October and November 2001 and February 2002 issues.

In practice, time limits other than the 30-month time limit will continue to apply, for various periods of time, in respect of certain designated or elected Offices. For regular updates on the applicable time limits (20, 21, 30 or 31 months, or other time limit), Office by Office, refer to the PCT Gazette ("Section IV" part published on a weekly basis), to the PCT Newsletter (on a monthly basis) and to the relevant National Chapters in Volume II of the PCT Applicant's Guide (the paper version of which is updated usually twice a year and the Internet version of which is updated usually on a weekly basis). Finally, a cumulative table of all applicable time limits for entering the national phase is available from WIPO's Internet site, via links from various pages the site including those of the Gazette, Newsletter and Guide, at <http://www.wipo.int/pct/en/index.html>.

Information about the requirements for filing a demand for international preliminary examination is set out in the PCT Applicant's Guide, Volume I/A, Chapter IX. Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination (at present, all PCT Contracting States are bound by Chapter II).

CONFIRMATION OF PRECAUTIONARY DESIGNATIONS

This notification lists only specific designations made under Rule 4.9(a) in the request. It is important to check that these designations are correct. Errors in designations can be corrected where precautionary designations have been made under Rule 4.9(b). The applicant is hereby reminded that any precautionary designations may be confirmed according to Rule 4.9(c) before the expiration of 15 months from the priority date (this time limit may not be extended). If it is not confirmed, it will automatically be regarded as withdrawn by the applicant. There will be no reminder and no invitation. Confirmation of a designation consists of the filing of a notice specifying the designated State concerned (with indication of the kind of protection or treatment desired) and the payment of the designation and confirmation fees. The Notice of confirmation and payment must reach the receiving Office within the 15-month time limit.

REQUIREMENTS REGARDING PRIORITY DOCUMENTS

For applicants who have not yet complied with the requirements regarding priority documents, the following is recalled.

Where the priority of an earlier national, regional or international application is claimed, the applicant must submit a copy of the said earlier application, certified by the authority with which it was filed ("the priority document"), to the receiving Office (which will transmit it to the International Bureau) or directly to the International Bureau, before the expiration of 18 months from the priority date, provided that any such priority document may still be submitted to the International Bureau before that date of international publication of the international application, in which case that document will be considered to have been received by the International Bureau on the last day of the 18-month time limit (Rule 17.1(a)).

Where the priority document is issued by the receiving Office, the applicant may, instead of submitting the priority document, request the receiving Office to prepare and transmit the priority document to the International Bureau. Such request must be made before the expiration of the 18-month time limit and may be subjected by the receiving Office to the payment of a fee (Rule 17.1(b)).

If the priority document concerned is not submitted to the International Bureau or if the request to the receiving Office to prepare and transmit the priority document has not been made (and the corresponding fee, if any, paid) within the applicable time limit indicated under the preceding paragraphs, any designated State may disregard the priority claim, provided that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within the time limit which is reasonable under the circumstances.

Where several priorities are claimed, the priority date to be considered for the purposes of computing the 18-month time limit is the filing date of the earliest application whose priority is claimed.

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Pat ntanwälte Patent Attorneys
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Europäisches Patentamt

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80331 München

Unser Zeichen:
022392wo/CS/gn

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Dipl.-Chem. Dr. Jörg Halbing
Dipl.-Ing. Alexander von Kirchbaum
Dipl.-Chem. Dr. Christoph Schrelber

01. Dezember 2003

Per Telefax und
Bestätigungskopie

Internationale Patent Anmeldung PCT/DE 02/03394
Alexander Beckmann

Auf den zweiten schriftlichen Bescheid vom 30. September 2003:

Als Anlage wird ein Satz neuer Patentansprüche überreicht, der der weiteren
Prüfung zugrundegelegt werden soll. /

In Anspruch 1 wurde aufgenommen, dass das Reaktionsprodukt CoS oder NiS
enthält.

Dies ist beispielsweise auf Seite 3, letzter Absatz der Beschreibung offenbart.
Hierdurch soll klargestellt werden, dass erfindungsgemäß kein Röstverfahren
durchgeführt wird, sondern eine Umsetzung des Erzes als Feststoff mit Schwefel
bzw. schwefelhaltigen Arsenverbindungen erfolgt.

Nach Ansicht der IPEA ist der Anspruch 1 nicht neu gegenüber D1 bzw. D2. Wie
im schriftlichen Bescheid dargestellt, betrifft D1 ein Verfahren zur Gewinnung
von Kupfer und Nickel aus sulfidischen Erzen umfassend die Schritte des Rösten
des Minerals, Sulfatierung, gefolgt von einem Laugungsschritt. Zur Sulfatierung
werden eingesetzt Schwefelsäure, Schwefeltrioxid, Metallsulfate und Schwefeldi-

mit elementarem Schwefel im festen, flüssigen oder gasförmigen Zustand bei 360 bis 900°C für mindestens 20 Minuten behandelt wird. Anschließend werden die löslichen Metalle aus dem Reaktionsprodukt gelöst (Ansprüche 1, 4; Sp.4, Z.51-55).

3. Neuheit

Die Merkmale der Ansprüche 1, 2 und 11 sind direkt aus D1 zu entnehmen.

Die Merkmale der Ansprüche 1, 2, 5, 8 und 9 sind aus D2 bekannt.

Die inerte Atmosphäre, die im Anspruch 4 beansprucht wird, ist automatisch durch die Präsenz von Sauerstoff und Schwefel in D2 vorhanden. Diese Lehre ist auch eindeutig aus D3 zu entnehmen.

Somit ist der Gegenstand der Ansprüche 1, 2, 4, 5, 8, 9 und 11 nicht neu gemäß Art.33(2) PCT.

4. Erfinderische Tätigkeit

Die Merkmale der abhängigen Ansprüche 3 und 6 bis 12 gehören zu bekannten Verfahrensschritten bei der Gewinnung von Metallen aus sulfidischen Erzen.

Somit ist es dem Fachmann sehr naheliegend, ein Bioleaching-Verfahren, wie aus D4 bekannt, als Methode zur Lösung von den Metallen im Reaktionsprodukt in D1 zu benutzen, da beide Druckschriften sich auf sulfidischen Nickelerzen beziehen.

Ähnlicherweise ist die Unterstützung der Röstung durch Mikrowellen für sulfidischen Erzen aus D5 bekannt und dem Fachmann naheliegend, wenn er die Gewinnung von Metallen verbessern möchte.

Die Länge der Umsetzung mit Schwefel ist zwar in D1 und D2 nicht ausdrücklich beschrieben. Eine Dauer von 0,5 bis 10 Stunden ist jedoch eine übliche Länge eines solchen Verfahrensschrittes. Dies ist aus D6 zu entnehmen, die sich zwar mit nicht-sulfidischen Erzen (Laterit) befasst, aber sonst die gleichen Schritte, wie in der jetzigen Anmeldung beinhaltet.

**SCHRIFTLICHER BESCHEID
BEIBLATT**

Internationales Aktenzeichen PCT/DE02/03394

D6 beschreibt auch der Zufuhr von Schwefel in verschiedenen Zustände. Da D6 sich gut mit D1 oder D2 kombinieren lässt, da sie alle mit dem Zufuhr von Schwefel zur Verbesserung der Gewinnung von Metallen befassen, kann kein erfinderisches Zutun in den Merkmalen der abhängigen Ansprüchen 8 bis 12 gesehen werden.

Somit ist der Gegenstand der Ansprüche 3 und 6 bis 12 nicht erfinderisch gemäß Art.33(3) PCT.

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1 de diciembre de 2003

Por Telefax y copia de confirmación

Solicitud de Patente Internacional PCT/DE02/03394

Alexander Beckmann

Respecto del segundo informe escrito del 30 de septiembre de 2003:

Como adjunto se ofrece un juego de nuevas reivindicaciones de la patente, en las cuales debe basarse el nuevo examen.

En la reivindicación 1 se supuso que el producto de reacción contiene CoS o NiS.

Esto se da a conocer, por ejemplo, en la página 3, último párrafo de la descripción. De esta manera queda en claro que, de acuerdo con la invención, no se lleva a cabo ningún proceso de calcinación, sino una reacción del mineral, como material sólido, con azufre o compuestos de arsénico que contienen azufre.

Según la opinión de IDEA, la reivindicación 1 no es novedosa con respecto a D1 o D2. Como se indica en el informe escrito, D1 se refiere a un procedimiento para la extracción de cobre y níquel a partir de minerales sulfurosos que comprende los pasos de calcinar y sulfatar el mineral, seguidos de un paso de lixiviación. Para la sulfatación se emplean ácido sulfúrico, trióxido de azufre,

sulfato metálico y dióxido de azufre, junto con oxígeno. Los productos obtenidos de esta manera están sulfatados, es decir, se tratan de las sales metálicas del ácido sulfúrico.

De acuerdo con la invención, mediante el procedimiento no se lleva a cabo una oxidación, sino que se obtienen CoS y NiS . La reivindicación 1 es entonces novedosa con respecto a D1.

D2 se refiere asimismo a un procedimiento para la calcinación de minerales, a saber, los denominados minerales refractarios de oro. De acuerdo con el renglón 6, antes de una lixiviación con cianuro se debe llevar a cabo una oxidación, en lo posible, completa de, entre otros, el azufre. Independientemente del hecho de que D2 no describe el procesamiento de minerales de cobalto o de níquel sino de minerales de oro, el presente procedimiento se diferencia en que no se lleva a cabo ningún paso de calcinación sino una transformación del mineral presente como sólido a un sulfuro de cobalto o de níquel.

A los demás documentos citados se recurre solo desde el punto de vista de realizaciones preferidas de ciertas reivindicaciones. Los mismos no son relevantes para el cuestionamiento de la novedad y la actividad inventiva del presente juego de reivindicaciones.

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Se solicita entonces reconocer la novedad, la actividad inventiva y la aplicabilidad industrial de todas las reivindicaciones.

El Agente de Patentes

(Fdo.)

Anexos: /

Röster

cat SO₂ etc 21 70

United States Patent [19]

Mißen

[11] Patent Number: 4,585,477
[45] Date of Patent: Apr. 29, 1986

[54] METHOD FOR SEPARATING AND RECOVERING NICKEL AND COPPER FROM COMPLEX MATERIALS

[75] Inventor: Thomas K. Mißen, Stockholm, Sweden

[73] Assignee: Bolldes Aktiebolag, Stockholm, Sweden

[21] Appl. No.: 699,506

[22] Filed: Feb. 11, 1985

Related U.S. Application Data

[63] Continuation of Ser. No. 539,628, Oct. 6, 1983, abandoned, which is a continuation of Ser. No. 403,649, filed as PCT SE 81/00334, Nov. 13, 1981, published as WO 82/01725, May 27, 1982, § 102(e) date Jul. 15, 1982, abandoned.

[30] Foreign Application Priority Data

Nov. 17, 1980 [SE] Sweden 8008053

[51] Int. Cl.⁴ C22B 15/00; C22B 23/00

[52] U.S. Cl. 75/117; 75/2; 75/72; 75/74; 75/82; 75/83; 75/101 R; 75/115; 75/119; 75/121; 423/27; 423/35; 423/36; 423/41; 423/42; 423/45; 423/140; 423/146; 423/150; 423/152; 423/154; 204/108

[58] Field of Search 423/41, 45, 151, 152, 423/153, 27, 35, 36, 42, 140, 146, 150, 154; 75/117, 101 R, 2, 72, 74, 82, 83, 115, 119, 121; 204/108

[56] References Cited

U.S. PATENT DOCUMENTS

1,315,761 9/1919 Coolbaugh 423/41
1,528,209 3/1925 Greenwald
1,844,937 2/1932 Hyblins 204/108

4,069,041 1/1978 Görting et al. 75/101
4,093,526 6/1978 Blanco et al. 204/104

FOREIGN PATENT DOCUMENTS

892475 2/1972 Canada
1082467 7/1980 Canada
200467 5/1907 Fed. Rep. of Germany
22259 11/1905 Sweden
322632 4/1970 Sweden
397204 10/1977 Sweden

OTHER PUBLICATIONS

Hanf, N. W. and Schmidt C. G., "The Roasting and Leaching of Witwatersrand Pyrite Concentrates" J. of S. Africa Inst. of Mining and Metallurgy Aug., 1979, pp. 365-371.

Primary Examiner—John Doll

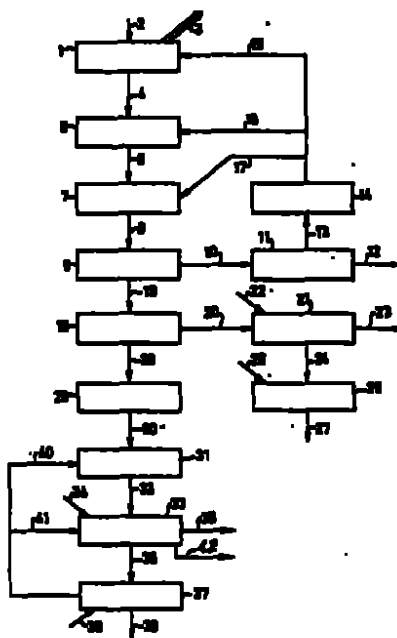
Assistant Examiner—Robert L. Stoll

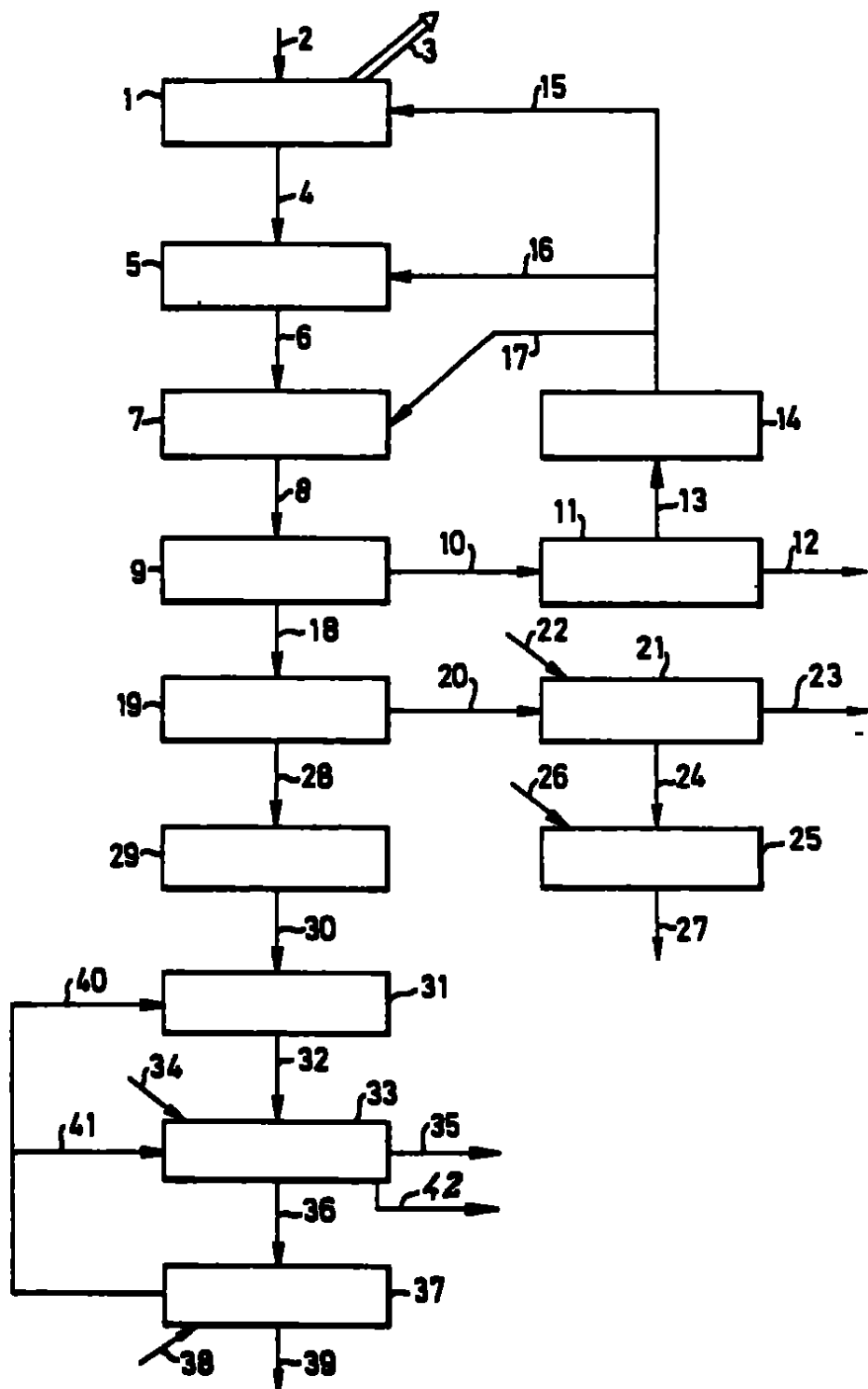
Attorney, Agent, or Firm—Nils H. Ljungman

[57] ABSTRACT

A method of recovering copper and nickel from sulphidic minerals containing copper, nickel and iron comprises the steps of roasting the mineral, preferably to provide magnetic sulphating, for example with sulphuric acid, sulphur trioxide, metal sulphate and/or sulphur dioxide together with oxygen; and a subsequent leaching of the sulphated material and recovery of copper from the leaching solution, for example by electrolysis. All or part of the leaching solution with its nickel content is recycled to the roasting stage, and the nickel content is removed in the form of nickel oxide together with the leaching residue, from which nickel can be recovered.

15 Claims, 1 Drawing Figure





METHOD FOR SEPARATING AND RECOVERING NICKEL AND COPPER FROM COMPLEX MATERIALS

This is a continuation of the U.S. application Ser. No. 539,628, filed on Oct. 6, 1983, now abandoned, which is a continuation from Ser. No. 403,649, filed as PCT SE81/00334, on Nov. 13, 1981, published as WO82/01725 on May 27, 1982, § 102(e) date on July 15, 1982, now abandoned.

The present invention relates to a method of separating and recovering nickel and copper from complex sulphide minerals, by subjecting said minerals to roasting, sulphating and leaching processes.

The working-up of complex sulphide minerals which contain nickel and copper presents a problem which is not readily solved. A number of commonly known pyrometallurgical processes cannot readily be applied to complex sulphide minerals. Complex sulphide minerals which contain nickel almost always also contain copper and iron. Such minerals include pentlandite, chalcopyrite and pyrrhotite. When wishing to produce pure copper and nickel concentrates, the method to which one is generally referred is one involving the hydrometallurgical separation by flotation, therewith to recover a copper concentrate, a nickel concentrate and a waste comprising mainly pyrrhotite which will contain a relatively high percentage of nickel and copper.

A relatively high energy input is required to finely divide the complex concentrate when separating the individual constituents thereof by flotation, and the separation process results in concentrates which are far too impure for direct use, without separating therefrom other, residual valuable minerals. As before indicated, pyrometallurgical methods for working-up complex sulphide minerals of the aforementioned kind present many problems, these problems being illustrated herein-after in more detail. Thus, dead roasting results in the formation of copper and nickel ferrites which are chemically stable at elevated temperatures. Chlorinating roasting is expensive, since copper and nickel are chlorinated simultaneously and must be separated in a separate process. In the case of sulphating roasting it is difficult to sulphate nickel effectively, which results in nickel losses.

Smelting processes, for example applied when producing a matte from a complex sulphide material containing copper and nickel, also give rise to problems, owing to the fact that it is difficult to prevent nickel from passing into the iron slag, and to the fact that the copper and nickel content cannot readily be separated from the matte, and that a satisfactory yield cannot be obtained.

It will therefore be obvious that there is a need for satisfactory technique by which nickel can be recovered pyrometallurgically from complex sulphide minerals in a manner to eliminate any iron present.

It is also known to treat complex sulphide minerals containing minor quantities of nickel through a combination of sulphating roasting and leaching processes, where the mineral is roasted, sulphated and leached, whereafter copper and nickel are separated by electrolytically precipitating copper and recovering nickel sulphate from the electrolyte. As beforementioned, the disadvantage with this method is that excessively high contents of nickel remain in the leaching residue, thereby rendering the method uneconomical when the mineral contains large quantities of nickel; see for exam-

ple the Canadian Patent Specification Ser. No. 1082467.

It has now been found that nickel can be economically recovered from complex sulphide minerals rich in nickel in a more satisfactory manner, by applying a new combination of procedural steps.

The novel method is set forth in the following claims.

In accordance with the novel method there is roasted a complex sulphide concentrate containing copper and nickel under conditions such as to avoid the formation of ferrites with the iron present. The roasted products or calcines are then sulphated in a separate reactor vessel under conditions lying outside the thermodynamical stability range for ferrites. The sulphating agent used is either sulphur trioxide, sulphuric acid, metal sulphates or sulphur dioxide together with oxygen. The sulphating step is known per se; see for example the Canadian Patent Specification Ser. No. 892475. During the sulphating step, the temperature is held at 600°-750° C., preferably 625°-700° C.

Thermodynamically, copper and nickel lie very close to one another and it is difficult to separate nickel and copper by selective sulphating processes carried out thermodynamically. Consequently, efforts have always previously been made to sulphate copper and nickel to the highest possible extent (Thorahill, Trans CIMM, 64:601 (1961)). It is known that nickel is difficult to sulphate, because the resultant nickel sulphate forms an impenetrable layer on the surface of the nickel-oxide grains, which inhibits further sulphating. Consequently, it has been necessary to add alkali sulphates to prevent the formation of this impenetrable nickel-sulphate skin on the nickel-oxide grains. In order to obtain a yield which is higher than 60% sulphated nickel, it is necessary to add 4-6% sodium sulphate. (Journal of the South African Institute of Mining and Metallurgy, August 1979, pages 365-371). The costs incurred by this addition of sodium sulphate makes it difficult to provide a process which is economically rewarding.

The present proposal of selectively sulphating copper and substantially leaving nickel in its oxide form is surprising to one of normal skill in this art, since it could not be expected that both copper and nickel could be recovered effectively by selectively sulphating solely copper. It is important in this respect that nickel is recovered practically completely in the process. When practicing the method according to the invention, it is permissible for copper to be sulphated less effectively than considered necessary in accordance with previously known sulphating methods, in order to obtain a maintained total yield. This is less significant from the aspect of economy, since copper in the leaching residue found subsequent to the sulphating and leaching processes can be recovered together with nickel, for example as a copper-nickel-alloy, or by working-up the leaching residue in a nickel plant, for example by smelting and converting the leaching residue together with the nickel matte and/or sulphidic nickel concentrate, to form an ordinary Bessemer matte with about 20% by weight sulphur or a sulphur deficient so called high grade matte with not more than 10% sulphur and with low iron content.

The copper sulphate which has leached out is further treated in a conventional manner, by electrolysis or by cementation, to recover copper metal. Any electrolyte remaining after the electrolysis stage is returned to the roasting stage; and part of said electrolyte may also be returned to the sulphating and leaching stages. When returned to the roasting stage, sulphated nickel may be split-off to form nickel oxide. In this way the advantage

is gained whereby the only nickel leaving the process is in the form of an oxide in the leaching residue obtained from the leaching stage. The leaching residue obtained when leaching-out sulphates can be treated in various ways. Thus, noble metals can be leached out, where-
with a certain quantity of nickel will also be leached out. The noble metals can be cemented out with copper or nickel metal and residual nickel in the leaching solution can be precipitated out as nickel hydroxide, by neutralizing said solution, and then returned to the roasting stage or combined with the leaching residues from the leaching stages.

The leaching residue obtained from the leaching stage or stages can suitably be dried, and melted by supplying thereto a reductant, such as carbon or oil.

In this way there is obtained an alloy containing iron, nickel and copper. If the iron is oxidised by injecting air or oxygen gas into the bath of molten iron, copper and nickel, a copper-nickel alloy will be obtained. The resultant nickel products, copper-nickel alloy (Monel) and nickel hydroxide, can be further worked-up or sold in this form.

Thus, the method according to the invention enables the nickel and copper content of the mineral to be recovered practically completely as commercially valuable products.

The invention will now be described with reference to the accompanying drawing, the single FIGURE of which is a block schematic of a preferred embodiment of the invention.

Charged to a roasting furnace 1 through a line 2 is a complex copper-nickel-concentrate, containing for example pentlandite, chalcopyrite and pyrrhotite in mixture. Roaster gases from the furnace 1 are passed, through a line 3, to suitable apparatus (not shown) for utilizing the heat content and sulphur dioxide, while the roasted products are passed to a sulphating reactor vessel 5 through a line 4. The sulphated roasted products, or calcines, are passed, through a line 6, to a leaching stage 7, where the sulphated roasted product is leached with a weak acid sulphate solution.

The leached product and leaching solution are passed from the leaching stage 7, through a line 8, to a separation apparatus 9, from which leaching solution is passed, through a line 10, to an electrowinning apparatus 11, where copper is precipitated onto copper cathodes and where the anodes used comprise a non-consumable metal, such as lead, or where consumable anodes comprising nickel and copper are used. The removal of the copper product from the system is indicated by the arrow 12. The copper-depleted electrolyte is passed, through a line 13, to an optional evaporation apparatus 14, and from there, through a line 15, to the roasting furnace 1, or, through a line 16, to the sulphating stage 5 and/or, through a line 17, to the leaching stage 7. The leaching solution is suitably divided between the lines 15, 16 and 17.

The leaching residues are passed from the separating apparatus 9, through a line 18, to a second leaching stage 19, in which noble metals are leached-out with a chlorine-containing chloride solution. The leaching solution is passed, through a line 20, to a cementation stage 21, where noble metals are precipitated out. As indicated by arrow 22, nickel or copper are added as cementation metals. Removal of noble-metal precipitates is shown by arrow 23. The leaching solution is then passed, through a line 24, to a neutralizing stage 25, to which calcium hydroxide is charged, as shown by

arrow 26. Nickel-hydroxide precipitate, and possibly copper-hydroxide, is removed, as indicated by arrow 27.

Leaching residues obtained from the second leaching stage 19 are passed, via a line 28, to a drying stage 29, and from there to a melting furnace 31 through a line 30. The resultant melt, which comprises an iron-copper-nickel-alloy, is passed, through a line 32, to a reduction stage 33, to which reductant and slag former are charged via a line 34, and a fayalite slag is taken out, as indicated by arrow 35. The smelting and reduction stages may, to advantage, also be carried out in one and the same furnace unit, for example an electric-arc furnace. The alloy formed by said reduction is passed, via a line 36, to a converter 37, to which there is charged an oxygen-containing gas through a line 38, and from where there is removed a molten copper-nickel-alloy, through a line 39. Slag is passed from the converter 37 either to a smelting furnace 31, via a line 40, or to the reduction stage 33, via a line 41. As indicated by arrow 42, a nickel-iron alloy also containing some copper can also be taken out.

EXAMPLE 108.5 tons of complex copper-nickel concentrate of the following composition were charged each day to a fluidized-bed furnace

Cu	12.8%	13.9 tons
Ni	2.1%	2.3
Fe	38.5%	41.8
S	31.4%	34.0
Residue	12.2%	13.3
	100%	108.5 tons

The concentrate was subjected to a magnetite-yielding roasting at a temperature of about 800°-1100° C. with a limited supply of oxygen; and the magnetite calcine then sulphated and leached in accordance with the invention.

In the first leaching stage, about 80% of the copper content in its steady state was leached out, and about 10% of the nickel content.

In the steady state, i.e. subsequent to returning the leaching solution to the roasting stage when copper had been recovered therefrom, all of the nickel, iron and noble metal content of the concentrate was found in the leaching residue, said residue therefore containing, after being dried

Cu	4.4%	2.8 tons/day
Ni	1.7%	3.3 tons/day
Fe	63.9%	41.8 tons/day
Residue	21.0%	13.3 tons/day
		63.4 tons/day

When the material did not contain appreciable quantities of noble metals, the dried leaching residue was passed directly to the melting stage. In the melting stage the iron content was slagged to 75% or 32.0 tons/day. An iron-copper-nickel-alloy of the following composition was obtained

Ni	28.7%	14 tons/day
Cu	15.3%	2.8 tons/day
Fe	55.0%	10.0 tons/day
		18.2 tons/day

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Finally the iron content was slagged to about 90%, there being obtained an alloy of the following composition

Ni	33.9%	5.3 tons/day
Cu	31.1%	2.8 tons/day
Fe	10.0%	0.9 tons/day
		9.0 tons/day

Thus, the process gave each day 9 tons of Monel, 40 tons of iron in the form of fayalite slag, and 11 tons of copper.

I claim:

1. A method of recovering copper and nickel from sulphidic minerals containing copper, nickel and iron, comprising roasting said minerals and then sulphating the roasted minerals in separate stages, and leaching the sulphated material and recovering copper from the leaching solution, characterized by returning all or part of the nickel content of the leaching solution to the roasting stage as nickel sulphate, at least partially transforming said returned nickel content to nickel oxide by splitting off in said roasting stage substantially simultaneously with transforming of any nickel sulphide content of said minerals to nickel oxide by roasting in said roasting stage, delivering said nickel oxide and any remaining nickel sulphate to the sulphating stage; and by recovering the nickel content in the form of an oxide, together with the leaching residue.

2. A method according to claim 1, characterized by recovering copper from the leaching solution by means of an electrolysis process.

3. A method according to claim 2, characterized by recirculating the leaching solution subsequent to recovering copper therefrom.

4. A method according to claim 1, characterized in that the sulphating agent used is either sulphuric acid, sulphur trioxide, metal sulphate and/or sulphur dioxide, together with oxygen.

5. A method according to claim 4, characterized in that at least part of the sulphating agent comprises leaching solution which has been recirculated subsequent to recovering copper therefrom.

6. A method according to claim 1, characterized in that the roasting stage is a magnetic yielding roasting and is effected at a temperature of 800°-1100° C.

7. A method according to claim 1, characterized in that nickel is recovered from the leaching residue by melting and reduction, to form a nickel-iron alloy.

8. A method according to claim 7 wherein said sulphidic minerals also contain noble metals, characterized by recovering noble metal from the leaching residue prior to the melting stage.

9. A method according to claim 1 wherein said sulphide minerals also contain noble metals, characterized in that the leaching residues are smelted together with the nickel matte; and that the resultant melt is converted

to nickel matte which is then worked-up to nickel metal, copper metal and noble metals.

10. A method of recovering copper and nickel from sulphidic minerals containing copper, nickel and iron, comprising:

roasting said minerals;
sulphating said roasted minerals in a separate stage;
leaching said sulphated minerals to form a leaching solution and a residue;

recovering copper from said leaching solution;
recycling said copper-depleted leaching solution to said roasting step, whereby what nickel sulphate which was formed in said sulphating step is transformed into nickel oxide; and

recovering the nickel content in the form of nickel oxide from said leaching residue, whereby substantially all of the nickel content of the mineral is recovered.

11. The method of claim 10, wherein said sulphating step is performed without the addition of an alkali sulphate, whereby the sulphating of the nickel content is minimized.

12. A method according to claim 1 wherein said sulphidic minerals also contain noble metals, characterized in that the leaching residues are smelted together with sulphidic nickel concentrate; and that the melt is converted to nickel matte which is then worked-up to nickel metal, copper metal and noble metals.

13. A method according to claim 1 wherein said sulphidic minerals also contain noble metals, characterized in that the leaching residues are smelted together with the nickel matte and sulphidic nickel concentrate; and that the resultant melt is converted to nickel matte which is then worked-up to nickel metal, copper metal and noble metals.

14. A method of recovering copper and nickel from sulphidic minerals containing copper, nickel and iron, comprising:

roasting said minerals; sulphating said roasted minerals in a separate stage;
leaching and sulphated minerals to form a leaching solution and a residue; recovering copper from said leaching solution;

evaporating said copper-depleted leaching solution; recycling said evaporated copper-depleted leaching solution to said roasting step, whereby what nickel sulphate which was formed in said sulphating step is transformed into nickel oxide; and

recovering the nickel content in the form of nickel oxide from said leaching residue, whereby substantially all of the nickel content of the mineral is recovered.

15. The method of claim 14, wherein said sulphating step is performed without the addition of an alkali sulphate, whereby the sulphating of the nickel content is minimized.

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[54] **RECOVERY OF NICKEL FROM BIOLEACH SOLUTION**

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[57] **ABSTRACT**

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A bioleaching method is provided for recovering nickel from an ore selected from the group consisting nickel-containing lateritic ores and nickel-containing sulfidic ores or concentrates thereof. Where the ore selected is a nickel-containing lateritic ore, at least one micro-organism selective to the leaching of the lateritic ore is provided as an aqueous solution thereof maintained at a pH ranging from about 1 to 3 including a nutrient for the micro-organism. The ore may be in the form of a heap, or a charge in a vat, or as a slurry. Where the ore selected is a nickel-containing sulfidic ore or concentrate thereof, at least one micro-organism comprising a biooxidizing bacterium selective to the leaching of sulfidic ore is added as an aqueous solution to the sulfidic ore or concentrate maintained at a pH of about 1 to 3, including a nutrient for the bacterium. The ore either as a slurry, a heap, or a charge in a vat is bioleached for a time sufficient to effect the dissolution of the nickel in the ore and form a solution thereof and a residue which is separated from the solution. The nickel is then selectively extracted from the solution using an ion exchange resin, and the nickel thereafter extracted from the resin using a mineral acid.

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[52] **U.S. Cl.** _____ 75/712; 75/743; 423/139; 423/DIG. 17

[58] **Field of Search** _____ 423/139, DIG. 17; 75/712, 743

[36] **References Cited**

U.S. PATENT DOCUMENTS

4,401,629 8/1983 Hancock et al. _____ 423/139
5,429,659 7/1995 Spencer et al. _____ 423/DIG. 17
5,491,078 2/1996 Clark _____ 423/68

14 Claims, No Drawings

RECOVERY OF NICKEL FROM BIOLEACH SOLUTION

This invention relates to the recovery of nickel from solutions generated from the processing of nickeliferous oxide or sulfide ores by bioleaching.

BACKGROUND OF THE INVENTION

It is known to recover nickel and/or copper from sulfidic ores by comminuting the ore to a finely divided state, subjecting the comminuted ore to froth flotation to upgrade the metal content thereof, and roasting the concentrate in an oxidizing atmosphere to remove the sulfur therefrom as SO_2 , followed by the reduction of the oxidized concentrate at an elevated temperature with a carbonaceous material to form molten nickel which is cast to provide pig nickel for use in the manufacture of stainless steel.

The foregoing method has certain disadvantages particularly with respect to the formation of SO_2 which is undesirable. Unless the SO_2 is converted to sulfuric acid on site, the SO_2 effluent released into the atmosphere presents environmental problems.

Nickel-containing sulfidic minerals and laterites are the two major raw material sources for nickel. The laterites are abundantly distributed throughout the world.

However, laterites, unlike nickel sulfide ores, cannot be concentrated by froth flotation or magnetically. Compared to other ores, the nickel content is low, for example, may range from 0.5 to 1.5% nickel by weight, with the exception of deposits in New Caledonia and Indonesia in which the amount of nickel is of the order of up to about 3% by weight which is quite high.

It has been predicted that by the end of this century, laterites will become the major source for the production of nickel.

The conventional process for recovering nickel from lateritic ores is somewhat energy intensive in that the nickel is extracted from the ore by high pressure leaching at elevated temperature in an autoclave.

For example, one process for recovering nickel and cobalt from lateritic ores is the well known Moa Bay process involving acid leaching at elevated temperatures and pressures at which iron oxide and aluminum oxyhydroxide are substantially insoluble.

In the Moa Bay process, lateritic ore at minus 20 mesh (95% passing 325 mesh U.S. Standard) is pulped to approximately 45% solids and the nickel and cobalt selectively leached with sufficient sulfuric acid at elevated temperature and pressure (e.g. 230° C. to 250° C. and 405 to 580 psia) to solubilize about 95% each of nickel and cobalt in about 60 to 90 minutes. After pressure let down, the leached pulp is washed by countercurrent decantation with the washed pulp going to tailings. The leach solution pH, which is quite low (e.g., between 0 and 0.5), is then neutralized with coral mud to a pH of about 2.4 in a series of four tanks at a total retention time of about 20 minutes and the thus-treated product liquor (containing about 5.65 gpl Ni, 0.8 gpl Fe and 2.3 gpl Al), after solid-liquid separation, is then subjected to sulfide precipitation. The leach liquor is preheated and the sulfide precipitation carried out using H_2S as the precipitating reagent in an autoclave at about 120° C. (250° F.) and a pressure of about 150 psig.

In the original scheme for treating the mixed sulfides, the sulfide precipitate was washed and thickened to a solids content of 65%. It was then oxidized in an autoclave at about 177° C. (350° F.) and a pressure of about 700 psig.

The solution containing nickel and cobalt was then neutralized with ammonia to a pH (5.35) sufficient to precipitate any residual iron, aluminum, and chromium present using air as an oxidizing agent.

The precipitate was thereafter separated from the solution and the nickel and cobalt solution then adjusted to a pH of about 1.5. H_2S was added to precipitate selectively any copper, lead and zinc present. The precipitate was separated from the solution by filtration and the nickel recovered by various methods. One method comprised treating the nickel-containing solution with hydrogen at elevated temperature and pressure to produce nickel powder.

The aforementioned method, as stated hereinbefore, had certain economic disadvantages. The conversion of mixed nickel-cobalt sulfide into saleable separate nickel and cobalt products was very expensive and there was no market for mixed sulfide precipitates.

It is known to subject gold-bearing sulfide ore to oxidative bioleaching. Such methods are disclosed in U.S. Pat. No. 4,729,788, No. 5,127,942 and No. 5,244,493. The sulfidic material is ground, placed in heaps or piles or pulped or slurried and bioleached to oxidize the sulfide mineral using bacteria at temperatures of about 15° C. to about 40° C. The sulfide particle containing gold occluded within it is biooxidized to physically free up the gold for removal by cyanide leaching or other types of leaching.

Attempts to use bioleaching to recover base metals, such as nickel, have not been attractive enough to warrant the building of a commercial plant, particularly since technology was not in place economically at the time for recovering nickel from the solution which were quite dilute at best, except for the use of solvent extraction by means of which more concentrated solutions could be produced for the subsequent recovery of nickel. The recovery of nickel from low grade bioleach solutions by solvent extraction has its problems in that (i) there are organic solvents that preferentially extract nickel from mixed ferric iron-nickel containing solutions such as shown hereinafter in Example 2 and (ii) the micro-organisms present in the bioleach solutions tend to adversely affect the separation of the organic phase from the aqueous phase.

The problem with ferric iron is that either the ferric ion will preferentially load on organic solvents, such as DEHPA (di-2-ethyl hexyl phosphoric acid) or it will oxidize the active ingredient in organic solvents such as Cyanex 272; 301 and 302. These reagents are sold by the American Cyanamid Company with the following active ingredients: phosphoric, phosphonic and phosphinic acids.

"Third phase" formation during solvent extractions sometimes limits the application of solvent extraction in leaching operations, particularly in a bioleaching circuit because bacteria and organic solvents are not compatible. For example, *Thiobacillus ferrooxidans* is in essence a sulfur-loving bacteria which presents problems in solvent extraction, particularly when the organic solvent contains sulfur, such as in di-nonyl-naphthyl sulfonic acid. Since many nickel sulfide ore bodies have a metal cut-off grade of around 0.2% to 0.5% Ni, it at once becomes apparent that a method is needed to enable the production of nickel solutions of sufficiently high concentration from which the nickel can be recovered economically. Thus, low grade nickel ores, in essence, could then be treated the same as a high grade ore with the same economical advantages.

Recent work conducted in the bioleaching of ores has indicated that low grade ores can be economically leached using bacteria as a means for effecting the dissolution of metal, e.g., nickel and/or cobalt, into an aqueous acid solution.

An advantage of bioleaching, while time dependent, is the fact that it is not energy and cost intensive. The pregnant solution obtained, however, is quite dilute.

One bioleaching method proposed for the recovery of nickel from sulfide ores is disclosed in Canadian Patent No. 2,065,491 which issued on Oct. 9, 1992.

According to the Canadian patent, a method disclosed comprises crushing the sulfide ore which is thereafter formed into a heap and the ore heap percolated with an iron sulfate solution which, optionally, carries bacteria, such as *Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans* or *Leptospirillum ferrooxidans*. By virtue of the oxidation of the sulfide ore, the generation of sulfuric acid occurs, thus forming a sulfate solution.

Sulfuric acid or an alkali, such as lime, is added to the solution, if necessary, to control the pH to a range of about 1.2 to 3, preferably from 2.3 to 2.5.

An anaerobic bacterium is added to the sulfate solution to cause the precipitation of the dissolved metal as an insoluble sulfide, thus upgrading the metal into a highly concentrated form which then must be treated to recover the metal, e.g., nickel.

To bring about sulfide generation of the dissolved metal (e.g., nickel), a bacterium, referred to as *Desulfovivrio Desulfuricans*, may be added to the solution. After the nickel sulfide precipitates, it is separated from the solution to provide a concentrate high in nickel which must be further treated, such as by high pressure leaching at an elevated temperature in the presence of sulfuric acid to produce a nickel sulfate solution from which the nickel is extracted by known conventional methods.

In a paper entitled "The Solubilization of Nickel, Cobalt and Iron From Laterites by Means of Organic Chelating agents" (Denis I. McKenzie et al. International Journal of Mineral Processing 21 (1987) P275-292), a group of carboxylic acids were mentioned as chelating agents, including Oxalic Acid, Citric Acid, Tartaric Acid, among others. The efficacy of the organic acids at natural pH were compared to H_2SO_4 (15 mM final concentration). Over a 456 hour period, using 15 mM concentrations of acids with 2 grams of ore (West Australian ore) in 150 ml of H_2O , Oxalic, Citric and Tartaric acids compared somewhat favorably with H_2SO_4 . Amount of nickel dissolved in ppm was 30.3 for H_2SO_4 , 18.5 for Oxalic acid, 20.2 for Citric acid and 16.3 for Tartaric.

The same acids employed on Indonesian ore showed that the nickel dissolved amounted to the following: Citric Acid 863 ppm, Tartaric Acid—708 ppm, Oxalic Acid—318 ppm, etc.

In a paper entitled "Microbial Leaching of Nickel from Low Grade Greek Laterites," *Mineral Bioprocessing*, TMS, 1991 page 191-205, the authors indicate a variety of heterotrophic micro-organisms that can produce such organic acids. They include: *aspergillus* and *penicillia* concentrations of around 40 grams of organic acid which were readily produced by these microorganisms.

Close to 70% of the Ni and less than 5% of the Fe were solubilized after a 51-day leaching period from a laterite ore containing about 1% Ni and 30% Fe. This work also showed an improved extraction when the organisms plus the culture medium were mixed with the laterite ore. An explanation was given: "Once the organisms attach themselves to the surface of the mineral grains, a high metal concentration gradient is experienced which could be toxic to the organisms spurring them to produce more citric acid (possibly as a defense response) which subsequently leaches out more

ions from the mineral grains." If the toxic metal were to be removed from the solution, as proposed in accordance with the present invention, either during the leaching process or interrupted by it, the leaching kinetics will be enhanced significantly so long as a low level of the toxic metal is maintained.

One method of heap leaching with nutrient solutions containing at least one micro-organisms include those selected from the group consisting of the fungi *Aspergillus Niger*, *Penicillium* Sp., *Aspergillus* Sp., *Penicillium Simplicissimus* and the bacteria *Enterobacter* Spp., *Bacillus* Spp., and *Achromobacter* Spp.

It would be desirable to provide a process for bioleaching relatively low grade as well as relative high grade nickel-containing lateritic ores and sulfidic ores or concentrates thereof in combination with a novel method for concentrating the nickel ions in solution from which nickel is economically recovered.

OBJECTS OF THE INVENTION

It is an object of the invention to provide a bioleaching process for the direct production of nickel metal by treating nickel-containing lateritic ores or nickel-containing sulfide ores or concentrates thereof (hereinafter referred to as nickel-containing sulfidic material) without going through an intermediate nickel sulfide production stage.

Another object is to provide a bioleaching process for treating nickel-containing ores in an economical and efficient manner.

These and other objects will clearly appear from the following disclosure and the claims.

SUMMARY OF THE INVENTION

Stating it broadly, the invention resides in a bioleaching and nickel recovery method for the extraction of nickel from an ore selected from the group consisting of nickel-containing lateritic ore and nickel-containing sulfidic material.

Where the ore is a nickel-containing lateritic ore, at least one micro-organism which systemically can produce an organic acid selective to the leaching of said ore is provided dispersed in an aqueous solution containing nutrients and the ore contacted by said solution.

The lateritic ore may be contacted by the leach solution in several ways. One method is to leach *in situ*, that is, by contacting an ore body in the ground with a micro-organism containing leach solution by drilling access holes into the ore body and allowing the solution to percolate into the ore body and stored therein for a residence time sufficient to allow the micro-organism to effect leaching of the ore. This type of leaching is time dependent in that the micro-organism containing solution is maintained in the ore body for a substantially long period of time. Another method is to employ heap leaching, agitation leaching, vat leaching or the like.

The micro-organism selected for leaching the lateritic ore is one which systemically produces an organic acid conducive to forming a complex with nickel, the micro-organism selected preferably being one that systemically produces such organic acids as Oxalic Acid, Pyruvic Acid, Citric Acid, Tartaric Acid, Malonic Acid, among others.

As illustrative of such micro-organisms, reference is made to *Aspergillus Niger* and *Penicillium Simplicissimus*. These micro-organisms are referred to as fungi which systemically secrete organic acids. These fungi grow well in a glucose solution.

It has been indicated that lateritic ores are leachable with these fungi in a glucose environment. The fungi may be used to manufacture solutions containing organic acids and the organic acids can then be used in combination with inorganic acids to leach and complex nickel and cobalt from laterite.

While it is known that the foregoing fungi have potential in the bioleaching of laterites to form a metal-containing lixiviant, very few, if any, address the need of recovering nickel from the lixiviant and to separate nickel from ferric iron to provide solutions containing sufficient amount of metal, e.g., nickel, for recovery by electrolysis or other methods.

Where the ore is a nickel-containing sulfidic material, the bacterial leaching, whether by stirred reactor, heap or vat leaching, is carried out using at least one biooxidizing bacterium selective to the leaching of the sulfidic ore.

As illustrative of biooxidizing bacteria, the following list of bacteria is given: *Thiobacillus thiooxidans*, *Thiobacillus ferrooxidans*, *Leptospirillum* species, *Sulfobacillus*, *Thermosulfidobacillus*, *Sulfobolus brierleyi*, *Sulfobolus acidocaldarius*, *Sulfobolus BC* and *Sulfobolus sulfataricus*. The *Sulfobolus* bacteria are particularly useful in that they can withstand temperatures over 40° C. and range up to about 80° C. or 90° C.

A preferred method for extracting the nickel from the bioleach solution and at the same time increase its concentration is by absorbing the nickel in a resin specifically selective to the absorption of nickel.

The preferred resin is one in which the active ingredient is bis-picolyamine. Such resins are produced by Dow Chemical under the trade names Dow XPS 4195, Dow XPS 4196 and Dow XPS 43084. We have found that these resins are particularly attractive not only for metal recovery but also for metal separation, such as the separation of nickel from cobalt and ferric and ferrous iron.

Conventional bioleaching for metal recovery, unlike the present invention, requires the use of low solids concentration in bioleach reactors in that too high a metal concentration in the bioleach solution adversely affects bacterial activity.

Generally speaking, the nickel-containing bioleach solution is subjected to resin absorption to selectively remove the nickel from the solution. Thus, the solution may be passed through a bed of one of the aforementioned Dow resins, e.g. XPS 4195, or the nickel extraction can be effected by employing the resin-in-pulp method which comprises grinding the ore or concentrate to a particular size smaller than the size of the resin employed (from 20 mesh to 50 mesh), blending the resin with ore and micro-organisms containing solution or concentrate, maintaining the slurry mixture in suspension for a predetermined amount of time, finally screening the coarser resin from the leach residue.

The nickel loaded resin is then stripped with a mineral acid, e.g., sulfuric acid. The amount or volume of sulfuric acid used should be sufficient to provide a concentration of nickel corresponding to about 10 gpl to 25 gpl. Electrolysis is a preferred method of recovering substantially pure nickel.

As illustrative of the invention, the following examples are given:

EXAMPLE 1

A lateritic ore analyzing 2.2% Ni, 10% Mg, 18% Fe and 30% SiO₂ is subjected to bioleaching by employing a

micro-organism which systematically produces a carboxylic acid selective to complexing the nickel in the ore.

The ore is slurried in an aqueous nutrient solution containing the nutrients 100 gpl sugar, 1.2 gpl NH₄H₂PO₄, 0.5 gpl KCl, 0.5 gpl MgSO₄·7H₂O in the presence of the fungi *Aspergillus Niger* at a pulp density of about 30% for about 120 hours. The fungus systematically produces the carboxylic acid citric acid which complexes the nickel to produce nickel citrate.

When the term "nutrient" is used with respect to the bacteria or fungi disclosed herein and other micro-organisms employed in bioleaching, it is to be understood that its meaning is well known to those skilled in the art as to the conventional nutrients employed.

Following the bioleaching of the lateritic ore, the bioleach slurry obtained is separated into a solid leach residue and an aqueous nickel containing solution.

The aqueous nickel-containing solution is thereafter contacted with a resin having the active ingredient bis-picolyamine dispersed therethrough by using any of the known methods of recovering elements from solution by ion exchange (fixed bed ion exchange, continuous counter current ion exchange, short bed reciprocating flow or the carousel method).

The foregoing method of bioleaching the ore may also be carried out by heap leaching wherein the bioleach solution is caused over a period of time to trickle gravimetrically through the interstices of the heap and the effluent thereof recycled to the heap, if necessary.

Vat leaching may also be employed wherein the ore is placed into a large vat and saturated with the bioleach solution which reacts with the nickel-containing ore over a prolonged period of time to effect dissolution of the nickel in the ore.

After a determination has been made that a substantial amount of nickel has been dissolved, the pregnant nickel solution is clarified, e.g., by filtering, and the clarified nickel solution then contacted with an ion-exchange resin specific to the absorption of nickel, the resin being one containing bis-picolyamine as the active ingredient as described hereinbefore.

EXAMPLE 2

A nickel-containing sulfidic ore or concentrate of the form pentlandite (Ni, Fe)₉S₈ in which cobalt may replace some of the nickel, and analyzing 0.5% to 12% Ni, 0.2% to 0.8% Co, 28.0 to 54% Fe, 21% to 34% S, 3.0% to 13% SiO₂, the balance gangue material is subjected to bioleaching by employing micro-organisms which enhance the selective solubilization of nickel by utilizing the energy derived from the electrochemical oxidation of sulfur to sulfate and ferrous to ferric iron for their metabolic functions.

The ore is slurried in an aqueous nutrient solution containing 0.8 gpl (NH₄)₂SO₄, 0.4 gpl KH₂PO₄, and 0.16 gpl MgSO₄·7H₂O in the presence of mesophilic thiobacillus type bacteria (35° C.), such as one or more of moderate thermophiles, TH3 (45° C.), and extreme thermophiles, *Acidilobus Brierleyi* (65° C.) and *Sulfobolus acidocaldarius* (85° to 90°). The pH of the slurry is initially adjusted to about 1.8 with sulfuric acid. The slurry may or may not contain resin at this stage.

Following the bioleaching of the nickel-bearing sulfidic ore, the slurry is separated into a solid leach residue and an aqueous nickel-containing solution. Where resin is present in the slurry, i.e., resin in pulp (RIP), the slurry is separated

into solid leach residue, a nickel-loaded resin, and a barren nickel-free solution.

Following solid-liquid separation, the resin is stripped with a mineral acid to obtain a pregnant solution containing about 10 to 25 gpl nickel such as nickel chloride, nickel sulfate and nickel nitrate, depending on the acid used.

The following nickel extraction data were experimentally obtained as follows:

Leaching Time - days	Nickel Dissolution (%)			
	Nickel Dissolution		Solution Concentration ⁽²⁾	
	Nickel Ore ⁽¹⁾	Nickel Concentrate ⁽²⁾	Nickel grams/liter	Iron grams/liter
0	0	0	0.05	0.20
3	8	6	0.41	1.06
7	14	33	2.10	0.98
10	17	60	3.80	5.06
14	27	79	5.00	5.99
17	37	87	5.50	6.06

⁽¹⁾Nickel Ore: Ni 0.59%, Co 0.17%, Fe 54%, S 34.4%, Si 1.4%

⁽²⁾Nickel Concentrate: Ni 12.3%, Co 0.17%, Fe 27%, S 21.2%, Si 6.1%

Although the present invention has been described in conjunction with preferred embodiment. It is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

What is claimed is:

1. A bioleaching method of recovering nickel from an ore selected from the group consisting nickel-containing lateritic ores and nickel-containing sulfidic material which comprises:

where the ore selected is a nickel-containing lateritic ore, at least one micro-organism selective to the leaching of the lateritic ore is added to an aqueous slurry thereof maintained at a pH ranging from about 1 to 3 including a nutrient for said micro-organism;

said at least one micro-organism used in leaching said lateritic ore being a fungi that systemically produces a carboxylic acid conducive for chelating the nickel in the ore and thus produce a solution containing nickel;

where the ore selected is a nickel-containing sulfidic ore or a concentrate thereof, at least one micro-organism comprising an ore biooxidizing bacterium selective to the leaching of sulfidic ore is added to an aqueous slurry of said sulfidic ore maintained at a pH of about 1 to 3 including a nutrient for said bacterium;

the biooxidation of said ore being effected by using at least one bacterium selected from the group consisting of *Thiobacillus thiooxidans*, *Thiobacillus ferrooxidans*, *Leptospirillum* species, *Sulfobacillus*, *thermosulfidooxidans* or similar species, *Sulfolobus brierleyi*, *Sulfolobus acidocaldarius*, *Sulfolobus* BC and *Sulfolobus sulfataricus*;

bioleaching a slurry of said selected ore for a time sufficient to effect the dissolution of said nickel in said ore and form a pregnant solution thereof and a residue; separating said nickel solution from said residue;

contacting said separated nickel solution with an ion exchange resin containing as an active ingredient bis-picolylamine specific to the absorption of said nickel and thereby form a nickel loaded resin;

extracting said absorbed nickel from said resin by contacting said resin with a mineral acid solution; and recovering said nickel from said mineral acid solution.

2. The method of claim 1,

wherein the carboxylic acid systemically produced by said fungi bacterium is selected from the group consisting of citric, tartaric, pyruvic, oxalic, lactic, glycolic and malonic acids.

3. The method of claim 1, wherein the micro-organism used in treating the lateric ore is selected from the group consisting of the fungi *Aspergillus Niger*, *Penicillium Aspergillus* Sp., *Penicillium Simplicissimus* and the bacteria *Enterobacter* Spp., *Bacillus* Spp. and *Achromobacter* Spp.

4. The method of claim 3 wherein said fungi is *Aspergillus Niger*.

5. The method of claim 1, wherein the ion exchange resin containing bis-picolylamine as an active ingredient is added in a particulate form to the leach slurry to produce thereby a nickel loaded resin, and the particulate nickel-loaded resin then removed from the slurry by screening.

6. A bioleaching method of recovering nickel from an ore selected from the group consisting nickel-containing lateritic ores and nickel-containing sulfidic ores which comprises:

where the ore selected is a nickel-containing lateritic ore, at least one micro-organism selective to the leaching of the lateritic ore is added to an aqueous slurry thereof maintained at a pH ranging from about 1 to 3 including a nutrient for said micro-organism;

said at least one micro-organism used in leaching said lateritic ore being a fungi that systemically produces a carboxylic acid conducive for chelating the nickel in the ore and thus produce a solution containing nickel;

where the ore selected is a nickel-containing sulfidic ore or a concentrate thereof, at least one micro-organism comprising an ore biooxidizing bacterium selective to the leaching of sulfidic ore is added to an aqueous slurry of said sulfidic ore maintained at a pH of about 1 to 3 including a nutrient for said bacterium,

said at least one bacterium being selected from the group consisting of *Thiobacillus thiooxidans*, *Thiobacillus ferrooxidans*, *Leptospirillum* species, *Sulfobacillus*, *thermosulfidooxidans* or similar species, *Sulfolobus brierleyi*, *Sulfolobus acidocaldarius*, *Sulfolobus* BC and *Sulfolobus sulfataricus*;

forming a heap of said selected ore or concentrate, bioleaching said heap by passing a solution containing said microorganism gravimetrically through said heap for a time sufficient to effect the dissolution of said nickel in said ore and form a pregnant solution thereof; collecting said pregnant nickel solution following heap leaching;

contacting said pregnant nickel solution with an ion exchange resin containing as an active ingredient bis-picolylamine specific to the absorption of said nickel and thereby form a nickel loaded resin;

extracting said absorbed nickel from said resin by contacting said resin with a mineral acid solution; and recovering said nickel from said mineral acid solution.

7. The method of claim 6,

wherein the carboxylic acid systemically produced by said fungi is selected from the group consisting of citric, tartaric, pyruvic, oxalic, lactic, glycolic and malonic acids.

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8. The method of claim 6, wherein the micro-organism used in treating the lateritic ore is selected from the group consisting of the fungi *Aspergillus Niger*, *Penicillium Aspergillus* Sp., *Penicillium Simplicissimus* and the bacteria *Enterobacter* Spp., *Bacillus* Spp. and *Achromobacter* Spp. 5

9. The method of claim 8 wherein said fungi is *Aspergillus Niger*.

10. A bioleaching method of recovering nickel from an ore selected from the group consisting nickel-containing lateritic ores and nickel-containing sulfidic ores which comprises: 10

where the ore selected is a nickel-containing lateritic ore, at least one micro-organism selective to the leaching of the lateritic ore is added to an aqueous slurry thereof maintained at a pH ranging from about 1 to 3 including a nutrient for said micro-organism; 15

said at least one micro-organism used in leaching said lateritic ore being a fungi that systemically produces a carboxylic acid conducive for chelating the nickel in the ore and thus produce a solution containing nickel, 20

where the ore selected is a nickel-containing sulfidic ore or a concentrate thereof, at least one micro-organism comprising an ore biooxidizing bacterium selective to the leaching of sulfidic ore is added to an aqueous slurry of said sulfidic ore maintained at a pH of about 1 to 3 including a nutrient for said bacterium which comprises: 25

said at least one bacterium being selected from the group consisting of *Thiobacillus thiooxidans*, *Thiobacillus ferrooxidans*, *Leptospirillum* species, *Sulfobacillus thermosulfidooxidans* or similar species, *Sulfolobus brierleyi*, *Sulfolobus acidocaldarius*, *Sulfolobus* BC and *Sulfolobus sulfataricus*; 30

forming a charge of said ore in the particulate state in a vat; 35

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bioleaching said charge of ore in said vat by saturating said charge with the bioleach solution for a residence time sufficient to effect the dissolution of said nickel in said ore and form a pregnant solution thereof and a residue;

separating said pregnant nickel solution from said residue;

contacting said separated nickel solution with an ion exchange resin containing as an active ingredient bis-picolylamine specific to the absorption of said nickel and thereby form a nickel loaded resin;

extracting said absorbed nickel from said resin by contacting said resin with a mineral acid solution;

and recovering said nickel from said mineral acid solution.

11. The method of claim 10,

wherein the carboxylic acid systemically produced by said fungi is selected from the group consisting of citric, tartaric, pyruvic, oxalic, lactic, glycolic and malonic acids.

12. The method of claim 10, wherein the micro-organism used in treating the lateritic ore is selected from the group consisting of the fungi *Aspergillus Niger*, *Penicillium Aspergillus* Sp., *Penicillium Simplicissimus* and the bacteria *Enterobacter* Spp., *Bacillus* Spp. and *Achromobacter* Spp. 25

13. The method of claim 12 wherein said fungi is *Aspergillus Niger*.

14. The method of claim 10, wherein the ion exchange resin containing bis-picolylamine as an active ingredient is added in a particulate form to the pregnant nickel solution to produce thereby a nickel loaded resin, and the particulate nickel-loaded resin then removed from the slurry by screening.

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AB - AU9517751 The process for removing arsenic impurities from nickel concentrates comprises roasting in an inert atmosphere under process conditions which facilitate the removal of the arsenic while preventing back reaction with calcium contained in the gangue minerals present in the nickel concentrate, providing material suitable for smelting.

- PREFERRED METHOD - The inert atmosphere comprises nitrogen or an oxidising atmosphere rendered inert by reaction with sulphur in the concentrate. Back reaction of the arsenic with calcium is prevented by the evolution of bound water and sulphur from the gangue minerals in the concentrate, being further assisted by using a purge gas to remove the evolved arsenic.

- USE - The removal of arsenic impurities from nickel concentrates provides material suitable for smelting.

- ADVANTAGE - The process reduces the level of arsenic in the material from 1.0 wt.% to 200-300 ppm. This is achieved by preventing the back reaction of the arsenic with calcium in the concentrate by using suitable heating conditions.

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IW - REMOVE ARSENIC NICKEL CONCENTRATE SMELT MATERIAL ROAST CONCENTRATE
INERT ATMOSPHERE PREVENT BACK REACT CALCIUM

IKW - REMOVE ARSENIC NICKEL CONCENTRATE SMELT MATERIAL ROAST CONCENTRATE
INERT ATMOSPHERE PREVENT BACK REACT CALCIUM

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TI - Removing arsenic from nickel concentrates to provide smelting material
- by roasting concentrate in inert atmos. preventing back reaction
with calcium

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(54) Process for the recovery of metals from their ores.

(57) A process for the recovery of metals from host materials, where the metal is present in the form of a compound which is more absorbent to microwaves than the rest of the host material. Microwave energy is used to selectively heat the metal compounds, such as sulfidic and oxidic compounds, in the ore, as respects the gangue, under conditions in which the compounds are converted into other compounds, such as oxides and chloride, from which the metal is more readily recoverable. Copper molybdenum and rhenium ores can be treated in this way.

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PROCESS FOR THE RECOVERY OF METALS FROM THEIR ORES

The present invention relates to a process for the recovery of a metal from a host material.

Recovery of metals from low-grade ore deposits can be very expensive due to the large amounts of rock which must be mined transported and treated. Conventional recovery processes may not be economically viable in these cases. For example an established method of recovering metal values from such low grade deposits has involved mining the deposits and then grinding the ore to a fine size to permit floating the liberated minerals. The grinding also produces some very fine particles of the ore which are too fine to be recoverable by flotation. This is particularly true in the case of very soft ores such as molybdenite.

Certain ores, such as oxides or silicates of copper are not amenable to flotation, and so the ore is often leached with acids to recover the copper. However, such acid leaching is not effective in recovering highly insoluble copper sulfide which may also be present and is in general susceptible to only a very poor recovery of the copper. The concentrates obtained from flotation steps may require further treatment for example by smelting or roasting to obtain the metal values and these are problems associated with these treatments.

For example molybdenite once recovered is converted to molybdenum oxide by roasting it in the presence of oxygen which may be supplied by air. In the course of the roasting a great deal of heat is generated because of the exothermic reactions producing molybdenum trioxide and sulfur dioxide. Additional or excess air over that required for oxidation is frequently used during the

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roasting to cool the burning mass to prevent it from becoming so that that it fuses, or that the molybdenum oxide volatilizes.

During the roasting of molybdenite, rhenium which may be present with the molybdenum is oxidized and at the temperature of roasting becomes volatile. Given the large volumes of gases emitted by burning organic feeds to initiate the roasting, the large volumes of sulfur dioxide from the roasting and the large volumes of air needed to cool the reaction, the recovery of this valuable rhenium is difficult and expensive.

In roasting of molybdenite, the molybdenum oxide being formed tends to coat the as yet unreacted molybdenite and form an insulating layer which inhibits further reaction. As the heat and oxygen necessary to reaction must pass through this layer, it is difficult to obtain a complete roasting of the molybdenite.

Various processes in which metal compounds contained in ores are converted to other more readily recoverable compounds have been proposed.

It is an object of the invention to provide a process for the economical recovery of metals from host materials such as low grade ore deposits.

According to the invention, there is provided a process for the recovery of a metal from a host material wherein the metal is present in the form of a first compound and the host material is less absorbent to microwaves than said first compound, characterized in that the process comprises subjecting the host material and first compound to microwave energy under conditions in which the first compound can be converted to the metal or to a second compound which is more readily recoverable from the host material.

By the use of microwaves, one can selectively heat the metal values for example copper (whether oxidic or sulfidic) or sulfidic molybdenum or rhenium without the necessity of heating the whole rock mass, because the gangue is substantially transparent to microwave radiation while the aforementioned metal values are very effective in absorbing the microwaves.

Microwave energy is used in processes requiring heat to recover for example copper from its oxidic or sulfidic ore and to recover molybdenum and rhenium from their sulfidic ore. The microwave energy is used in processes known to the art in place of conventional heat sources thereby causing very rapid chemical reactions with substantial energy savings. Because the microwaves heat and activate primarily the metal component of the ore and not the gangue, they are useful for treating lower grades of ore than could be ordinarily economically treated.

The effects of microwaves on metal values contained with ores does not appear to be related in any predictable way to the chemical or physical properties of such metal values. For example, it has been found that copper in its oxide, sulfide or silicate forms is very susceptible to heating by microwaves of 915 megahertz or 2450 megahertz, whereas zinc oxide or sulfide does not respond, or responds only slightly. Likewise, it has been found that the sulfides of molybdenum and rhenium absorb microwaves. It has also been found that nickel, cobalt and manganese oxides absorb microwaves, but the oxides of iron and chromium, which are transition metals, do not absorb microwaves.

Therefore the process can be applied to copper ores

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in the form of sulfides such as chalcopyrite; bornite, chalcocite and covellite, or oxides such as cuprite or tenorite, the hydroxy carbonates such as malachite or azurite, or as the silicates such as chrysocolla, or to molybdenum ores containing molybdenum disulfide or molybdenite.

In the treating of copper sulfide ores or concentrates, the ore or concentrate may be heated by microwaves in the presence of oxygen either as a pure gas or diluted as in air. The microwaves may be applied to heat the copper sulfides sufficiently in the presence of oxygen to convert them to sulfates (a "sulfation roast", well known in the art), or to heat the sulfides sufficiently to produce the oxide and sulfur dioxide. Heating to produce the sulfate is preferred as requiring less energy.

The copper, now as a water soluble sulfate or acid soluble oxide, can be leached and recovered. As an example, it might be recovered from the water leach by solvent extraction and then stripped with sulfuric acid, and electrowon. The use of organic solvents to extract copper and the electrowinning of the extracted copper is well known and practiced commercially. Heretofore, however, there was no practical means to convert the copper sulfides to soluble sulfates without expending an excessive amount of energy. It was necessary either to grind the ore to liberate the copper sulfides, float to a concentrate and then roast the ore, or use an excessive amount of heat to heat the whole ore, both desired mineral and gangue, to reaction temperature.

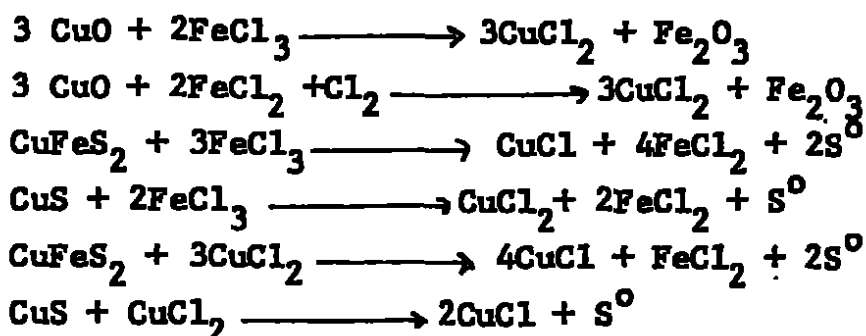
In the conventional grinding and flotation of copper sulfide ores, a portion of the ore reports to slimes which can be finer than 10 microns and very difficult or impossible

to recover by flotation. These slimes can readily be separated by cyclones and other physical means, but the resulting sulfide concentrate is too low grade to be recovered conventionally. Because the microwaves used will selectively heat all the copper sulfides to a temperature where they will be converted by a flow of oxygen to sulfates or oxides which are water or acid soluble, the problem of fine grains of ore reporting to the slimes is eliminated and it becomes practical to recover the copper from such concentrates.

An alternative to the oxidation of copper sulfide concentrates is the chlorination of sulfide and oxide ores. Frequently, large copper sulfide ore bodies are overlain by mixed copper oxide-copper sulfide ores in which the copper is difficult to recover. Such ores, when heated with a chlorine ion donor such as ferric chloride or cupric chloride to a sufficient temperature in the absence of air, can be converted to copper chlorides which are water soluble and from which the copper can be recovered by techniques which are well known. Heretofore the expense of heating the whole rock mass was considered too great for an economic recovery of the copper. These types of ores and such oxidic ores as malachite, azurite and chrysocolla lend themselves to recovery by blending the ore with a source of chloride ion such as chlorine gas, ferrous chloride or ferric chloride, cuprous chloride or cupric chloride, and drying. The dried copper mineral and chloride ion source are then irradiated with microwaves in the absence of air, and if ferrous or cuprous chloride is used, in the presence of chlorine. The microwaves heat the copper minerals to reaction temperature, forming water

soluble or brine soluble chlorides.

The reactions may be illustrated as follows:



Where molybdenite and rhenium sulfide occur with a silicate gangue, the microwaves selectively heat the molybdenite and rhenium sulfide to a temperature where roasting with air or oxygen produces molybdenum and rhenium oxides and sulfur dioxide. Because the microwaves are selective for the sulfides, it is not necessary to heat the entire mineral mass to roasting temperature.

The formed molybdenum and rhenium oxides are then conveniently recovered by leaching with ammonia or with caustic soda, and then treated by well known processes to precipitate molybdenum and rhenium compounds. Alternatively, the molybdenite and rhenium sulfide can be chlorinated to molybdenum and rhenium chlorides which are volatile by selectively heating them in their ores in the presence of chlorine. Again, because only the molybdenite and rhenium are heated by the microwaves, the whole gangue mass does not have to be heated. The chlorination reaction has a preferred temperature of at least about 600°C. This is readily achieved with the microwaves.

In roasting of a molybdenite concentrate the molybdenite can be brought to roasting temperature by the use of microwaves. This obviates the need for combustion

of fuel to supply heat and thereby permits a more closely controlled roast and one in which the total gases produced are less. Because the microwaves pass through the transparent molybdenum oxide as it is formed and heat the molybdenum sulfide, the fact that there are oxide coatings does not inhibit the reaction and a more complete roasting can be accomplished in a shorter time. The thermal difference between the heated molybdenum sulfide and the unheated molybdenum oxide is sufficient to destroy the continuity of the oxide coating.

Inasmuch as the molybdenite and rhenium sulfide are heated internally by the microwaves, it is not necessary to grind ore so fine that the particles are liberated. It is sufficient that a surface be exposed so that the roasting conversion to molybdenum and rhenium oxides or the chlorination reaction to molybdenum and rhenium chlorides can occur. The removal of the necessity for fine grinding can greatly decrease the overall energy required for the recovery of molybdenum and rhenium.

Processes embodying the invention will now be particularly described by way of example.

The process is applicable to the treatment of sulfides or oxidic (including oxides, hydrocarbonates and silicates) minerals of copper and to treatment of sulfitic minerals of molybdenum and rhenium in the presence of oxygen or chlorine.

It is preferred that the ore or concentrate of copper be crushed so that it is readily handled in the microwave reacting unit. It is not necessary that the ore or concentrate be finely ground. Generally, with respect to a copper ore, grinding to 1/2 inch or finer is satisfactory. It is preferred that the molybdenum and rhenium ores be ground to a size of 12 mesh or smaller so that the indi-

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vidual particles of molybdenite and rhenium sulfide have at least one surface exposed to the gases to be used for reaction.

It is preferred that the ore or concentrate be dried by conventional means prior to the microwave reaction. Water is an excellent absorber of microwaves and can readily be removed by microwave irradiation, but this is an expensive means of removing water and if there are substantial amounts present, it may be preferable to remove it by conventional means. However, where only a little water is present or where there is insufficient water present to justify its separate removal, it can be removed in the course of the microwave irradiation.

In a sulfation roast where copper sulfides are converted to copper sulfates, it is preferred to irradiate with microwaves for a sufficient time to heat the sulfide minerals to temperatures of between 350°C and 700°C. At higher temperatures there is a tendency for copper iron oxide ferrites to form which are soluble only with difficulty. Air or oxygen can be used as the source of oxygen. Generally, irradiation times of less than 15 minutes will be sufficient to raise the copper sulfide particles in the ore or concentrate to reaction temperatures, although the precise time of irradiation will depend upon the power of the microwave source and the precise nature of the gangue associated with the copper sulfide. The time must be sufficient to convert substantially all of the copper metal value to soluble compounds.

Following irradiation of the copper sulfide, the ore or concentrate may be leached with water or with acidified water to dissolve any copper oxides as well as the copper

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sulfate formed. The soluble copper may be recovered by solvent extraction and electrowinning.

In a chlorination reaction it is preferred to treat the ore or concentrate with a ferrous chloride solution containing sufficient ferrous chloride so that there will be at least a stoichiometric quantity of ferrous chloride which will convert to ferric chloride in the presence of chlorine gas and react with the copper minerals present. The ore or concentrate can then be dried. It is not necessary to dry completely nor to remove the water of hydration associated with the ferrous chloride. Alternatively one may use cuprous chloride and chlorine gas, although ferrous chloride is preferred. Also, alternatively, one may use ferric chloride in place of the ferrous chloride and chlorine. If ferric chloride is used, it is preferred to blend the dry ferric chloride with the dry ore prior to irradiation. The ore and reagents are then reacted by being heated by the microwave radiation. It is preferred that temperatures of the copper mineral be at least 300°C for all reactions except the sulfation roast. The mass of the gangue will of course not reach such temperatures. The time of irradiation will depend upon the power of the microwave source and the gangue minerals present, but in general will be shorter than 10 minutes.

Microwave heating can be used to selectively heat the molybdenite and rhenium sulfide to reaction temperature in the presence of chlorine to produce molybdenum and rhenium chloride and elemental sulfur. The operative temperature for this reaction is at least 300°C and 600°C

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is preferred. After chlorination, the molybdenum and rhenium chlorides can be processed by known means such as hydrogen reduction to produce the metals, or by reaction with water and ammonia or caustic to produce the oxides. The reaction time for either roasting or chlorination will depend upon the grade of the material being treated. Very low grade feeds will have a certain amount of heat loss to the surrounding gangue by conduction away from the heating molybdenum and rhenium sulfides. There will be a proportionately small heat loss from the exothermic oxidation and chlorination reactions. The sulfides in very low grade materials will generally be converted in 15 minutes, and in high grade material in 3 to 5 minutes. Because of the high speed of reaction in the microwave field, equipment size is minimal and great capital savings result.

In the roasting of molybdenite, zones of microwave energy can be advantageously used to provide additional heat to the molybdenite, which is almost completely roasted, carrying the reaction to completion. It is possible to combine the useful effects of microwave heating with conventional processes.

The following examples illustrate the process and principles employed therein.

Example 1

The following materials were all irradiated with microwave radiation of 2450 megahertz. Samples weighing 25 grams were irradiated for 6 minutes at power levels of 300 watts. Water was used as a ballast to prevent excess heating of the microwave source because of the poor

absorption of some of the material. The temperature was measured as quickly as possible after irradiation.

<u>Material</u>	<u>Temperature °C after 6 minutes irradiation</u>
Sand	36
Iron Oxide	34
Sphalerite	34
Zinc Oxide	38
Cupric Oxide	195
Chalcopyrite	324
Bornite	>600
Chalcocite	124
Chrysocolla	108
Covellite	244

It is seen from the above results that zinc sulfide and the oxides of zinc and iron are not appreciably heated, while the oxides, sulfides and silicates of copper are. It is also noted that sand, which is representative of the host material for the copper minerals, is not appreciably heated.

Example 2

Twenty-five gram samples of the following materials were irradiated 6 minutes at 915 megahertz and a power level of 250 watts. Water was present as a ballast to prevent damage to the microwave source because of the poor adsorption of some of the materials. As soon as possible after irradiation the temperature of the material was measured showing the relative absorption of the microwave energy.

<u>Material</u>	<u>Temperature °C after 6 minutes irradiation</u>
Sand	29
Iron Oxide	28
Sphalerite	34
Zinc Oxide	29
Lead Oxide	32
Cupric Oxide	70
Chalcopyrite	58
Bornite	73

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Chalcocite	42
Chrysocolla	46
Covellite	79

The results show that the oxides, sulfides and silicates of copper are significantly more absorbent to microwaves than sand, the oxides of iron, zinc and lead and the sulfide ore of zinc.

Example 3

A mixed copper oxide-copper sulfide ore from the oxidized zone of the large porphyry copper ore body contained 1.6 percent copper. Fifty-three percent of the copper was present as copper oxides and 47 percent of the copper was present as copper sulfides. A 113.4 gram sample of this copper ore, crushed to minus 1/2 inch but not ground, was put in a container having a flow of oxygen and subjected to 600 watts of 2450 megahertz radiation for 15 minutes. Sulfur dioxide was noted in the off-gases. The residue was leached with sulfuric acid and water at pH 1.0. Sixty-one percent of the copper was found to be soluble.

Example 4

A 120 gram sample of the ore of Example 3 was blended with 11 grams of concentrated sulfuric acid and 3 grams of iron as ferrous chloride. It was irradiated for 10 minutes with 600 watts of 2450 megahertz radiation under a chlorine atmosphere. After cooling, the reaction mass was leached with a brine solution. Eighty-six percent of the copper was soluble.

Example 5

A 94 gram sample of the ore of Example 3 was ground to minus 30 mesh and then was blended with 11 grams of concentrated sulfuric acid and 3 grams of iron as ferrous chloride, and dried. It was irradiated for 10 minutes

with 600 watts of 2450 megahertz radiation. When cool, it was leached for 30 minutes with a brine leach at pH 2.2. Ninety-six percent of the copper was soluble.

Example 6

Fifty grams of a mixed copper oxide-copper sulfide ore in which 85 percent of the copper is oxidic and the copper content is 0.77 percent was blended with 5.4 grams of the sulfuric acid and 3 grams of iron as ferrous chloride. The blend was dried and ground to minus 20 mesh. Under a chlorine atmosphere it was reacted for 3 minutes with 600 watts 2450 megahertz radiation. It was then water leached for 1/2 hour at pH 1.9 and 90 percent of the copper was water soluble.

Example 7

One-hundred grams of a porphyry copper ore containing 0.6 percent copper principally as chalcopyrite was ground to minus 12 mesh. Under a flow of oxygen it was irradiated at 600 watts with 2450 megahertz radiation for 20 minutes. It was then leached for 30 minutes with acidified water to pH 1.0 at room temperature. Forty-two percent of the copper was water soluble.

Example 8

One hundred grams of a porphyry copper ore containing 0.6 percent copper, principally a chalcopyrite, was ground to minus 12 mesh. One gram of iron was blended as ferrous chloride. The blend was dried and under a chlorine atmosphere was irradiated for 6 minutes at 600 watts of 2450 megahertz radiation. The cooled solids were leached with a brine water solution for 30 minutes. Ninety-one percent of the copper was brine soluble.

Example 9

Twenty-five grams of a chalcopyrite copper concentrate containing 20 percent copper was blended with 5 grams of

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iron as ferrous chloride and dried. A blend of inert gas and chlorine was used to chlorinate the chalcopyrite during the microwave irradiation. To prevent excessive temperatures, the irradiation was on for one minute and off for three minutes. The irradiation was on for nine minutes at 300 watts and finally two minutes at 600 watts over a time span of 40 minutes. The cooled reaction mass was leached with water with a little peroxide to oxide cuprous to cupric chloride. Ninety-six percent of the copper was dissolved.

Example 10

The following materials were all irradiated with microwave radiation of the indicated wavelength and at power levels of 600 watts for the 2450 megahertz radiation. Water was used as a ballast to prevent over-heating of the microwave generator where the adsorption of radiation was slight. The radiation was continued for 6 minutes and then the temperature of the substance was measured as quickly as possible to determine the relative absorbence of the microwave energy.

<u>Substance</u>	300 watts
	<u>2450 megahertz</u> <u>Temp °C</u>
Sand	36
Iron Oxide	34
Zinc Sulfide	34
Molybdenite	212
Rhenium Sulfide	162
Molybdenum Oxide	33

It is seen from the above results that molybdenum and rhenium sulfides strongly absorb microwaves, while sand, iron and molybdenum oxides and zinc sulfide do not appreciably absorb microwaves.

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Example 11

The following materials were all irradiated with microwaves of 915 megahertz and at a power level of about 280 watts for 6 minutes. Water was used as a ballast to prevent the overheating of the generator.

<u>Material</u>	<u>Temperature Increase °C</u>
Sand	11
Iron Oxide	10
Zinc Sulfide	14
Molybdenite	25
Rhenium Sulfide	28
Molybdenum Oxide	11

As may be noted, molybdenum and rhenium sulfides are better absorbers of the radiation than the other materials tested.

Example 12

A molybdenite mine rock waste which was too low grade for recovery of molybdenum by conventional practice, assaying 0.054 percent molybdenum, was ground to minus 14 mesh. The minus 48 mesh fraction was 24.1 percent of the weight, assayed 0.094 percent molybdenum, and represented 40 percent of the molybdenum in the head sample. Fifty grams of this minus 48 mesh material was blended with 0.5 grams of iron as ferrous chloride and one gram of potassium chloride. The sample was dried. It was irradiated for six and one-half minutes with 600 watts of 2450 megahertz radiation in a chlorine atmosphere. Fifty-five percent of the molybdenum was found to be soluble in dilute acid, leaving a tailing assaying only 0.041 molybdenum.

Example 13

A flotation reject which assayed 6 percent molybdenum was subjected to a flow of oxygen and 2450 megahertz radiation for 15 minutes. The mass was allowed to cool and was leached with caustic at pH 13. Sixty-five percent

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of the molybdenum was found to have been roasted and to be soluble.

Example 14

One hundred grams of a commercial molybdenite concentrate assaying 53 percent molybdenum was de-oiled by irradiating with 600 watts of 2450 megahertz radiation for 5 minutes. It was then subjected to a flow of oxygen and irradiated for 14 minutes to initiate the roasting reaction. Subsequently, the irradiation was periodically imposed in short pulses to return the unreacted molybdenite to reaction temperature as it cooled. The irradiation was on for 32 minutes over a two and one-half hour period. At the end of the roast 91 percent of the molybdenum was soluble in caustic.

Example 15

Five grams of a commercial molybdenite concentrate containing 53 percent molybdenum was irradiated at 300 watts and 2450 megahertz for 35 minutes in a flow of chlorine. The molybdenite was chlorinated. At the end of the reaction the small residue was leached with caustic to remove soluble molybdenum which had not been volatilized. The yield of volatile and soluble molybdenum was 92 percent.

Example 16

Five grams of a molybdenite concentrate rich in rhenium was irradiated in a flow of chlorine with 300 watts of 2450 megahertz radiation for 45 minutes. A caustic solution was used to scrub the gases leaving the reactor, and the residue was leached with caustic to pH 13. Molybdenum recovered in soluble form was 61 percent of the total molybdenum. Rhenium extraction was 99 percent of the total rhenium.

From the above examples, it is seen that the above described process is effective for the recovery of copper, molybdenum and rhenium from their ores, including ores too poor for the recovery of metals by conventional processes.

While the recovery of copper, molybdenum and rhenium from their ores have been particularly described, the process in accordance with the invention is by no means limited to these uses. It has been found that the process is equally effective for the recovery of nickel, cobalt, and manganese from their oxides and silicates wherein the source of heat is microwave energy and it is used alone to produce the metal or in conjunction with a reducing agent, such as, hydrogen gas or a chlorinating agent, such as, ferric chloride which serves as a chlorine donor. The reduced metals are recovered by conventional processes and metal values are recovered from the formed soluble chlorides by conventional processes.

In contrast, it has been found that the above described process is not operable for many ores in their host materials. For example, it has been found, as illustrated herein, that sphalerite and the oxide ores of zinc and iron are not appreciably heated over their host materials so that the process cannot be used to recover these metal values from these compounds in their host minerals. These examples are only illustrative of many combinations of host materials and ores upon which the process is probably not operative. It can however, as a generality, be said that the process is operable on any host material-ore combination in which the ore or compound containing the metal value is selectively heated over the host material by the microwave energy.

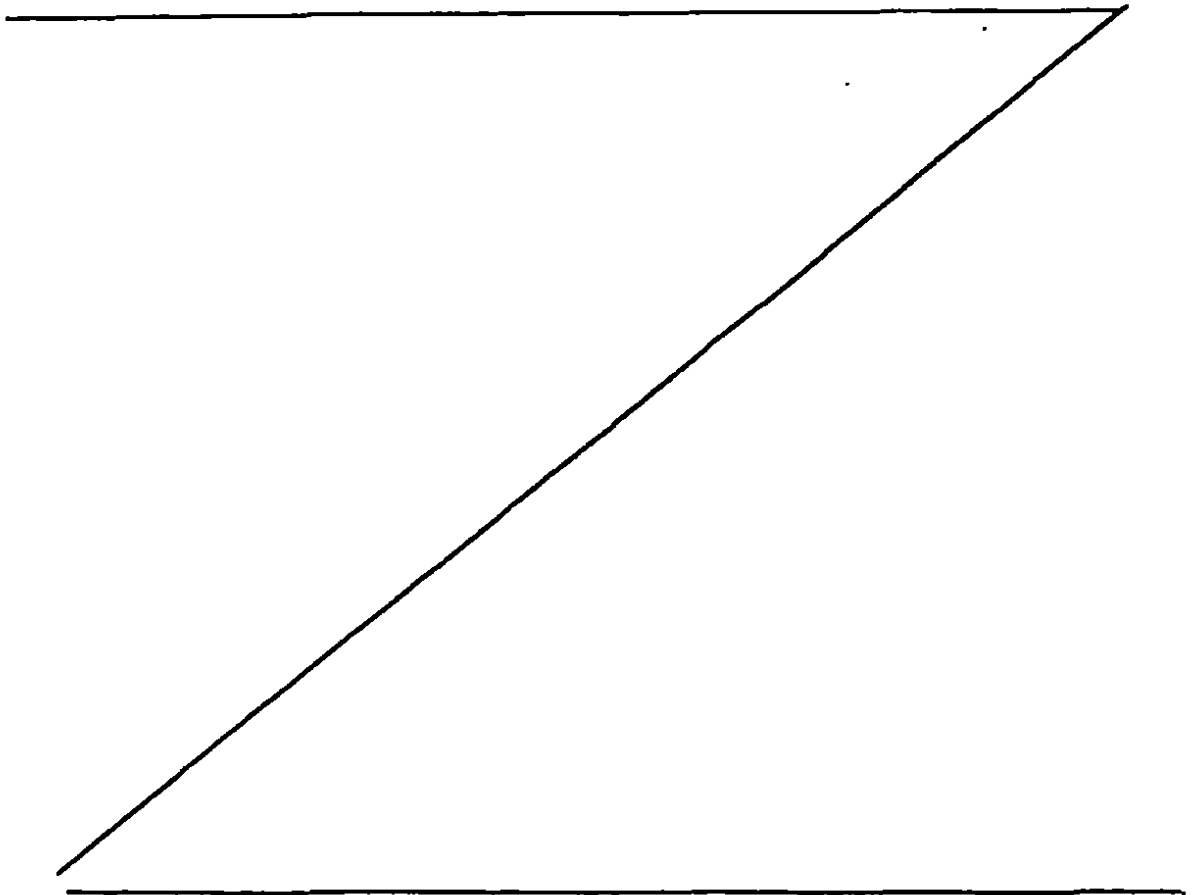
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The process can be used for the recovery of metals from mixtures of compounds of different metals in mineral gangues or host materials which are less absorbent to microwaves than the compounds.

The absorption of microwave energy by a given material is a complex function which varies with frequency, and therefore response will vary over a range of frequencies and with different materials. Lower frequencies are preferred. Microwaves of different frequencies may be used at the same time, or on the same batch. Energy should be applied for a sufficient time to convert substantially all of the metal compound in the ore to the required compound in the interest of efficiency.



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CLAIMS

1. A process for the recovery of a metal from a host material wherein the metal is present in the form of a first compound and the host material is less absorbent to microwaves than said first compound, characterised in that the process comprises subjecting the host material and first compound to microwave energy under conditions in which the first compound can be converted to the metal or to a second compound which is more readily recoverable from the host material.
2. A process according to claim 1, wherein the metal is copper, molybdenum or rhenium and the host material is a copper oxide ore, including a hydroxy carbonate or silicate form, or copper sulfide ore, molybdenum sulfide ore or rhenium sulfide ore respectively.
3. A process according to claim 2, wherein the ore is molybdenite, molybdenum disulfide, chalcopyrite, bornite, chalcocite, covellite, malachite, azurite, chrysocolla, cuprite or tenorite.
4. A process according to any one of the preceding claims wherein the first compound is a sulfide and is heated with microwaves to a temperature of at least about 300°C.
5. A process according to claim 4, wherein the sulfide is heated in the presence of oxygen to convert it to a sulfate or an oxide.

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6. A process according to claim 5, wherein the sulfide is copper sulfide and it is heated with microwaves to a temperature of from about 350°C to 700°C to convert it to copper sulfate.

7. A process according to any one of claims 1 to 4, wherein the host material and first compound are subjected to microwaves in the presence of a source of chlorine to convert the first compound to a chloride.

8. A process according to claim 7, wherein the first compound is rhenium sulfide or molybdenum sulfide and is heated with microwaves to a temperature of at least about 600°C.

9. A process according to claim 7, wherein the first compound is copper sulfide or copper oxide and is heated with microwaves to a temperature of at least about 300°C.

10. A process according to any one of claims 7 to 9, wherein the source of chlorine is chlorine gas, ferrous chloride, ferric chloride, cuprous chloride, cupric chloride or mixtures thereof.

11. A process according to claim 10, wherein ferrous chloride is added to the ore and the chlorination reaction is initiated by the addition of chlorine gas to promote the formation of ferric chloride.



European Patent
Office

EUROPEAN SEARCH REPORT

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Application number

EP 81 30 2495.7

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	<u>US - A - 2 177 070</u> (H. KIKUCHI) —		C 22 B 1/00 C 22 B 4/00
A	<u>DE - C - 891 231</u> (R. KÜRTH) —		
A,P	Patents Abstracts of Japan Vol. 4, No. 119, 23 August 1980, page 143C22		
A	& <u>JP - A - 55 - 76028</u> (7.6.80) —		
A,P	<u>US - A - 4 234 402</u> (C.G. KIRKBRIDE) —		TECHNICAL FIELDS SEARCHED (Int. Cl.)
A	ELEKTROTECHNIK UND MASCHINENBAU, Vol. 93, No. 9, September 1976, Wien E. BONEK "Industrielle Anwendungen von Mikrowellen" pages 371 to 378 —		B 01 J 19/12 C 22 B 1/00 C 22 B 4/00
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
X The present search report has been drawn up for all claims			A: member of the same patent family, corresponding document
Place of search	Date of completion of the search	Examiner	
Berlin	10-09-1981	SUTOR	

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METHOD IN CONNECTION WITH ROASTING, ESPECIALLY WITH SULPHATIZING OR CHLORIDIZING ROASTING

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Claims priority, application Finland, Apr. 13, 1966, 946/66

Int. Cl. C21b 1/02; C21b 1/06, 1/08
U.S. Cl. 75-7 5 Claims

ABSTRACT OF THE DISCLOSURE

A method in connection with roasting especially with sulphatizing or chloridizing roasting according to which after a suitable roasting time the processed material is removed from the roasting apparatus and the material is separated into two or more fractions in a suitable manner, so that for example one of the said fractions, the smaller one in quantity, contains mainly unreacted material, while the main part of the fully reacted material is contained in the other fraction. By returning only that fraction which contains mainly unreacted material back to treatment, the treatment time of the entire quantity can be considerably reduced.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to a method in connection with roasting especially with sulphatizing or chloridizing roasting and the object of the invention is to reduce considerably the treatment time for the material in roasting from what heretofore has been necessary.

Description of the prior art

In roasting of metal sulphides it is previously known that the different sulphides have different reaction velocities and therefore the total retention time for the material in the roasting furnace is determined by the slowest reacting sulphide which one may be only a small part of the total material to be roasted. Therefore by treating such sulphide mixtures the roasting apparatus has to be correspondingly large. As an example of the reaction velocity of the most common sulphides treated in this manner, reference is made to the following series in which the sulphides are put in sequence according to their reaction velocity starting with the highest velocity;



SUMMARY OF THE INVENTION

According to the principal characteristics of the present method after the roasting operation has been carried out the portion of the product that has reacted incompletely is separated from the material by utilizing physical separation methods known per se. The thus separated incompletely reacted portion is returned to the roasting operation. The fully reacted material is passed on for eventual additional treatment.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

According to the method of the invention, when carrying out roasting, e.g. in a fluidized bed furnace, the processed material is removed after a suitable reaction time. It is separated into two or more fractions in a suitable manner, with one of the said fractions, the smaller one in quantity, containing mainly unreacted material while the main portion of the reacted material is contained in the

other fraction. By returning the fraction containing mainly unreacted material back into the furnace for further treatment, the treatment time of the entire quantity can be considerably reduced.

The object of returning the fraction is accordingly to avoid increasing the treatment time for the main portion on which sufficient reaction results have already been reached just to sufficiently react the fraction.

In the separation of said slowly reacting or incompletely reacted components any conventional physical separation methods can be utilized, the selection of the method depending upon which method can be expected to give the best results.

The method of separation can be selected e.g. on the basis of the differences between the product to be removed and the portion to be returned. The portion to be returned can be separated as an individual portion by magnetic separation. It is sometimes necessary to carry out a grinding operation to make separation like this possible.

Magnetic separation in this case is possible because e.g. the completely roasted Fe_2O_3 particles are almost non-magnetic while the grains that are only partially roasted contain also magnetite Fe_3O_4 and innermost the sulphide FeS and are magnetic.

An example is the situation where the pyrite or pyrrhotite concentrate contains small amounts of Co, Ni, and Cu sulphides, say about 0.5 to 2% of the amount of the concentrate. In order to recover these materials a so called sulphatizing roasting is carried out, whereby with suitable conditions e.g. in a fluidized bed furnace, a soluble Cu-, Ni- and Co-sulphate can be produced, and can then be removed leaching.

It has been found that the sulphatizing of e.g. cobalt as stated above is slow and that during e.g. 4 hours about 80% of the cobalt is soluble, whereas to raise the solubility to the range of 90 to 95% requires a treating time of 10 hours or a time which is 2.5 times longer.

By carrying out a magnetic separation of the sulphatizing roasted product after 4 hours of process treatment a fraction was obtained amounting to between 5 and 7% of the total quantity and where the content of unreacted cobalt was at least equal to or greater than the material fed in.

By returning the obtained fraction it was possible with 4 hours' treatment time to reach the same amount of reacted cobalt, that before the separation required a treatment time of 10 hours, so that with this method it was possible to reduce the amount of cobalt in the leach residue at the same time maintaining the process treatment time short.

The magnetic separation can be carried out either immediately after the roasting, or e.g. in combination with a leaching, or on a finally washed product, which contains only insoluble components.

Which of these alternatives is applied depends on the requirements of the after treatment process and the possibilities the same gives in respect of the effectivity of the separation.

As already mentioned above, the separation method can be other than magnetic, such as an electrostatic separation, a flotation or the like, as long as it gives the desired result and depending on the characteristics of the roasted material, on the basis of which it is a simple task for persons skilled in the art to select the most suitable procedure.

What is claimed is:

1. A process for shortening of the treatment time and for raising the effective capacity of the apparatus employed in the sulphatizing or chloridizing roasting of sulfide or oxide ores including side metals which are changed into soluble sulfates and chlorides, which comprises,

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roasting a quantity of the material to be treated, terminating the roasting while a portion of the material remains in incompletely reacted state and after a shorter time period than required for completely reacting the whole of the material, separating the incompletely reacted portion of the material from the completely reacted portion thereof, returning the incompletely reacted portion to the roasting apparatus and subjecting the completely reacted portion to further treatment.

2. A method according to claim 1, comprising that the product is ground before the separation of the incompletely reacted portion.

3. A method according to claim 1, comprising that the separation is carried out as a dry or wet magnetic separation.

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4. A method according to claim 1, comprising that the separation is carried out electrostatically.

5. A method according to claim 1, comprising that the separation is carried out by flotation.

References Cited

UNITED STATES PATENTS

1,398,051	11/1921	Thom	209-8
2,785,050	3/1957	Swaine	75-9 XR
2,789,034	4/1957	Swaine	75-9 XR
2,943,929	7/1960	Norman	75-9

FRANK W. LUTTER, *Primary Examiner.*

U.S. Cl. X.R.

75-9; 209-4, 8, 11

United States Patent [19]
Flynn, Jr. et al.

[11] **Patent Number:** **4,888,207**
[45] **Date of Patent:** **Dec. 19, 1989**

[54] **RECOVERY OF ARSENIC FROM ORES AND CONCENTRATES**

[76] **Inventors:** Charles M. Flynn, Jr.; Thomas G. Carrahan, both of 1605 Evans Ave., Reno, Nev. 89512

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[22] **Filed:** Mar. 15, 1984

[51] **Int. Cl.⁴** C01G 28/00

[52] **U.S. Cl.** 423/87; 423/617

[58] **Field of Search** 423/87, DIG. 2, 617; 75/121

[56] **References Cited**

U.S. PATENT DOCUMENTS

1,952,290 3/1934 Shopper 423/87
2,939,467 11/1960 Yusuf 423/87
4,220,670 9/1980 Fuglsberg et al. 423/87
4,241,039 12/1980 Koh et al. 423/87

4,401,632 8/1983 Maden et al. 423/87
4,438,079 3/1984 Nakano et al. 423/87
4,452,762 6/1984 Fuglsberg et al. 423/87

FOREIGN PATENT DOCUMENTS

914647 3/1982 U.S.S.R. 423/87
2093003 8/1982 United Kingdom 423/87

Primary Examiner—Robert L. Stoll

[57] **ABSTRACT**

Arsenic, in the form of As_2O_3 , is recovered from arsenical ores or concentrates by leaching with a hot acidic ferric salt solution to extract arsenic, followed by cooling the pregnant leach solution to crystallize As_2O_3 . Leaching of some ores or concentrates is facilitated by addition of silver sulfate or mercuric sulfate to catalyze the leaching reaction.

5 Claims, No Drawings

RECOVERY OF ARSENIC FROM ORES AND CONCENTRATES

This invention relates to recovery of arsenic, in the form of As_2O_3 , from arsenical ores and concentrates. Typical of such ores are arseno-pyrite, cobaltite, niccolite, enargite, and speiss. Concentrates of the ores are prepared by conventional means such as flotation.

Arsenic is conventionally recovered from its ores or concentrates by roasting them to produce arsenic trioxide, As_2O_3 , which volatilizes and is subsequently condensed. Arsenic trioxide, however, poses serious problems by reason of its high toxicity, carcinogenicity and volatility. Hence, compliance with health and safety regulations is difficult or impossible to achieve on a regular basis with pyrometallurgical processes for treating the ores or concentrates. In the case of cobaltite, and other sulfur-containing arsenical ores or concentrates, SO_2 , an objectionable pollutant, is also generated during roasting.

Hydrometallurgical processes have also been proposed for treatment of arsenical ores. In these, arsenic is commonly precipitated as an arsenate, and is then discarded. However, the arsenates are subject to weathering leaching by hydrolysis or by acidic or basic solutions, thereby causing water pollution problems.

U.S. Pat. No. 4,220,627 discloses a process for treatment of arsenic and metal-bearing raw materials to obtain an arsenic-free metal sulfate and a metal-free arsenic product. The process comprises leaching of the raw material with sulfuric acid under strong oxidizing conditions, obtained by addition of gaseous oxygen or air, at elevated temperature to form a sulfate solution containing both the metal and arsenic, the latter being in the As^{3+} form. The resulting solution is cooled to selectively precipitate the metal in the form of sulfate. Recovery of the arsenic from the sulfate solution is then accomplished by extraction with butyl phosphate, or by reduction of the arsenic to arsenite, whereby As_2O_3 is precipitated.

U.S. Pat. No. 2,959,467 discloses an oxidation leach of metal values and arsenic from ores which also contain iron. The leach solution in this process consists of a combination of sulfuric and nitric acids, and the solutions are employed in a manner designed to adjust the ratio of iron to arsenic in the pregnant leach solution close to one.

It has now been found, according to the present invention, that arsenic may be recovered, in the form of As_2O_3 , from arsenical ores or concentrates by means of a process comprising leaching of the ore or concentrate with a hot acidic ferric salt solution, followed by cooling of the leach solution to precipitate As_2O_3 . Thus, most of the arsenic may be recovered as As_2O_3 , without the necessity of a reduction step.

The preferred leach solution comprises an aqueous solution of ferric sulfate and sulfuric acid, since this solution is economical, provides a high recovery of As_2O_3 , and does not result in formation of gaseous reaction products. Other leach solutions, such as ferric chloride or nitrate in solutions of the corresponding acid, may, however, be used in the process of the invention.

The leach solution preferably contains a maximum concentration of ferric salt, generally about 200 g/l or higher. Suitable acid concentrations are about 20 to 500 g/l, with about 400 to 450 g/l generally being preferred. The preferred ratio of ferric salt to arsenic ore or con-

centrate is the stoichiometric amount necessary to solubilize the arsenic. Excess ferric salt is generally undesirable since it is liable to oxidize the arsenic to arsenate at an undesirably high rate.

Certain arsenical minerals, such as enargite, however, leach slowly even at boiling temperature. It has been found that such minerals may be effectively treated by the process of the invention if silver or mercury salts, particularly the sulfates, are added to catalyze the leaching reaction. Silver sulfate is generally most effective, and is employed in amounts of about 0.05 to 0.5 g/l of leach solution, with mercuric sulfate being used in amounts of about 1 to 5 g/l.

In addition, ores containing significant percentages of valueless minerals reactive to the leach solution may require a preleach with a dilute acid to remove them. An important consideration is the removal of calcium minerals to avoid contamination of the product As_2O_3 by coprecipitated gypsum. The minimum calcium content of the ore requiring such a preleach depends on the Ca/Fe ratio in the ore and the leaching reagent requirements of the ore. To avoid gypsum precipitation, calcium concentrations in the leach liquor should not exceed 0.5 g Ca/l. Any strong mineral acid is acceptable for preleaching although hydrochloric acid is preferred because chloride salts are usually very soluble. The preferred preleach temperature is 20°-40° C.

The preferred leaching temperature in the process of the invention is about 100° to 120° C., the boiling point of the leach solution, depending on the ferric salt and acid employed, and their concentrations. At lower temperatures the leaching rate is too low, whereas at temperatures above 150° C. the solubility of the ferric salt decreases greatly. Preferred pressure is atmospheric, except at temperature above 100° to 120° C., where pressurization may be required to prevent loss of water from the reaction mixture. Solution arsenic trioxide concentrations exceeding 15 g/l can be obtained in the leaching reaction.

Following leaching, the leach solution is filtered hot to remove remaining solids, and is then cooled to crystallize the As_2O_3 . Crystallized As_2O_3 is recovered by filtration and washing. Generally, the lower the final temperature during crystallization, the greater the recovery of As_2O_3 . Ambient temperature, i.e., about 15° to 35° C., is preferred because no refrigeration is required. The most likely cocrystallizing salts are ferrous salts, such as ferrous sulfate, which can generally be readily removed during washing of the As_2O_3 . However, it is usually possible to adjust the acid concentration of the pregnant leach solution so as to prevent cocrystallization of ferrous salts. Furthermore, much of the byproduct ferrous salts precipitate during leaching and are removed in the hot filtration when the acid concentration of the leach solution is sufficiently high, e.g., about 30 pct or higher in the case of sulfuric acid. For example, a solvent composition of about 30 to 37 pct sulfuric acid will result in crystallization of As_2O_3 free of ferrous sulfate at 25° C.

A minor portion of the arsenic that is solubilized in the acid-ferric salt leach is present as As^{5+} , i.e., as arsenate. This arsenate must be reduced to As^{3+} before it can be recovered from the solution as As_2O_3 . Accordingly, reduction of any As^{5+} to As^{3+} is required for maximum recovery of arsenic. This may be accomplished by treatment of the hot pregnant leach solution with a conventional reducing agent, such as SO_2 .

The crystallized As_2O_3 can be purified if necessary by recrystallization from water or dilute acid. However, if much calcium is present in the ore, some of it will co-crystallize as gypsum during crystallization of the As_2O_3 , and is difficult to remove by recrystallizing. Hence, calcium should be removed from the ore by means of a preleach with dilute acid, as discussed above.

The leach solution contains other metal values, such as Co, Ni and Cu in addition to arsenic. These metals can be recovered by conventional techniques such as electrolysis, cementation, solvent extraction-electrolysis, or hydrogen reduction, after arsenic removal. If salts of valuable metals, such as Co, Ni, and Cu, remain in the leach residue, the residue is water leached, and this solution is combined with the filtrate from As_2O_3 crystallization prior to recovery of the metals by the above-mentioned conventional means. The solution is bled to control iron buildup, the barren solution, after removal of valuable metals, being oxidized by conventional techniques, such as with air or oxygen, to regenerate the iron salt, and the solution may be recycled for further leaching.

The invention will be more specifically illustrated by the following examples.

EXAMPLE 1

Weighed amounts of ore concentrates were boiled with solutions composed of 80 grams anhydrous $Fe_2(SO_4)_3$ and 318 grams of 30.8 pct aqueous H_2SO_4 for 6 hours. During this leaching period, the volumes of the solutions, initially about 280 ml, were allowed to decrease to about 220 ml, corresponding to a solvent composition of about 37 pct H_2SO_4 , by evaporation of water. Water lost beyond that amount was replaced. At completion of the leaching, the slurries were filtered while hot to separate leach residues and precipitated sulfate salts from the pregnant solution. The filter cakes were washed with 10 to 20 ml of water, which was added to the filtrates. The filtrates were cooled, during which As_2O_3 crystallized. The products were separated by filtration, washed with water and air dried. The water washing removed soluble cocrystallized sulfate salts, with the exception of gypsum.

The leaching residue filter cakes from the hot filtration were stirred with dilute H_2SO_4 to dissolve soluble salts. The slurries were filtered, and the solids and solutions were analyzed, as were the arsenic trioxide products and the filtrates from the arsenic trioxide crystallizations. The results of leaching four different arsenic feeds are presented in table 1. The arsenic trioxide products contained <0.1 pct Fe and <0.01 pct Co or Cu.

The procedure was very effective for leaching cobaltite and speiss, partially effective for arsenopyrite and ineffective for enargite. The purity of the crystallized As_2O_3 was 98 pct or higher in the three tests where As_2O_3 was crystallized. Gypsum was the major impurity in all of the arsenic trioxide products.

TABLE 1

Feed	Ore concentrate			
	Arsenopyrite	Cobaltite	Speiss	Enargite
Total, g	14.0	20.0	17.0	16.0
As, g	6.8	8.6	7.4	1.3
Fe, g	3.3	1.9	2.2	.5
Water insoluble leach residue				
Total, g	7.5	4.8	5.2	14.8

TABLE 1-continued

	Ore concentrate			
	Arsenopyrite	Cobaltite	Speiss	Enargite
As, g	3.5	.4	.8	1.1
Fe, g	2.1	.1	.3	.2
Water soluble sulfate salts in hot filtration filter cake				
As, g	.1	.8	.5	—
Fe, g	11.2	15.6	18.0	—
As_2O_3 crystals				
As, g	2.0	3.7	3.3	—
Filtrate from As_2O_3 crystallization				
As, g	1.2	3.7	2.8	.2
Fe, g	12.3	9.5	6.2	22.6
Pct As extraction	51	95	89	9
Pct As recovery as As_2O_3	29	43	49	0
Pct purity of As_2O_3 crystals	99	99	98	—
Pct arsenate formed	<1	33	14	—
Associated metals, M	Co	Co	Co	Cu
Pct M extraction	70	90	90	1
Pct M in sulfate salts	20	40	40	0
Pct Fe elutriated in sulfate salts	32	65	73	0

EXAMPLE 2

The feed materials, arsenopyrite and enargite, that did not leach well in the experiments of example 1 were further tested. The procedure was the same as for example 1 except that 250 mg of Ag_2SO_4 /l or 1,200 mg of $HgSO_4$ /l were added to the leaching solutions. The leaching results are shown in table 2.

TABLE 2

	Feed	Percent extraction		
		As	Cu	Co
No additive	Enargite	9	8	—
250 mg Ag_2SO_4 /l added	Enargite	97	94	—
1,200 mg $HgSO_4$ /l added	Enargite	47	45	—
No additive	Arsenopyrite	51	—	70
250 mg Ag_2SO_4 /l added	Arsenopyrite	71	—	90

Table 2 shows that the addition of Ag_2SO_4 is very effective for improving the leaching of arsenic and the associated base metals from these feed materials. The addition of $HgSO_4$ to the leaching solution was intermediate in effectiveness between no additive and the Ag_2SO_4 additive. Neither leaching solution additive had any effect on the recovery or the purity of the As_2O_3 crystals. Both leaching solution additives remained in the filtrate and could be reused for leaching fresh ore concentrate.

EXAMPLE 3

Cobaltite, the ore with which the most arsenate was formed or was present as such initially, was leached as in example 1 except that the weights of reagents were doubled and the weight of cobaltite was 48.0 grams. The leaching reaction was run 5 hours, then the hot filtration was done. The hot pregnant leach solution was split in halves. One half was allowed to cool in air to crystallize the As_2O_3 . The second half of the solution was put into a pressure bottle and treated with SO_2 at 25 to 30 psig during cooling. The solution, initially at 66° C., cooled to 28° C. in 2.0 hours during this SO_2 treatment. The SO_2 was then removed from the cooled mix-

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ture by aeration. The As_2O_3 was isolated from the SO_2 -treated and untreated solutions and the solutions were analyzed as in example 1. The results showed that about 65 pct of the arsenate was reduced to As_2O_3 by the SO_2 . This conversion could likely be improved by starting SO_2 treatment at a higher temperature, using a higher SO_2 pressure, or by cooling the solution more slowly. The As_2O_3 formed from arsenate in the SO_2 reduction appears as an increased recovery of As_2O_3 crystals. This test was conducted with about 15 pct excess ore, and it also showed that arsenate in the solution is not reduced at a significant rate to As_2O_3 by excess ore.

We claim:

1. A process for recovery of arsenic, as As_2O_3 , from arsenical sulfide ores or concentrates comprising:

(a) leaching of the ores or concentrates with an acidic ferric compound-containing leach solution at a temperature of 100° to 150° C. to extract arsenic in the As^{3+} state, wherein the acidic ferric compound is selected from the class consisting of ferric sulfate and sulfuric acid, ferric nitrate and nitric acid, and ferric chloride and hydrochloric acid, and wherein

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said leach solution additionally contains a leaching catalyst selected from the class consisting of silver sulfate and mercuric sulfate;

(b) separating the pregnant leach solution from the leach residue, and

(c) cooling the pregnant leach solution to crystallize As_2O_3 .

2. The process of claim 1 in which the temperature of the leach solution in step (a) is about 100° C. to 120° C.

3. The process of claim 1 in which the As_2O_3 is crystallized by cooling the pregnant leach solution to about 15° to 35° C.

4. The process of claim 1 wherein when the ores or concentrates contain calcium, they are treated with dilute acid to remove calcium prior to the leaching step with the ferric compound-containing leach solution.

5. The process of claim 1 wherein after step (b) including the additional step of treatment of the pregnant leach solution with SO_2 to reduce any pentavalent arsenic to trivalent arsenic prior to crystallization of As_2O_3 .

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[54] SELECTIVE SULFATION PROCESS FOR
PARTITIONING FERROUS AND
NON-FERROUS VALUES IN AN ORE

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[75] Assignor: Kennecott Copper Corporation, New
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[21] Appl. No.: 896,493
[22] Filed: Sep. 26, 1977

Related U.S. Application Data

- [63] Continuation of Ser. No. 657,849, Feb. 13, 1976,
abandoned.

- [51] Int. Cl.² _____ C22B 1/06
[52] U.S. Cl. _____ 75/1 R; 75/101 R;
423/DIG. 12; 423/41; 423/43; 423/49; 423/62;
423/68; 423/146; 423/150
[58] Field of Search _____ 75/1 R, 1 T, 21, 97 R,
75/101 R, 115, 116, 117, 119, 121; 423/DIG.
12, 41, 43, 49, 62, 68, 89, 98, 146, 150, 53

[56] References Cited

U.S. PATENT DOCUMENTS

1,364,804	1/1921	Randall	_____	423/98
2,719,082	9/1955	Sprinkle et al.	_____	75/1 R
2,813,016	11/1957	Thorahill	_____	75/9
2,930,687	3/1960	Thorahill et al.	_____	75/9
3,252,750	2/1966	Kazimierz	_____	75/119
3,367,740	2/1968	Zubryckij et al.	_____	75/101 R
3,451,804	6/1969	Malstrom et al.	_____	75/7
3,880,650	4/1975	Penzler	_____	75/117

OTHER PUBLICATIONS

Delarue, G.; *Chimie Analytique*, vol. 44, No. 3, 3/62, pp. 91-102.
Flood, H.; "The Acidic and Basic Properties of Oxides", *Acta Chemica Scandinavica*, vol. 1, (1947), pp. 781-789.
Zubryckij, N., et al.; "Preferential Sulfation of Nickel and Cobalt in Lateritic Ores", *Journals of Metals*, (5/65) pp. 478-486.
Weast, R. C. ed., *Handbook of Chemistry and Physics* 52 ed.; The Chemical Rubber Co., Cleveland, Ohio. p. B62,140 QD63C4 (1971).
Hodgman C. D. ed., *Handbook of Chemistry and Physics* 43rd ed.; The Chemical Rubber Co. pp. 519, 604, 605 (1961).

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Assistant Examiner—Michael L. Lewis

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[57] ABSTRACT

Process for quantitatively converting non-ferrous metals chosen from the group consisting of copper, nickel, cobalt, vanadium, and manganese in an ore concentrate to soluble sulfates and simultaneously convert the ferrous values in the ore to insoluble oxides. The process comprises roasting finely divided ore particles at a temperature in excess of 650° C in the presence of a roaster gas comprising at least a stoichiometric amount of oxygen and at least 1% SO₂. The roasting is performed in the presence of a sufficient amount of a mixture of salts to allow the formation of a liquid coating on the ore particles. In a preferred embodiment, the mixed salt which forms the liquid coating comprises Na₂SO₄ and K₂SO₄ with the ratio of sodium to potassium being between 1.0 and 2.0.

28 Claims, 3 Drawing Figures

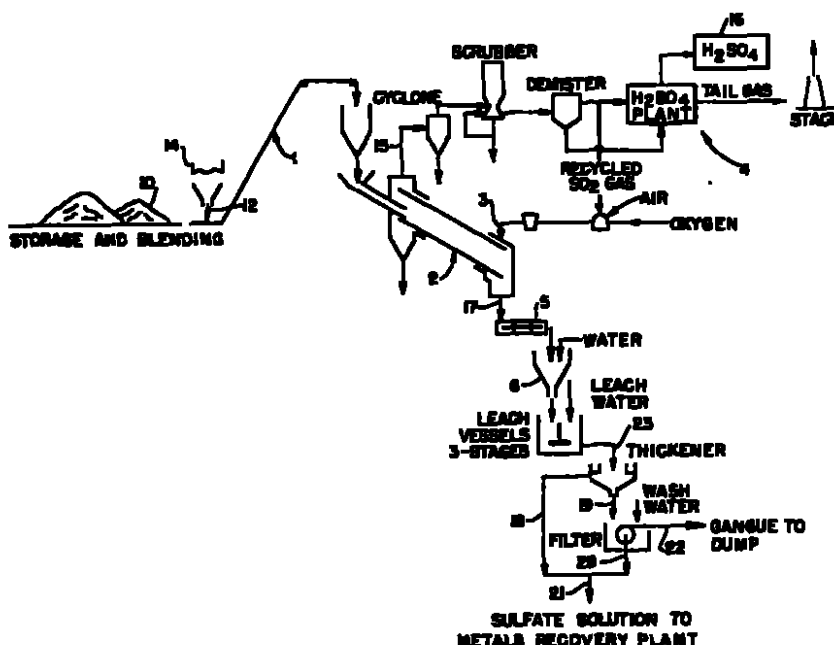


FIG 1

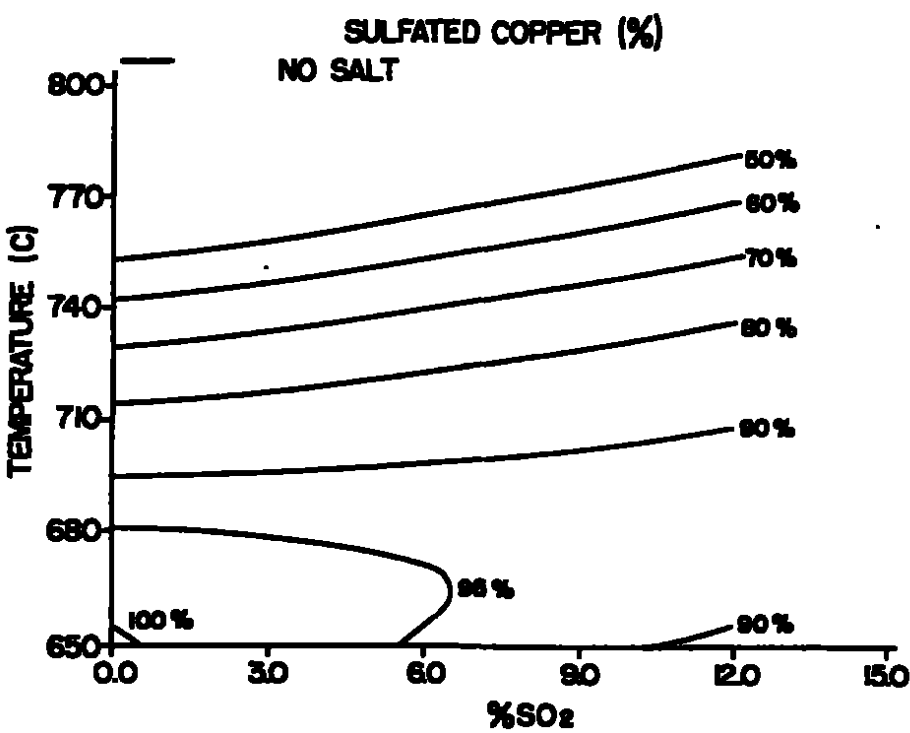
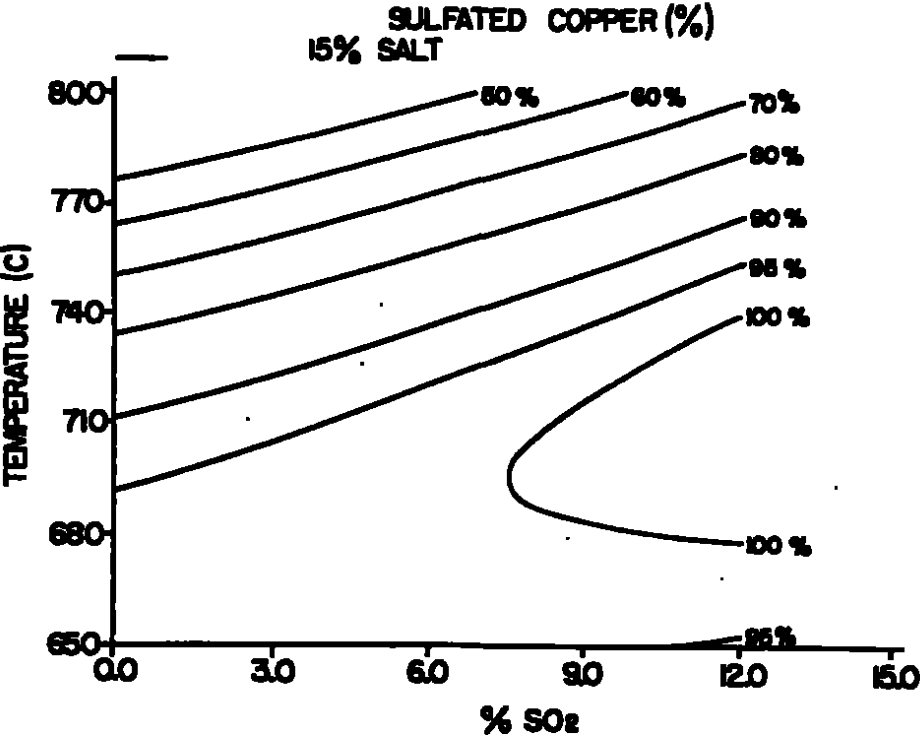


FIG 2



SELECTIVE SULFATION PROCESS FOR PARTITIONING FERROUS AND NON-FERROUS VALUES IN AN ORE

This is a continuation, of application Ser. No. 657,849
Filed Feb. 13, 1976, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to a method of processing ores
containing one or more metal values selected from the
group consisting of copper, nickel, cobalt, vanadium,
and manganese which are present in the ore in associa-
tion with iron. The process rapidly and quantitatively
separates the non-ferrous metals from the iron. More
particularly, the invention relates to an improvement in
the process of selective sulfation of such ores to render
the non-ferrous metals leachable and the ferrous metals
non-leachable.

It is well known that ores containing pentlandite,
pyrrhotite, chalcopyrite, cubanite, other sulfides of
copper, other sulfates of nickel, small amounts of cobalt,
vanadium and manganese, and various mixtures thereof
may be treated to yield metal values by selective sulfa-
tion. In general, this process involves oxygen roasting
the concentrates in the presence of sulfur dioxide or a
sulfate salt to produce sulfates from the copper, nickel,
and/or non-ferrous metals present and to convert the
ferrous metal values to Fe_2O_3 . Since the sulfates of the
non-ferrous values are soluble, after such treatment, it is
possible to water leach the mixture, leaving the ferrous
values behind and conveniently extracting the non-fer-
rous values.

While this process has considerable theoretical poten-
tial, it has achieved only limited success in large scale
commercial use because of several difficulties which
make it economically unfeasible. The most basic disad-
vantage of the sulfation process is that the temperature
and the roaster gas composition are difficult to control
so that the production of sulfates of the non-ferrous
values is maximized. Although the reaction of iron to
form iron oxide generally requires a temperature in
excess of about 675° C, at such temperatures much of
the copper, nickel, etc. may also be oxidized to a non-
leachable state. Below about 675° C, much of the iron is
converted to sulfate. Unless a high degree of partition-
ing between the ferrous and non-ferrous metals can be
achieved, the water leach extracts an unacceptably high
percentage of the ferrous metal values along with the
metal values of interest.

The prior art is replete with attempts to improve the
yield of water soluble copper values in the sulfation
process. For example, U.S. Pat. No. 3,441,403 to R. E.
Frederickson et al. teaches that the yield of soluble cop-
per may be increased by adding gaseous HCl to the
roaster gas. In U.S. Pat. No. 2,719,082 to W. K. Sproule
et al., a method for producing high grade hematite from
nickel, copper, and cobalt containing iron sulfide ores is
disclosed which takes advantage of this sulfation pro-
cess to remove small amounts of non-ferrous metal
sulfide contaminants and small amounts of silica, lime,
alumina, and magnesia from the ore. This process in-
volves removing the bulk of the contaminants by con-
ventional separation techniques and then roasting the
concentrated and partially purified ore under oxidizing
conditions to form a permeable iron oxide calcine con-
taining not more than 1% nickel and 0.1% copper. The
calcine is then sulfated by heating it between 630°-687°

C (1200°-1300° F) with between 2% and 8% by weight
sodium sulfate in the presence of a roasting gas compris-
ing between 4 and 6% sulfur dioxide and more than 5%
oxygen. This process is said to be capable of rendering
"substantially all" of the small amount of copper pres-
ent and up to 86% of the nickel present water soluble.
However, it is taught that these results can only be
achieved when the ore has been pretreated to contain
the small recited percentages of copper and nickel.

U.S. Pat. No. 3,791,812 to R. L. Frank et al. discloses
a process for extracting copper, cobalt, and manganese
values from ores as water soluble salts. In this process,
a sulfide ore bearing the metal values of interest is mixed
with an inorganic chloride to form a mixture containing
from about 30-93 weight percent ore and from about 7
to about 70 weight percent inorganic chloride. A
charge of the mixture in a gas permeable state is roasted
with oxygen at a temperature of about 300° to 425° C
and the sulfur dioxide produced is transferred to a sec-
ond stage roasting zone where the oxides produced in
the first zone are converted to sulfates. The primary
object of the invention disclosed in this patent is to
reduce sulfur dioxide emissions, and no data is presented
which indicates that the ferrous metals and non-ferrous
metals are efficiently partitioned. In fact, the tempera-
ture range disclosed in this patent indicates that a sub-
stantial amount of soluble iron sulfate and iron chloride
would be produced by the process and that a substantial
amount of iron would therefore be leached along with
the non-ferrous metals.

In general, it is believed that all the prior art sulfation
processes designed to render substantial amounts of
non-ferrous metal values in extractable form, yield a
non-ferrous metal sulfate which is contaminated by
unacceptably large quantities of iron sulfate and generally
require a roasting time which is greater than optimal. In
contrast, embodiments of the process of this invention
yield up to 99% of the copper, 97% of the nickel, 90%
of the cobalt, and comparable percentages of other
non-ferrous metals while excluding between 96% and
99% of the iron in a short period of time and under
conditions of temperature and pressure which are easily
regulated.

SUMMARY OF THE INVENTION

In general, the invention provides a process for parti-
tioning non-ferrous metal values from ferrous metal
values in a finely divided ore by rendering the non-fer-
rous metal values water soluble to the essential exclu-
sion of the ferrous metal values. The process comprises
coating the ore particles with a mixture of molten salts
having a melting point below 630° C and reacting the
coated particles at a temperature between 630° and 800°
C, in the presence of a roaster gas comprising SO_2 and
at least a stoichiometric equivalent of O_2 . In preferred
embodiments, the molten salt mixture comprises a mix-
ture of sulfates, preferably sodium and potassium sul-
fate, and more preferably, a sodium-potassium sulfate
mix having a sodium or potassium ratio between 10 and
0.1. During the process, pyrosulfates are produced
which help to stabilize the nonferrous metal sulfates,
dissolve any ferrites which may have formed, and sub-
stantially prevent non-ferrous metal sulfates decomposi-
tion. During the course of the roast, sulfides are con-
verted to oxides and the oxides are sulfated. The use of
the salt coating in the presence of sulfur dioxide on the
order of between 1% and 25%, preferably about 5%, in
the roasting gas mixture, allows roasting at tempera-

tures where greater than 96% of the ferrous metal values are converted to insoluble forms. To effectively coat the ore with molten salt, the mass ratio of molten salt to ore should be greater than about 0.05. However, as the salt-ore ratio is increased beyond the preferred range of 0.10 to 0.25, the economic advantages of the process are increasingly lost. The ore or ore concentrate, roaster gas, and molten salt must be intimately mixed during the roasting, and one preferred method of mixing comprises bubbling the roaster gas through the salt-ore mixture. The temperature at which essentially quantitative selective sulfation of non-ferrous values is economically effected is between 650° and 800° C, preferably between 675° and 750° C. During the process, an easily leachable molten solution of the salt mixture and non-ferrous metal sulfates is produced which may be separated from the insoluble residue by conventional techniques.

Accordingly, it is an object of the present invention to rapidly (within 0.25-2 hours) extract copper, nickel, cobalt, etc. from an ore or ore concentrate.

Another object of the invention is to effect a quantitative separation of copper, nickel, and cobalt from iron such that the soluble sulfates produced are four percent or less of the available iron in the ore or ore concentrate being treated in the process.

Still another object of the invention is to achieve concentrate extractions of up to 99% copper, 97% nickel, and 90% cobalt in a relatively short time.

Still another object of the invention is to dissolve ferrites and to recover non-ferrous metal from sulfidic, oxidic, ferritic, siliceous, or other ore concentrates.

Yet another object of the invention is to provide a process for recovering non-ferrous metal values from a variety of heretofore difficult to treat ore concentrates of various grades.

Yet another object of the invention is to provide such a process having a chemistry which is independent of ore concentrate grade.

Another object of the invention is to provide a selective sulfation process wherein temperature and atmospheric requirements are easily regulated.

Other objects and features of the invention will be apparent to those skilled in the art from the following description of a preferred embodiment and from the drawing.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a graph showing the results of a series of roasts without a salt coating;

FIG. 2 is a graph showing the results of a series of roasts conducted in accordance with the present invention; and

FIG. 3 is a flow diagram schematically illustrating a commercial process embodying the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

At the outset, the invention is described in its broadest overall aspects with a more detailed description following.

The process of the invention partitions ferrous and non-ferrous metal values in an ore or ore concentrate. The process is characterized by the steps of adding a finely divided ore to a reactor together with a mixture of inorganic salts, intimately mixing the ore and salt mixture, heating the mixture to melt the salt and to cause a coating to form about the ore particles, contact-

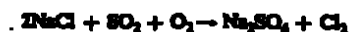
ing the ore and salt mixture with SO₂ and O₂ to produce soluble non-ferrous metal sulfates and insoluble iron oxides, and water quenching the ore and salt mixture to remove the non-ferrous metal sulfates while leaving the iron behind.

The types of ores and ore concentrates with which the present invention is concerned are those in which copper, nickel, cobalt, vanadium, or manganese are found in sulfidic, oxidic, ferritic, or siliceous states mixed with, inter alia, iron sulfides, oxides, or silicates and ores containing compounds of these metals with iron. While the following description and examples will deal essentially with copper and nickel, it will be apparent to those skilled in the art, that since cobalt, vanadium, and manganese are chemically similar to copper and nickel, these metals can be treated in accordance with the invention with little or no modification of the process. Minerals which are particularly well-adapted for treatment in accordance with the process of the invention include pendlandite, pyrrhotite, chalcopyrite, and cubanite. Frequently, trace amounts of sulfidic or oxidic salts of cobalt, vanadium, and/or manganese are found mixed with such minerals, and it is contemplated that, when desired, these minerals may be recovered together with the copper and nickel.

Since, as disclosed below, the chemistry of the process is independent of the concentrate grade, the process of the present invention is operable with a wide range of concentrate grades which may be made by conventional techniques. In any industrial use of the process, some form of concentrate is highly preferred over the raw ore.

In the process of the invention, the ore in finely divided form is placed in a rotary kiln, fluid bed, or other suitable reactor together with a mixture of salts, preferably a mixture of sodium and potassium sulfate. A sufficient amount of the salt mixture should be added to provide at least a thin coating of salt on the ore particles. The ratio of salt to concentrate affects the recovery of both copper and nickel with the larger effect being on nickel recovery. Generally, the mass ratio of salt to concentrate should lie within the range of 0.05 to 0.50, and the higher the ratio, the higher the degree of extraction up to some value of the ratio where 98±2% of the metal values are converted to sulfates. Further increases of the ratio do not adversely affect the sulfation, but require handling unnecessary amounts of molten salt. Higher roasting temperatures generally require larger amounts of salt within the range specified.

The nature of the salt bath must be chosen with the following considerations in mind. First, the function of the salt is to provide a gas permeable coating about the ore particles and a reaction environment in which both a high temperature, on the order of 650 to 800° C, and a high concentration of available SO₂ will be provided. NaCl, Na₂SO₄, KCl, K₂SO₄, and other salts are operable. However, the non-sulfate salts are rapidly converted to sulfates in the presence of SO₂ and oxygen. For example:



However, the addition of Cl₂ has no effect on the degree of copper and nickel extraction, indicating that the sulfate salts are the active extraction aid. Thus sulfate salts are preferred although other salts, e.g., halides, may be used if desired.

A mixture of salts is essential to the invention insofar as the melting point of a mixture is depressed in accordance with well-known melting point depression theory. Since a liquid coating on the ore particles is essential, it is important that the salt used have a melting point well below the roasting temperature. Copper and nickel sulfates produced during roasting of the mixture form a molten solution with the mixture of sodium and potassium sulfates to produce a copper and/or nickel sodium-potassium salt solution which is a liquid at the roast temperature.

A series of experiments has shown that a mixed salt is more efficient in extracting copper than any single salt and that the ratio of sodium to potassium is important for high nickel extraction. In the case of sulfates, changing the sodium to potassium ratio from 4 to 0.25 increased nickel extraction from 79% to 92% after a 120 minute roast. Copper extraction was not significantly affected by variations in the sodium-potassium ratio, but a separate set of experiments using only potassium sulfate in one and an equimolar sodium sulfate-potassium sulfate mixture in the other increased copper extraction from 87% in the former to 98% in the latter. The implication of these experiments is that while a copper sulfate-potassium sulfate mix does not form a low melting mixed salt, a copper sulfate-sodium sulfate-potassium sulfate system does, and will allow the required liquid coating to form. The melting point of sodium sulfate is 884° C and that of potassium sulfate is even higher, but the melting point of the salt mix useful in this invention is below 650° C, and typically should be well below this temperature, e.g., 500° C. When the sodium-potassium sulfate salt mix is used, the operable sodium-potassium ratio is within the range of 10 to 0.1, and the preferred range is 1.0 and 0.20. The best sodium-potassium ratio for a given concentrate must be determined specifically for that concentrate. When different salts are used, the best ratio for the mix should be determined.

To the molten mixture of concentrate and salt is added a roaster gas comprising oxygen and between 1% and 25%, preferably 1% to 5% sulfur dioxide. The gas should contain at least enough oxygen to allow the reactions involved to go to completion, but a gas containing far in excess of the stoichiometric amount of oxygen is also acceptable. In cases where the ore contains a large amount of sulfide, SO₂ is generated as a natural product of reaction with oxygen at the temperature of the roast and only minimal amounts of sulfur dioxide need be added to supplement that produced in the initial stages of the roasting. In any case, it is essential to maintain an SO₂ containing atmosphere over the reacting liquid-solid to prevent yield loss by CuSO₄ and NiSO₄ decomposition and subsequent ferrite formation. The above disclosed amount of SO₂ gas is designed to accomplish the above.

At the temperature of the roast, the oxygen and sulfur dioxide combine to form sulfur trioxide according to the equation:



It is believed that the sulfur trioxide thereby produced, being highly reactive, is the basic sulfating agent and that this agent acts either directly or through the formation of a pyrosulfate.

It is also important in the process of the present invention to assure that the ore particles, salt mix, and roaster gases are intimately mixed. On preferred method of mixing involves bubbling the gas through the

ore-salt mixture during the roast, thereby providing continuous agitation of the reactants. In this circumstance, the mixed sulfate salts, when exposed to sulfur trioxide, are in part converted to pyrosulfates in accordance with the equation:



The presence of the molten salt coating on the solid particles acts to improve the rate and degree of metal extraction by providing an SO₃ rich environment in accordance with the above reactions. The pyrosulfates are capable of giving up SO₃ to sulfate the copper and nickel by acting as an SO₃ donating system. One other advantage of the pyrosulfate formation is that the pyrosulfates are capable of dissolving CuO, NiO, and copper, or nickel ferrites formed during the roast, e.g.:



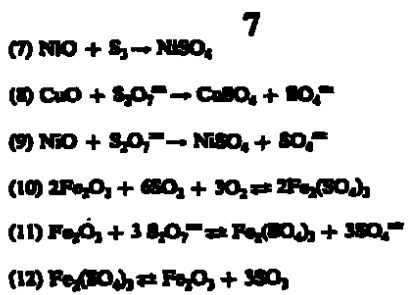
The combined effect of pyrosulfate formation and the liquid salt coating is to make the roast process less sensitive to temperature variations and thus reduce the requirements of precise process control which characterizes conventional roasts. Furthermore, higher process temperatures result in the rejection of iron as Fe₂O₃ to a much greater degree than in conventional sulfation roasts, and since extracted Cu and Ni are present as a complex Ni-Cu-Na-K sulfate salt, the salts and metal values are water leached in about 30 minutes at 50° C, i.e., much faster than in conventional roast-leach processes.

The invention will be further understood from the following examples which should not in any way be construed as limiting.

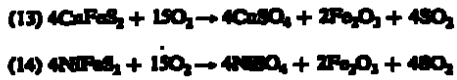
EXAMPLE 1

3.316 grams of a concentrate containing 14.2% Cu as chalcocopyrite and 2.5% Ni as pentlandite were placed in an alumina crucible with 1.005 g of an equimolar mixture of sodium sulfate and potassium sulfate and heated to 700° ± 5° C in a conventional laboratory furnace. Air was introduced to the reactor at a rate of 500 ml per minute. 25 ml per minute SO₂ was used to maintain the reaction atmosphere. After 120 min., the sample was removed, cooled to room temperature, and water leached. 95.0% of the nickel, 97% of the copper, and 1.8% of the iron was rendered water soluble. The reactions taking place were as follows:





Overall reactions:



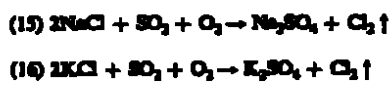
The presence of SO_3 and the pyrosulfate push reactions 6-11 to the right and the temperature of the roast favors completion of reaction 12.

A separate series of experiments show that the sodium-potassium ratio is important for high nickel extraction. The following examples are illustrative of these experiments.

EXAMPLE 2

An experiment was performed in accordance with Example 1 except that 0.80 grams of sodium sulfate and 0.20 grams of potassium sulfate were used in place of the equimolar mixture of Example 1. ($\text{Na}/\text{K}=4$). This treatment yielded over 98% of the copper to leachable form but only 79% of the nickel. In contrast, when the sodium-potassium ratio was changed to 0.25, i.e., 0.20 grams of sodium sulfate mixed with 0.80 grams of potassium sulfate, over 97% of the copper and 92% of the nickel was extracted.

A large number of experiments have been performed to establish the effect of various process parameters. For example, when sodium and potassium chlorides are used as salt additives, the chlorides are rapidly converted to sulfates with the release of chlorine in accordance with the equations:



EXAMPLES 3-7

A set of experiments was run to determine the effects of the sodium-potassium ratio and the use of Cl_2 gas on copper and nickel extraction in the process of the invention. Each experiment was conducted using a 2.000 g. sample of the concentrate of Example 1 with 0.300 g of sulfate salt added having the indicated Na/K mole ratio. The furnace temperature was $700^\circ \pm 5^\circ \text{C}$ and the reaction atmosphere was maintained by a flow of 200 ml/min air and 10 ml/min SO_2 . Cl_2 gas was added as indicated to simulate chloride salt reaction per reactions (15) and (16) above. All samples were treated for 120 minutes.

Example	% Cl_2	% Soluble Metal			
		Na/K	Cu	Ni	Fe
3	0	4.0	96	82	2.0
4	0.6	4.0	98	86	2.7
5	0	0.25	96	92	2.1
6	0.6	0.25	97	86	3.0
7	0.3	1.0	97	80	1.4

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As can be seen from a study of these data, a low Na/K ratio results in higher nickel extraction. Since, of the two possible pyrosulfates, $\text{K}_2\text{S}_2\text{O}_7$ is the more stable, one might suspect that the improved result may be explained solely in terms of a pyrosulfate effect. If this suspicion were correct, pure K_2SO_4 would provide an extraction aid superior in performance to a mixture of Na_2SO_4 and K_2SO_4 . However, since this hypothesis contradicts observation as evidenced by the following examples, it is apparent that the improvement in results may be traced to the combined effect of pyrosulfate formation and the formation of a liquid coating.

EXAMPLES 8 and 9

In these examples, 4.0 g of chalcopyrite concentrate, 1.0 g FeS_2 and 5.0 g of barren silicate rock were reacted with 1.5 g of salt for 120 minutes at 700°C in a rotating reactor. Reactor atmosphere was maintained by a gas flow of 500 ml/min air and 25 ml/min SO_2 . The results disclosed below clearly indicate that only a mixture of salts capable of forming a low melting salt solution will act as an efficient extractant.

Example	Salt	% Soluble Metal	
		Cu	Fe
8	equimolar Na_2SO_4 - K_2SO_4	98	3.3
9	K_2SO_4	87	3.3

Experience indicates that when copper extraction is incomplete, nickel extraction is even more incomplete. An examination of the phase diagrams of Na_2SO_4 - CuSO_4 , K_2SO_4 - CuSO_4 and Na_2SO_4 - K_2SO_4 - CuSO_4 , as disclosed in the published literature, (e.g. Phase Diagrams for Ceramists, E. M. Levin, C. R. Robbins, and H. F. McMurdie, ed., American Ceramic Society, Columbus, Ohio, 1969) shows that a salt mixture is required to lower the melting point of the salt solution to a temperature substantially below that used in the roast process. Of course, other salt combinations which fulfill the dual requirement of low melting point and pyrosulfate forming ability will be obvious to those skilled in the art in view of this specification. Combinations including halide salts are one non-limiting example of such equivalent extraction aids.

EXAMPLES 10 AND 11

1.32 g of the concentrate used in Example 1 were roasted with varying amounts of a salt mixture comprising 50% by weight of equimolar NaCl - KCl and 50% by weight Na_2SO_4 . The roast was conducted for 120 minutes at a temperature of $700^\circ \pm 5^\circ \text{C}$ while maintaining a reactor atmosphere with a gas flow of 500 ml/min air and 25 ml/min SO_2 . The results of these experiments are indicated below.

Examples	Wt. Salt Mixture	% Soluble Metal		
		Cu	Ni	Fe
10	0.13 g	97	99	4.0
11	0.66 g	98	100	3.2

EXAMPLES 12-15

Additional experiments (12, 13, 14) were conducted in the manner of Examples 10-11, except that larger amounts of concentrate and salt were used so as to impede the flow of gas to the bulk of the concentrate

particles and their liquid coatings. These experiments were designed to show that intimate mixing of all three phases, gas, solid, and liquid, is needed to achieve the desired results. For purposes of comparison, Example 15 was conducted using a procedure identical to that of Examples 12, 13, and 14, except that a slowly rotating reactor was used so that gas-liquid-solid mixing was achieved. The results of these experiments are indicated in the table below.

Example	Wt. Salt	Wt. Conc.	% Soluble Metal		
			Cu	Ni	Fe
12	.59g	1.30g	97	97	1.5
13	.59g	1.26g	90	83	1.4
14	2.64g	1.28g	90	86	1.7
15	2.00g	10.00g	100	—	3.1

EXAMPLE 16

A principal advantage of using the process chemistry described herein is that reaction time is considerably shorter than in conventional roasting processes. To illustrate this phenomenon, a series of samples were prepared in 15 mm x 25 mm alumina boats. The samples each contained 0.375 g of the concentrate used in Example 1 and 0.125 g of alkali sulfate salt with a Na/K = 0.21. A specially designed reactor was prepared so that a series of samples could be introduced to the hot zone without disturbing the reactor atmosphere or temperature. The former was maintained by a flow of 950 ml/min air and 50 ml/min SO₂. The latter was kept at 725° ± 5° C. Extractions as a function of residence time, shown below, indicate essentially complete copper extraction in 20 minutes and complete nickel extraction in 40 minutes.

Time (min.)	% Soluble Metal		
	Cu	Ni	Fe ²
20	94	72	10
40	100	93	11
60	97	89	11
80	96	89	7
100	99	89	5

In contrast, conventional sulfation roasts involve roasting times up to 6 hours for Ni extractions which generally do not exceed 85%. See, for example, U.S. Pat. No. 2,719,082 (87% Ni extraction in 3 hours) and U.S. Pat. No. 2,556,215 (89% Ni extraction in 48 hours).

EXAMPLE 17

In another series of experiments, the procedure of Example 1 was repeated except that the ratio of salt to concentrate was varied between 0.05 and 0.50 instead of being maintained at 0.30. It was found that variations in the salt to concentrate ratio affected the extraction of nickel more than the extraction of copper. The higher the ratio, the higher the degree of extraction up to some value of the ratio. This value is within the range recited and is characterized by a conversion of 98 ± 2% of the non-ferrous metal values to sulfates, but varies slightly for different ores. The preferred range for this ratio is 0.1 to 0.25. Further increase in the ratio above about 0.50 does not affect the sulfation but does increase cost because of the necessity of handling increased amounts of molten salt.

EXAMPLE 18

So called "hot spotting" invariably occurs in the course of sulfation roasting on a commercial scale. When hot spotting occurs, local temperatures rise considerably and result in the formation of water insoluble ferrites as per the following reactions:



To illustrate that the chemistry of the process of this invention is capable of overcoming the effects of hot-spotting, experiments were conducted in the manner of Example 16, except that pure NiFe₂O₄ and CaFe₂O₆ were placed in the reaction trays instead of the concentrate. These ferrites were roasted at 722° ± 2° C. in an atmosphere of 4.0% SO₂ in air. After 60 minutes, 92% of the copper had been extracted from the copper ferrite and, in a separate experiment, 42% of the nickel had been extracted from the nickel ferrite. The extraction was incomplete in the latter case because the melting point of the Na₂SO₄-K₂SO₄-NiSO₄ salt solution formed increased to a temperature above that used in the roast and thus terminated the reaction.

EXAMPLE 19

A series of 46 experiments were conducted using the procedure of Example 16 and a conventional chalcopyrite concentrate having a composition of 25% Cu, 25% Fe, and 29% S. Operational parameters were varied as followed:

Temperature: 650°-800° C.

% SO₂: 1.0%-10%

% Salt: 5%-25%

Time: 10-120 min.

The data obtained from these experiments were subjected to a multiple linear regression analysis on a computer. Equations were generated to reflect the extraction of Cu as a function of the operating parameters and these equations were plotted. FIG. 1 shows a series of computer generated curves of temperature versus % SO₂ used for a series of sulfations using no salt (results taken after 40 minute roast). FIG. 2 is a computer generated series of curves calculated from results taken under identical process conditions except that 15% salt was included. These results clearly show a greatly increased range of operating parameters over which 95% or higher copper extractions are achieved. Translated into commercial operations, these curves demonstrate that a greatly reduced degree of process control is required using the process of the invention while nevertheless maintaining economically attractive copper recovery in relatively short periods of time.

It has been observed that higher process temperatures and leaner ore concentrates require larger amounts of added salt. This behavior is consistent with the suggested mechanism whereby liquid salt coats the concentrate particles and pyrosulfates are formed. Because of this observation, it is believed that the pyrosulfates are mainly responsible for supplying the SO₂ activity which sulfates the metal values and stabilizes the copper and

nickel sulfates formed. The following example illustrates this phenomenon.

EXAMPLE 20

A salt bath consisting of 21 grams Na_2SO_4 and 79 grams NaCl was heated in an electric furnace to $820^\circ \pm 5^\circ \text{C}$. After the salt has melted and come up to temperature, 5.0 grams of pre-roasted chalcopyrite (CuFeS_2) was added to the salt. The pre-roasting converts the chalcopyrite to cupric and iron oxides as per equations 1, 17, and 18. The melt is stirred by bubbling gas consisting of 1500 ml per minute air plus 7.5 ml per minute SO_2 through the melt using a single hole 6 mm outside diameter quartz tube. Thirty minutes after the start of gas bubbling, the melt was sampled and analyzed for water soluble copper and water soluble iron. Then 5.0 grams more of pre-roasted chalcopyrite were added to the melt. The process was continued until a total of 30.0 grams of concentrate had been added. The table below summarizes the results of this experiment.

Table

Time	Conc. added	Sol. Cu	Sol. Fe
0 min.	5.0 g	—	—
30	5.0	1.04 g	0.03 g
60	5.0	1.40	0.03
90	5.0	1.82	0.03
120	5.0	1.61	0.03
150	5.0	7.32	0.04
210	—	9.43	0.02

The theoretical maximum soluble Cu was 9.55 g and, as can be seen from the Table, since 9.43 g are successfully extracted, 98.7% of the total soluble copper was recovered. The copper-iron partition was 487:1. This example indicates that higher temperatures than those disclosed in the preceding examples may be employed if additional amounts of salt are used. Note that the salt to concentrate ratio in this example was 3.33. While such modifications of the selective sulfation process are within the scope of the invention, it is highly preferable to keep the amount of salt used at a minimum so as to avoid the necessity of handling unduly large quantities of molten salt.

In addition, this example indicates that salts other than sulfates are useable, although, as indicated above, such salts are rapidly converted to sulfates in the SO_2 atmosphere. After conversion of the NaCl to Na_2SO_4 (a reaction which goes essentially to completion if the chlorine produced is removed) the roast takes place in Na_2SO_4 only. Obviously, since the melting point of Na_2SO_4 is 884°C ., the Na_2SO_4 mixed with the copper sulfates produced to form a mixed salt having a melting point below the temperature of the roast (820°C .). The presence of the chloride-sulfate mixture in the initial stages of the roast accounts for the salt melting below 820°C .

At the end of the process of this invention, the non-ferrous sulfates may be separated from the Fe_2O_3 , and other insoluble substances such as plagioclase, olivine, pyroxene, and ilmenite which are often found in the types of ore described above. In this regard, it is contemplated that conventional separation techniques may be employed. To take advantage of the process, a separation technique based on the solubility difference between the Fe_2O_3 and non-ferrous metal sulfates should be used, e.g., a water leach.

More specifically, the solution of molten salt and copper and/or nickel sulfates, which at the end of the roast coat the Fe_2O_3 , and any gangue solids, should be

removed from the kiln while at a temperature above its melting point (typically approximately 500°C .). Water quenching at this temperature effectively separates the insoluble iron oxides from the non-ferrous metal sulfates and yields a concentrated solution of the non-ferrous metal values. Solubility product constants and pure salt solubility for some salts are given below.

Salt	Pure Salt Solubility g/100 ml		K_{sp} at 25°C
	0°	100°	
K_2SO_4	10	24	2.7×10^{-3}
Na_2SO_4	48	42	2.7×10^{-3}
CuSO_4	14	71	.21
NiSO_4	29	83	.34

The metal values in the concentrated sulfate solution can be recovered by a wide selection of process configurations e.g., electrowinning. Any recovery process chosen, by necessity, will involve reduction.

Referring to FIG. 3, a schematic diagram illustrating an exemplary commercial process is shown. Copper or nickel bearing sulfide concentrate 10 is fed to a conveyor 1. A salt mixture 12 is added to the conveyor from a hopper 14. The resulting mixture is fed to kiln roaster 2 together with SO_2 gas and air (or oxygen as desired) which may conveniently be obtained from the output 3 of an off gas reclamation and treatment system 4. It should be noted that a fluid bed reactor (not shown) or other suitable roasting apparatus may be substituted for kiln roaster 2 as desired. When the concentrate, as described, is a sulfide ore, and the roasting is performed in a fluid bed roaster, no external source of SO_2 need be supplied to the fluid bed roaster.

The roasted ore is collected at 8, water quenched in quench tank 6, and the metal values of interest are leached in, e.g., a 3 stage leach system. Thereafter, the leach liquor is thickened and filtered to remove gangue solids. The thickened pregnant liquor may thereafter be treated to recover the metal values employing conventional techniques, e.g., liquid ion.

The material balances for the process illustrated in FIG. 3 appears below. The composition of concentrate 10 is:

- 18% Cu & Ni
- 23% S
- 24% Fe
- 25% gangue

It should be noted that the material balances which follow can be used to treat a concentrate containing 0-18% copper and 0-18% nickel. However, the total of the copper and nickel for the material balances given is 18% by weight.

In the table below, the numbers to the left correspond to the reference numerals of FIG. 3.

(1)	Concentrate	900 TPD
	Sodium Sulfate	90 TPD
	Potassium Sulfate	45 TPD
	Total	1035 TPD
(15)	Roaster off gases	
(16)	40,000 SCF at 1300°F	
(17)	Sulfuric Acid 380 TPD	
	Calcine at 1300°F	
	1160 TPD	
(23)	Leach Slurry	2730 TPD
	Solids	630 TPD
	Liquid	2100 TPD
(18)	Thickener Overflow	
	1470 TPD Liquid	
(19)	Thickener Underflow	
	1260 TPD solids slurry	

-continued

20)	(30% solids)
	Filtrate from filter
21)	625 TPD Liquid
	Total leach liquor
	2085 TPD
22)	90 gpi Cu
	Gasgas to dump 905 TPD
	Dry analysis 47.6% Fe_2O_3

The invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The present embodiment is therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

What is claimed is:

1. A process for separating non-ferrous metal values from ferrous metal values in an ore containing iron and at least one metal selected from the group consisting of copper, nickel, cobalt, vanadium, and manganese, said process comprising the steps of:

mixing the ore, in particulate sulfide form, with a mixture of inorganic salts, which mixture has a melting point below the roasting temperature of the ore the ratio of salt mixture to ore being at least 0.05;

heating the ore and salt mixture to melt the salt mixture and to form a liquid salt coating on the ore; contacting the ore coated with the liquid salt coating with a roaster gas comprising at least 1% SO_2 and O_2 , the amount of O_2 being sufficient to convert non-ferrous metals to sulfates and the ferrous metals to Fe_2O_3 , said contacting being conducted at a temperature above 650°C . and for a sufficient amount of time to produce non-ferrous metal sulfates and iron oxide; and

separating the non-ferrous metal sulfates from the iron oxide.

2. The process as set forth in claim 1 wherein the roaster gas comprises 1% to 25% SO_2 .

3. The process as set forth in claim 1 wherein the roaster gas comprises 1% to 5% SO_2 .

4. The process as set forth in claim 1 wherein the mixture of inorganic salts has a melting point below 650°C .

5. The process as set forth in claim 1 wherein the salt mixture comprises a mixture of sodium and potassium sulfates.

6. the process as set forth in claim 5 wherein the sodium sulfate-potassium sulfate mole ratio is between 10 and 0.1.

7. The process as set forth in claim 5 wherein the sodium sulfate-potassium sulfate mole ratio is between 1.0 and 0.20.

8. The process as set forth in claim 1 wherein the ratio of salt mixture to ore is between 0.05 and 10.0.

9. The process as set forth in claim 1 wherein the ratio of salt mixture to ore is between 0.1 and 0.25.

10. The process as set forth in claim 1 wherein the salt mixture has a melting point below 650°C . and the ore is heated to a temperature within the range of 650°C . and 800°C .

11. The process as set forth in claim 10 wherein the ore is heated to a temperature within the range of 675°C . and 750°C .

12. The process as set forth in claim 1 wherein the ore contains at least one metal selected from the group consisting of copper and nickel.

13. The process as set forth in claim 1 wherein the ore and liquid salt mixture is contacted with a stoichiometric excess of O_2 .

14. The process as set forth in claim 1 wherein the ore, coated with the liquid salt coating, is contacted with a roaster gas by bubbling the roaster gas through the ore - liquid salt mixture.

15. A process for partitioning non-ferrous metal values from ferrous metal values in an ore containing iron and at least one non-ferrous metal value selected from the group consisting of copper, nickel, cobalt, vanadium, and manganese by selective sulfation of the non-ferrous metal values to render the non-ferrous metal values water leachable, wherein the improvement comprises:

coating ore particles in sulfide form with a mixture of molten sodium and potassium salts; and

reacting the coated particles, at a temperature between 650°C . and 800°C ., with a roaster gas comprising at least 1% SO_2 and at least a stoichiometric equivalent of O_2 to produce Fe_2O_3 and a molten solution of salts which includes at least one non-ferrous metal ion selected from the group consisting of copper, nickel, cobalt, vanadium, and manganese ions.

16. The improved process as set forth in claim 15 wherein the non-ferrous metal values partitioned are selected from the group consisting of copper and nickel.

17. The improved process as set forth in claim 16 wherein the ore particles are coated with a mixture of molten potassium and sodium sulfate.

18. The improved process as set forth in claim 17 wherein the sodium sulfate-potassium sulfate mole ratio of the molten sodium and potassium salt mixture is between 10 and 0.1.

19. The improved process as set forth in claim 17 wherein the sodium sulfate-potassium sulfate mole ratio of the molten sodium and potassium salt mixture is between 1.0 and 0.20.

20. The improved process as set forth in claim 16 wherein the roaster gas comprises between 1% and 25% by volume SO_2 .

21. The improved process as set forth in claim 16 wherein the roaster gas comprises between 1 and 5% SO_2 .

22. The improved process as set forth in claim 16 including the further step of separating the Fe_2O_3 from the sulfate salt which includes a non-ferrous metal ion by utilizing the solubility difference between Fe_2O_3 and the non-ferrous metal sulfate in aqueous solution.

23. A Process for separating metal values selected from the group consisting of copper and nickel from iron in a finely divided sulfide concentrate comprising the steps of:

(A) contacting the sulfide concentrate, at a temperature above 650°C ., with a sufficient amount of a molten mixture of inorganic salts having a melting point below 650°C . to form a liquid salt coating on particles of the ore;

(B) contacting the concentrate coated with the liquid salt coating with a roaster gas comprising oxygen and sulfur trioxide to form molten sulfates including a non-ferrous metal ion selected from the group consisting of copper and nickel and to form iron oxide; and

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(C) water leaching the sulfate salts produced in step B to solubilize the non-ferrous metal ions.

24. The process as set forth in claim 23 wherein the molten mixture of inorganic salts comprises a molten mixture of sodium and potassium sulfates and pyrosulfates are produced during said process.

25. The process as set forth in claim 24 wherein the concentrate contains copper values and wherein the molten mixture of sodium and potassium sulfates comprises a mixture having a mole ratio of sodium sulfate to potassium sulfate between 10 and 0.10.

26. The process as set forth in claim 24 wherein the concentrate contains nickel values and wherein the molten mixture of sodium and potassium sulfates com-

prises a mixture of sodium sulfate and potassium sulfate having a mole ratio of sodium sulfate to potassium sulfate between 1.0 and 0.20.

27. The process as set forth in claim 23 further comprising the step of recovering the non-ferrous metal values from the water leach solution of non-ferrous metal ions produced in step C.

28. The process as set forth in claim 23 further comprising the step of reducing the copper or nickel ion component of the leached sulfate salt to recover at least one metal selected from the group consisting of copper and nickel.

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United States Patent [19]
Tolley et al.

[11] **4,328,192**
[45] **May 4, 1982**

- [54] **AMMONIACAL NICKEL LEACH OF LATERITES**
[75] **Inventors:** William K. Tolley, Arlington Heights; Francisco J. Curral, Des Plaines, both of Ill.
[73] **Assignee:** UOP Inc., Des Plaines, Ill.
[21] **Appl. No.:** 140,048
[22] **Filed:** Apr. 14, 1980
[51] **Int. Cl.³** C01G 53/00
[52] **U.S. Cl.** 423/150; 75/119
[58] **Field of Search** 423/144, 150; 75/119
[56] **References Cited**

U.S. PATENT DOCUMENTS

3,773,424	11/1973	Stevens	423/150
3,845,189	10/1974	Müller	423/150
4,069,294	1/1978	Stevens	423/150

4,187,281 2/1980 Stalter 423/150

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[57] **ABSTRACT**

In a hydrometallurgical process for the recovery of metal values from a metal bearing source in which a metal bearing source is treated at a temperature in the range of from about 300° to about 900° C. in a reducing atmosphere in contact with an additive such as a hydrogen halide and sulfur followed by cooling and extracting the source with a basic or acidic solution, the recovery of the desired metal value may be improved by adding the hydrogen halide to the source at a temperature below about 500° C.

6 Claims, No Drawings

BACKGROUND OF THE INVENTION

Of the several hydrometallurgy approaches used commercially for treating this type of ore, the practice on a highly serpentinic ore, such as at Nicaro, Cuba, involves roasting the ore in a multibarth furnace while a reducing gas, such as producer gas, passes countercurrent to the ore. Temperatures in this case range from about 900° to about 1350° F. Following the roasting step, the ore is cooled in the absence of air, mixed with an ammoniacal ammonium carbonate solution and vigorously agitated and aerated. This results in the dissolution of nickel and cobalt, separating them from the bulk of the ore. This solution then is treated with steam, driving off ammonia and precipitating nickel carbonate.

DESCRIPTION OF THE INVENTION

In one aspect, an embodiment of this invention resides in a process for the recovery of metal values from a metal bearing source which comprises treating said source at a temperature in the range of from about 300° to about 900° C. in a reducing atmosphere and in contact with at least one additive selected from the group consisting of hydrogen halide and a sulfur-containing compound, cooling the thus treated source, extracting the cooled source with a basic or acidic solution, and recovering the resultant metal value, the im-

provement which comprises adding said hydrogen halide to said source at a temperature below about 500° C.

A specific embodiment of this invention is found in a process for the recovery of metal values from a metal bearing source which comprises treating a metal bearing source such as a lateritic ore in a reducing atmosphere, adding hydrogen chloride to the ore at a temperature below about 500° C., thereafter roasting the ore at a temperature in the range of from about 500° to about 900° C., cooling the treated ore, extracting the cooled ore with an ammoniacal ammonium carbonate solution, and recovering the resultant nickel value.

Other objects and embodiments will be found in the following further detailed description of the present invention.

As hereinbefore set forth the present invention is concerned with a method for the hydrometallurgical recovery of metal values from a metal bearing source. The term "metal bearing source" as used in the present application and appended claims will refer to sources such as ore, slag, scrap, etc. In the interest of brevity, it is to be understood that reference to ore in the present specification will also include reference to the other metal bearing sources hereinbefore set forth. The improved process for the recovery of a desired metal value is particularly applicable to the recovery of nickel from such sources. However, it is to be understood that the process may also be used for the recovery of other metal values including, for example, copper, cobalt, manganese, etc.

The hydrometallurgical recovery of metal values may be effected utilizing conventional apparatus and in addition may utilize some conventional steps which have been set forth in prior art processes. Accordingly, the ore such as a lateritic nickel ore or other metal bearing source is first prepared in a manner suitable for the process, whereby the ore is subjected subject to treatment in order to form finely divided or comminuted particles, said grinding or other treatment being any which are well known in the art. The particles may be within a size range of from 35 to about 325 mesh or less and preferably within a range of from about 48 to about 200 mesh. The ground particles are then dried in a conventional manner in order to lower the moisture content of said particles of from about the usual 25 to 50% down to about 8 to 10% or less. The drying step is generally effected by treating the particles in a rotary kiln at conventional temperatures.

Following the drying of the particles, said particles are then roasted at a temperature in the range of from about 300° up to about 900° C., said roasting being effected in a reducing atmosphere and in contact with at least one additive, the presence of said additive preventing the incorporation of nickel into a phase which will make it unavailable and which will at a later point enable the nickel to be recovered from the extraction step in a higher percentage. By roasting the ore in a reducing atmosphere in the presence of additives at this temperature, the magnesium compounds which are present will be prevented from converting to magnesium silicate in the form of forsterite, which formation usually acts to reduce the amount of nickel in an extractable form. The reducing zone in which the ore is roasted may be of conventional nature and may include, for example, a multihearth furnace, a fluo-solids roaster, a Herreshoff furnace, etc. The reduction of the ore is effected by means of a suitable reducing gas mixture which, if so desired, may be of the general type which is used in

conventional processes. Any suitable reducing gas mixture may be used and preferably comprises a mixture of hydrogen, carbon monoxide, carbon dioxide and water vapor. The gaseous mixture may come from any suitable source such as producer gas, gases formed by the combustion of city gas, gases formed by combustion of oil, etc. The specific gaseous mixture will be selected to effect the desired reduction of the nickel compounds to an extractable state. As an example, an illustrative gas mixture comprises a CO:CO₂ ratio within the range of from about 0.1 to 10:1, a CO:H₂ ratio of from about 0.1:1 to 10:1 and a H₂:H₂O vapor ratio of from about 1.1:1 to 10:1, all being on a volumetric basis. In one embodiment, it is desirable to maintain the gas mixture within the ratios set forth above because an excessive concentration of one or more of the components in the gas mixture may have undesired effects such as, for example, incomplete reduction of the metal compound to the metallic state, excessive absorption of the gas in the ore particles, etc. It is to be understood that the gas mixture may contain other components as, for example, nitrogen, when advantages appear therefor. Other illustrative gas mixtures comprise hydrogen, nitrogen and water vapor or natural gas.

The roasting of the ore in a reducing atmosphere is effected in the presence of at least one additive, and preferably a combination of additives. One of the additives which is present in the roasting step comprises a hydrogen halide, examples of hydrogen halides which may be employed including hydrogen halide gases such as hydrogen chloride gas, hydrogen bromide gas, hydrogen iodide gas, or hydrogen fluoride gas, the latter two being used but not necessarily with equivalent results. It is also contemplated within the scope of this invention that precursors of hydrogen halide may be introduced into the roasting zone in a manner hereinafter set forth in greater detail and converted to hydrogen halide. Some examples of these precursors which may be employed will include boron trichloride, boron tribromide, boron trifluoride, carbon tetrachloride, carbon tetrabromide, carbon tetrafluoride, phosphorous tribromide, phosphorous pentachloride, phosphorous trifluoride, phosphorous pentafluoride, silicon tetrachloride, silicon tetrabromide, methyl chloride, methylene chloride, methyl bromide, methylene bromide, methyl iodide, ethyl chloride, dichloroethylene, dibromoethylene, vinyl chloride, vinyl bromide, etc. At the relatively high temperatures which are encountered in the roasting step, the precursor will be decomposed to liberate the hydrogen halide or the halogen which is then reduced to the hydrogen halide form. Other additives which are employed will include sulfur or sulfur compounds. The sulfur may be in gaseous form or may be in solid form including powder, flour, granules, pellets, etc., or molten or otherwise liquefied sulfur. Examples of sulfur-containing compounds will include pyrite, methyl xanthate, ethyl xanthate, propyl xanthate, butyl xanthate, pentyl xanthate, hexyl xanthate, etc., or metal salts thereof such as sodium methyl xanthate, potassium methyl xanthate, calcium ethyl xanthate, sodium propyl xanthate, sodium butyl xanthate, sodium hexyl xanthate, potassium hexyl xanthate, etc. When utilizing sulfur as the additive the sulfur may be admixed with the ore at an elevated temperature as it is being withdrawn from the drying step. The sulfur is usually present in an amount ranging from a concentration of from about 0.1 to about 5% and preferably from about 0.15 to about 3% by weight of the ore. It is to be understood that any

suitable means of introducing the sulfur-containing compound into the reducing zone may be utilized.

As hereinbefore set forth, it has now been discovered that by effecting the addition of the hydrogen halide compound at a relatively low temperature it is possible to attain improved yields of the desired metal value. While the reductive roast of the metal bearing source is effected at temperatures in the range hereinbefore set forth, that is, from about 300° to about 900° C. the hydrogen halide which is to constitute one of the additives present in the reductive roast is added during the initial stages of the roast and preferably is added at a period prior to the point at which the temperature of the roasting step reaches about 300° C., and preferably at a temperature within the range of from about 360° to about 500° C. The concentration of hydrogen halide which is used as an additive in the roasting step will range from about 0.001 to about 2% and preferably from about 0.01 to about 1.5% by weight of the source such as an ore. In the event that the hydrogen halide is in gaseous form, it may be added in any suitable manner including direct addition to the hydrogen halide gas into the roasting zone. In the event that the hydrogen halide is in aqueous form such as hydrochloric acid, hydrobromic acid, etc., the reducing gas of the composition hereinbefore set forth may be bubbled through an aqueous solution of the hydrogen halide and thus the hydrogen halide is carried into the reducing zone in this manner. In another embodiment the free halogen such as chlorine, bromine, etc., may be injected directly into the roasting zone wherein, upon contact with the reducing gas, it may be rapidly converted to the corresponding hydrogen halide. By adding the hydrogen halide additive to the reduction zone in such a manner and at such a temperature, that is, below about 500° C., it is possible, as will hereinafter be shown in greater detail, to obtain an improved extraction yield of desired metal values such as nickel.

After roasting in the reducing atmosphere and in contact with additives such as those hereinbefore set forth, the particles are withdrawn from the reducing zone, cooled and processed in a conventional manner for the hydrometallurgical extraction of the desired metal value such as nickel, cobalt, etc. The cooling is done by reducing the temperature several hundred degrees preferably under a nitrogen blanket in order to avoid the possibility of oxidation of the metals to the oxide or to other oxygen-containing forms. The leaching of the metal value may be effected in either a basic or acidic solution. For example, the quench liquid which is employed may comprise an ammoniacal ammonium carbonate or an ammoniacal ammonium chloride solution while the acidic solution may comprise aqueous inorganic acids such as hydrochloric acid, hydrobromic acid, nitric acid, phosphoric acid, sulfuric acid, the preferred acids being hydrochloric or sulfuric due to the greater availability thereof. In addition, the quenching or leaching of the metal source is also effected in the absence of oxygen in order to avoid the possibility of the oxidation of the metal. The leaching of the metal source is effected at temperatures below about 95° C. and is preferably effected at ambient temperature. After leaching for a period of time which may range from about 30 minutes to about 2.5 hours or more, the solution of the desired metals is withdrawn from the leaching or extraction zone and thereafter treated in any suitable manner to precipitate the desired metal values such as nickel, cobalt, etc., and to recover the same.

One method of accomplishing this precipitation, when utilizing a basic leach, is to steam heat the solution to precipitate the nickel carbonate and to volatilize off ammonia, carbon dioxide and water. Other methods will include neutralization, cementation, solvent extraction, electrolysis, etc.

As will hereinafter be shown in greater detail by utilizing the process of the present invention including the introduction of the hydrogen halide to the metal source at a temperature below about 500° C., it will be possible to attain a greater yield of the desired metal than is possible when treating the metal source during the roasting step in a reducing atmosphere at a temperature above 500° C.

The following examples are given for purposes of illustrating the process of this invention. However, it is to be understood that these examples are merely illustrative in nature, and that the present invention is not necessarily limited thereto.

EXAMPLE I

A series of experimental runs was made utilizing a lateritic ore having the following assay:

	%
Ni	1.24
Co	0.14
Fe	36.9
SiO ₂	14.7
Al ₂ O ₃	2.1
MgO	5.4

In the first series 50 gram samples were mixed with 0.5 grams of sulfur and placed in a quartz furnace tube. The tube was then purged with nitrogen and placed into a furnace which was preheated to 360° C. and roasted for a period of 10 minutes. After being roasted at 360° the ore was roasted for a second 10 minute period at this temperature under a flow of reducing gas having the following composition:

Gas	ML/min.
N ₂	369
H ₂	291
CO ₂	214
CO	97
H ₂ O	2

In addition 40 ml/min. of hydrogen chloride was added to this gas stream. At the end of the 10 minute period the introduction of hydrogen chloride was discontinued and the temperature was increased at a constant rate from 360° to 780° C. during a period of 33 minutes. Upon completion of the 33 minute reduction period the furnace tube was removed from the furnace and cooled while maintaining the reduced ore sample under a slight flow of dry nitrogen. After cooling, the reduced ore was transferred to leaching under a nitrogen pressure and leached for a period of 2.5 hours utilizing ammoniacal ammonium carbonate as the leaching agent. At the end of the 2.5 hour period during which the slurry was vigorously agitated, the mixture was filtered, the filtrate was then assayed for nickel content which disclosed a 91.5% extraction of the nickel.

When the experiment was repeated two more times and the hydrogen chloride gas was charged during the first 10 minute roast at 360° C. in the first run and in the

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second run was charged to the furnace during the first portion of the 33 minute reduction period while the furnace temperature was being raised from 360° to 500° C., nickel extractions of 91.2% and 90.3% were obtained.

EXAMPLE II

The above experimental runs were again repeated by treating a lateritic ore of the composition set forth in Example I above to a reductive roast utilizing a reducing gas of the same composition as hereinbefore set forth. Again the lateritic ore was placed in a quartz furnace tube after admixture with sulfur, the tube was purged with nitrogen and placed into a furnace which had been preheated to 360° C. After roasting the ore for a period of 10 minutes the reducing gas was charged thereto and the ore again roasted for a period of 10 minutes at this temperature. The temperature of the furnace was then raised at a constant temperature rate from 360° to 780° C. During the last two 10 minute periods of the roast during which time the temperature of the ore was in a range of from 500° to 780° C. 40 ml/min. of hydrogen chloride was added to the gas stream which was passing over the lateritic ore. In the first run during which time the hydrogen chloride gas was passed during the middle 10 minute period of the 33 minute reduction period, analysis of the ore which was recovered after ammoniacal ammonium carbonate leaching disclosed that there had been an 88.5% extraction and when the hydrogen chloride gas was passed into the reductive roast during the last 10 minute period when the temperature was approaching 780° C., there was an 88.3% extraction of the nickel.

EXAMPLE III

As a comparison the above experimental run was repeated utilizing a lateritic ore of similar composition and a reducing gas of similar composition to those hereinbefore set forth. Similar conditions were employed to those hereinbefore set forth in the above examples. However, the difference was that the hydrogen chloride additive was charged to the furnace during the entire 30 minute reduction period during which time the temperature was being raised from 360° C. to 780° C. Assay of the filtrate after treating the ore to an ammoniacal ammonium carbonate leach for a period of 2.5 hours determined that there had been a 91.0% nickel

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extraction. It is to be noted that this is the same extraction for nickel that had been obtained when the ore was chlorinated for only the first 10 minutes of the reduction ore when the hydrogen chloride was added in either prior 10 minute period, each addition being made when the temperature was in a range of from 360° to 500° C. This illustrates the fact that short periods of exposure to the additive at relatively low temperatures result in the extraction of a similar amount of nickel as can be obtained when subjecting the ore to longer periods of exposure to additive at higher temperatures, that is, above about 500° C. By utilizing the process of the present invention, it is possible to effect a similar extraction of nickel using a smaller amount of hydrogen halide additive thus reducing the expense of the entire operation with the concurrent recovery of metal values at a lower cost.

We claim as our invention:

1. A process for the increase in the recovery of nickel metal values from a lateritic ore which comprises treating said ore first with at least one additive selected from the group consisting of hydrogen halide, elemental sulfur and a sulfur containing compound in a reducing atmosphere at a temperature beginning at about 360° C. and extending to below 500° C. for a period of time of not less than 10 minutes while said temperature is held to below 500° C. and then increasing said temperature after said passage of not less than 10 minutes up to about 900° C., cooling said treated ore and additive, extracting said increased amount of nickel metal values from said treated and cooled ore with a basic ammoniacal leaching solution, and recovering said resultant increased amount of nickel metal values.
2. The process as set forth in claim 1 in which said hydrogen halide is hydrogen chloride.
3. The process as set forth in claim 1 in which said hydrogen halide is hydrochloric acid.
4. The process as set forth in claim 1 in which said elemental sulfur is gaseous sulfur.
5. The process as set forth in claim 1 in which said basic leaching solution is an ammoniacal ammonium carbonate.
6. The process as set forth in claim 1 in which said basic leaching solution is an ammoniacal ammonium chloride.

* * * * *

Roste

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⑤ Verfahren zum Rösten refraktärer Golderze

⑥ Refraktäre Golderze werden in oxidierender Atmosphäre
in einer Wirbelschicht unter Zusatz von Brennstoffen bei
einer Temperatur von 450 bis 850°C unter Zufuhr von
sauerstoffhaltigen Gasen geröstet. Zur Erzielung einer nied-
rigen Rösttemperatur werden Schwefel und/oder Pyrit als
Brennstoff zugegeben.

S zur Temperaturerregung
H₂, CO?

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Beschreibung

Die Erfindung betrifft ein Verfahren zum Rösten refraktärer Golderze in oxidierender Atmosphäre in einer Wirbelschicht unter Zusatz von Brennstoffen.

5 Refraktäre Golderze sind solche Erze, die sich nicht direkt mit NaCN laugen lassen und als Goldträger Arsenopyrite oder Pyrite mit mehr oder weniger organischem Kohlenstoff enthalten. Sie haben einen relativ niedrigen Goldgehalt. Für solche Erze ist vor der Cyanidlaugung eine möglichst vollständige Oxidation des Schwefel- und Kohlenstoffgehaltes erforderlich. Diese Oxidation erfolgt durch Röstung mit sauerstoffhaltigen Gasen. Bei vielen refraktären Golderzen reicht der vorhandene Gehalt an Arsenopyrit, Pyrit und organischem Kohlenstoff nicht zur Erzeugung der erforderlichen Reaktionswärme aus, und es muß Brennstoff zugesetzt werden. Eine Vielzahl von refraktären Golderzen muß bei relativ niedriger Temperatur geröstet werden, damit ein gutes Goldausbringen bei der anschließenden Laugung erzielt wird.

10 Aus der EP-A 0 508 542 ist bekannt, daß Golderze bei einer Temperatur von 475 bis 600°C und insbesondere bei 500 bis 575°C geröstet werden sollen. Als Brennstoffzusatz werden Kohle, Butan oder Propan genannt. Die Zündtemperatur soll dem des Propanes entsprechen oder niedriger liegen. Propan und Butan werden jedoch nur zu einem unbefriedigenden Teil zu CO₂ und H₂O verbrannt. Bei der Verbrennung entstehen erhebliche Mengen an CO mit einer Zündtemperatur von 600 bis 650°C und H₂ mit einer Zündtemperatur von 560 bis 580°C.

15 Golderze erfordern eine schonende Röstung, um Erhitzungen an der Partikeloberfläche zu vermeiden. Die Goldausbeute ist u. a. stark von der Rösttemperatur abhängig. Die Rösttemperatur muß unterhalb der Versinterungstemperatur der Bestandteile des jeweiligen Erzes gehalten werden.

20 Die meisten Golderze weisen niedrige Anteile an Pyrit und/oder anorganischem Kohlenstoff auf. Bedingt durch Wärmeverluste, die beim Aufheizen entstehen, durch Abgasverluste sowie Austragsverluste und dergleichen reicht der im Golderz enthaltene Heizwert nicht aus, um eine autotherme Röstung selbst bei Temperaturen von etwa nur 500°C durchzuführen. Daher ist der Einsatz von zusätzlichem Brennstoff mit einer niedrigen Zünd- und Verbrennungstemperatur erforderlich, um die Goldausbeute nicht zu verringern.

25 Der Erfindung liegt die Aufgabe zugrunde, einen Brennstoff einzusetzen, der bei niedrigen Temperaturen zuverlässig zündet und bei dessen Verbrennung keine oder niedrige Anteile an CO, H₂ und Kohlenwasserstoffen im Abgas vorhanden sind.

30 Die Lösung der Aufgabe erfolgt erfindungsgemäß bei dem eingangs genannten Verfahren dadurch, daß als Brennstoff Schwefel und/oder Pyrit in die Wirbelschicht zugegeben werden und die Röstung bei Temperaturen von 400 bis 650°C unter Zufuhr von sauerstoffhaltigen Gasen erfolgt. Der Vorteil des erfindungsgemäßen Verfahrens liegt darin, daß CO, H₂ und Kohlenwasserstoffe bei der Verbrennung von Schwefel und/oder Pyrit nicht gebildet werden.

35 Schwefel und Pyrit zeigen eine überraschend zuverlässige Zündbereitschaft bei niedrigen Rösttemperaturen. Schwefel brennt im Temperaturbereich von 200 bis 300°C, Pyrit brennt im Temperaturbereich von 450 bis 600°C. Die Zugabe von Schwefel und/oder Pyrit kann durch vorherige Mischung mit dem Golderz oder direkt in die Wirbelschicht erfolgen.

40 Die Röstung refraktärer Golderze erfolgt erfindungsgemäß in einer klassischen oder in einer zirkulierenden Wirbelschicht. Die sauerstoffhaltigen Gase werden als Fluidisierungsgas unterhalb des Düsenbodens in die Wirbelschicht eingeleitet. Erfindungsgemäß ist vorgesehen, daß sauerstoffhaltige Gase zusätzlich als Primär- und Sekundärgas seitlich in den Wirbelschichtreaktor eingeleitet werden können. Die sauerstoffhaltigen Gase sind Luft oder sauerstoffangereicherte Luft.

Eine bevorzugte Ausgestaltung besteht darin, daß die Röstung bei Temperaturen von 500 bis 550°C erfolgt. Bei diesen Temperaturen werden besonders gute Goldausbeuten erzielt.

45 Eine bevorzugte Ausgestaltung der Erfindung besteht darin, daß als Brennstoff Schwefel und/oder Pyrit und mindestens ein zusätzlicher Brennstoff, ausgewählt aus Kohlenwasserstoffen mit einer C-Atomzahl von 1 bis 16, Alkoholen mit einer C-Atomzahl von 1 bis 6 und einer OH-Gruppenzahl von 1 bis 2, organischen Äthern mit einer C-Atomzahl von 2 bis 8 und einer O-Atomzahl von 1, CS₂ oder H₂S in die Wirbelschicht zugegeben werden. Durch das gemeinsame Verbrennen von Schwefel und/oder Pyrit mit einem oder mehreren dieser zusätzlichen Brennstoffe wird die Zündtemperatur dieser Brennstoffe herabgesetzt, wenn die Zündtemperatur dieser zusätzlichen Brennstoffe höher liegt als die Zündtemperatur von Schwefel oder Pyrit. Das bedeutet, daß sie in einem solchen Gemisch schneller zünden und leichter verbrennen. Liegt die Zündtemperatur eines dieser zusätzlichen Brennstoffe niedriger als die Zündtemperatur von Schwefel oder Pyrit, so wird die Zündtemperatur von Schwefel oder Pyrit im Gemisch mit einem solchen zusätzlichen Brennstoff herabgesetzt.

50 Im Gemisch mit Schwefel und/oder Pyrit muß die Konzentration der zusätzlichen Brennstoffe höher liegen als die Konzentration für die untere Zündgrenze dieser Brennstoffe. Die untere Zündgrenze eines Brennstoffes bedeutet die Mindestkonzentration, mit der ein Brennstoff im Gasgemisch vorliegen muß, damit noch eine Zündung des Brennstoffes erfolgt. Die zusätzlichen Brennstoffe werden oberhalb ihrer Zündgrenze zugegeben, wenn der Wärmeinhalt im Reaktor nicht ausreicht, um die erforderliche Rösttemperatur zu erreichen. Der Wärmeinhalt im Reaktor ist gegeben durch die in refraktären Golderzen vorhandenen Mengen an Kohlenstoff und Schwefel und durch die Menge des als Brennstoff zugegebenen Schwefels und/oder Pyrits. Die Rösttemperatur kann somit durch Dosierung der zusätzlichen Brennstoffe gesteuert werden. Die zusätzlichen Brennstoffe werden in solchen Mengen zugegeben, daß die Rösttemperatur 650°C, vorzugsweise 550°C, nicht übersteigt und das Abgas aus der Wirbelschicht einen H₂-Gehalt von < 10 vppm, vorzugsweise < 5 vppm, einen CO-Gehalt von < 0,1 Vol.-%, vorzugsweise < 100 vppm, und einen Kohlenwasserstoffgehalt von < 100 vppm, vorzugsweise < 50 vppm, aufweist.

55 Als zusätzliche Brennstoffe werden Kohlenwasserstoffgemische, die als Destillationsfraktionen, wie z. B. Kerosin usw. oder Raffinerie-Abfallprodukte anfallen, verwendet. Neben Kohlenwasserstoffgemischen werden

als zusätzliche Brennstoffe auch Alkoholgemische, die bei der Destillation von Äthanol als Abfallprodukte anfallen, verwendet.

Eine bevorzugte Ausgestaltung der Erfindung besteht darin, daß die Korngröße des Golderzes unter 1 mm liegt. Diese Korngröße ergibt gute Ergebnisse.

Eine bevorzugte Ausgestaltung der Erfindung besteht darin, daß 60 bis 90% des Golderzes eine Korngröße unter 75 µm aufweisen. Diese Korngröße ergibt besonders gute Ergebnisse. Der Begriff "Korngröße" steht für den mittleren Korndurchmesser d_{50} .

Eine bevorzugte Ausgestaltung der Erfindung besteht darin, daß der O_2 -Gehalt in dem Gas, das in die Wirbelschicht eingeleitet wird, 20 bis 50 Vol.-% beträgt. Die sauerstoffangereicherte Luft ergibt eine bessere Zündung des Brennstoffgemisches. Die Verwendung der sauerstoffangereicherten Luft ist besonders wirtschaftlich.

Der Vorteil des Einsatzes der zusätzlichen Brennstoffe liegt darin, daß sie bei niedriger Temperatur weitgehend verbrennen, die Anteile an CO , H_2 und Kohlenwasserstoffen im Abgas sehr niedrig sind und daher nicht durch Nachverbrennung aus dem Abgas entfernt zu werden brauchen. Bei einer nachfolgenden Schwefelsäure-Herstellung ist es günstig, daß die Anteile an CO , H_2 und Kohlenwasserstoffen sehr niedrig sind, da diese Stoffe bei der Oxidation von SO_2 zu SO_3 als Katalysatorgifte wirken.

Eine bevorzugte Ausgestaltung der Erfindung besteht darin, daß ein Teilstrom des Abgases nach der Entstaubung des heißen Abgases abgezweigt wird und dem Fluidisierungsgas vor der Einleitung in die Wirbelschicht zugemischt wird. Durch die Rückführung eines Teils des Abgases und Vermischen mit dem Fluidisierungsgas wird erreicht, daß das Fluidisierungsgas aufgewärmt wird. Durch die Kreislaufführung eines Teils des Abgases wird eine Anreicherung von SO_2 im Abgas erhalten.

Eine bevorzugte Ausgestaltung der Erfindung besteht darin, daß das beim Rösten refraktärer Golderze gebildete und im Abgas abgeführte SO_2 -Gas der Schwefelsäure-Herstellung zugeführt wird. Das erfindungsgemäße Verfahren wird dadurch zusätzlich wirtschaftlich, daß das bei der Röstung gebildete und mit dem Abgas abgeführte SO_2 -Gas ohne Nachverbrennung der Schwefelsäure-Herstellung zugeführt werden kann. Es ist vor der Einleitung des SO_2 -Gases in die Schwefelsäure-Herstellungsanlage eine Gaswäsche vorgesehen.

Eine bevorzugte Ausgestaltung der Erfindung besteht darin, daß die Röstung in einer zirkulierenden Wirbelschicht erfolgt.

Das System der zirkulierenden Wirbelschicht besteht aus dem Wirbelschichtreaktor, dem Rückführzyklon und der Rückführleitung. Dieses Wirbelschichtprinzip zeichnet sich dadurch aus, daß im Unterschied zur "klassischen" Wirbelschicht, bei der eine dichte Phase durch einen deutlichen Dichtesprung von dem darüber befindlichen Gasraum getrennt ist, Verteilungszustände ohne definierte Grenzschicht vorliegen. Ein Dichtesprung zwischen dichter Phase und darüber befindlichem Staubraum ist nicht vorhanden, jedoch nimmt innerhalb des Reaktors die Feststoffkonzentration von unten nach oben ständig ab. Aus dem oberen Teil des Reaktors wird eine Gas-Feststoff-Suspension ausgetragen. Bei der Definition der Betriebsbedingungen über die Kennzahlen von Froude und Archimedes ergeben sich die Bereiche:

$$0,1 \leq \frac{3}{4} \cdot Fr^2 \cdot \frac{\rho_g}{\rho_k - \rho_g} \leq 10,$$

bzw.

$$0,01 \leq Ar \leq 100,$$

wobei

$$Ar = \frac{d_k^3 \cdot g (\rho_k - \rho_g)}{g \cdot \gamma^2} \quad \text{und}$$

$$Fr^2 = \frac{u^2}{g \cdot d_k}$$

sind.

Es bedeuten:

u die relative Gasgeschwindigkeit in m/sec,
 Ar die Archimedes-Zahl,
 Fr die Froude-Zahl,
 ρ_g die Dichte des Gases in kg/m³,
 5 ρ_k die Dichte des Feststoffteilchens in kg/m³,
 d_k den Durchmesser des kugelförmigen Teilchens in m,
 ν die kinematische Zähigkeit in m²/sec,
 g die Gravitationskonstante in m/sec².

10 Die aus dem Wirbelschichtreaktor ausgetragene Suspension wird in den Rückführzyklon der zirkulierenden Wirbelschicht geleitet, dort weitgehend vom Feststoff befreit, und der abgeschiedene Feststoff wird derart in den Wirbelschichtreaktor zurückgeleitet, daß innerhalb der zirkulierenden Wirbelschicht der stündliche Feststoffumlauf mindestens das Vierfache des im Wirbelschichtreaktor befindlichen Feststoffgewichtes beträgt.
 Die Erfindung wird anhand der Beispiele erläutert.

Beispiel 1

Es wurde ein refraktäres Golderz mit einem Goldgehalt von 8 g/t und 1,8 Gew.-% Schwefel, der als Pyrit vorlag, und 0,08 Gew.-% Kohlenstoff eingesetzt. Die Korngröße betrug $d_{50} = 30 \mu\text{m}$ und $100\% < 200 \mu\text{m}$.

20 Die Röstanlage war eine zirkulierende Wirbelschichtanlage, hauptsächlich bestehend aus dem Wirbelschichtreaktor, einem Rückführzyklon, der direkt an den Gasaustritt am Oberteil des Reaktors angeschlossen war, und einer Rückführleitung. Der im Zyklon abgeschiedene Feststoff wurde über die Rückführleitung in den Reaktor zurückgeführt.

Es wurde ein Gemisch aus 48 g Pyrit pro kg Erz hergestellt. Dann wurden 40 kg/h des hergestellten Gemisches über eine Falleitung in den Wirbelschichtreaktor aufgegeben.

In den Windkasten des Wirbelschichtreaktors wurden 22 Nm³/h Luft mit 21 Vol.-% O₂ mit einer Temperatur von 400°C eingeleitet. Das Trägergas strömte durch die Öffnungen des Auströmbodens. Die Temperatur im Reaktor betrug 520°C. Das Röstgas hatte einen Gehalt von 3,3 Vol.-% SO₂, 0,2 Vol.-% CO₂, 20 vppm CO und 16,3 Vol.-% O₂. Die Gehalte an H₂ und Kohlenwasserstoffen lagen unterhalb der Nachweisgrenze von 1 vppm.

30 Nach einer alkalischen Waschung des Abgases wurde das von SO₂ befreite Abgas in den Kamin geleitet. Das Röstgut hatte einen Schwefelgehalt von < 0,05 Gew.-% und einen Kohlenstoffgehalt von < 0,01 Gew.-%. Bei der Weiterverarbeitung wurde eine Goldausbeute von 94% erzielt.

Beispiel 2

35 Beispiel 2 wurde wie Beispiel 1 durchgeführt, mit dem Unterschied, daß das Trägergas 32 Vol.-% O₂ und durch zurückgeführtes Abgas 7 Vol.-% SO₂ enthielt. In den Wirbelschichtreaktor wurde ein Gemisch aufgegeben, das 50 g Schwefel pro kg Erz enthielt. Das Röstgas hatte einen Gehalt von 12,7 Vol.-% SO₂, 0,1 Vol.-% CO₂, 5 vppm CO und 24,2 Vol.-% O₂. Die Gehalte an H₂ und Kohlenwasserstoffen lagen unterhalb der Nachweisgrenze von 1 vppm. Das Röstgut hatte einen Schwefelgehalt von < 0,04 Gew.-% und einen Kohlenstoffgehalt von < 0,01 Gew.-%. Bei der Weiterverarbeitung wurde eine Goldausbeute von 96% erzielt.

Das in den Beispielen 1 und 2 verwendete Golderz hatte die folgende Zusammensetzung:

8 g/t Au
 45 3,3 Gew.-% FeS₂
 0,07 Gew.-% Fe[AsS].

Der im Beispiel 1 verwendete Pyrit hatte die folgende Zusammensetzung:

50 91 Gew.-% FeS₂
 2 Gew.-% FeS
 7 Gew.-% SiO₂, Al₂O₃ und restliche Bestandteile.

Der im Beispiel 2 verwendete Schwefel hatte die folgende Zusammensetzung:

55 98 Gew.-% S
 2 Gew.-% Verunreinigung.

Patentansprüche

60 1. Verfahren zum Rösten refraktärer Golderze in oxidierender Atmosphäre in einer Wirbelschicht unter Zusatz von Brennstoffen, dadurch gekennzeichnet, daß als Brennstoff Schwefel und/oder Pyrit in die Wirbelschicht zugegeben werden und die Röstung bei Temperaturen von 400 bis 650°C unter Zufuhr von sauerstoffhaltigen Gasen erfolgt.

65 2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Röstung bei Temperaturen von 500 bis 550°C erfolgt.

3. Verfahren nach den Ansprüchen 1 oder 2, dadurch gekennzeichnet, daß als Brennstoff Schwefel und/oder Pyrit und mindestens ein zusätzlicher Brennstoff, ausgewählt aus Kohlenwasserstoffen mit einer C-Atom-

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zahl von 1 bis 16, Alkoholen mit einer C-Atomzahl von 1 bis 6 und einer OH-Gruppenzahl von 1 bis 2, organischen Äthern mit einer C-Atomzahl von 2 bis 8 und einer O-Atomzahl von 1, CS₂ oder H₂S in die Wirbelschicht zugegeben werden.

4. Verfahren nach den Ansprüchen 1 bis 3, dadurch gekennzeichnet, daß die Korngröße des Golderzes unter 1 mm liegt.

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5. Verfahren nach den Ansprüchen 1 bis 4, dadurch gekennzeichnet, daß 60 bis 80% des Golderzes eine Größe unter 75 µm aufweisen.

6. Verfahren nach den Ansprüchen 1 bis 5, dadurch gekennzeichnet, daß der O₂-Gehalt in dem Gas, das in die Wirbelschicht eingeleitet wird, 20 bis 50 Vol.-% beträgt.

7. Verfahren nach den Ansprüchen 1 bis 6, dadurch gekennzeichnet, daß ein Teilstrom des Abgases nach der Entstaubung des heißen Abgases abgezweigt wird und dem Fluidisierungsgas vor der Einleitung in die Wirbelschicht zugemischt wird.

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8. Verfahren nach den Ansprüchen 1 bis 7, dadurch gekennzeichnet, daß das beim Rösten refraktärer Golderze gebildete und im Abgas abgeführte SO₂-Gas der Schwefelsäure-Herstellung zugeführt wird.

9. Verfahren nach den Ansprüchen 1 bis 8, dadurch gekennzeichnet, daß die Röstung in einer zirkulierenden Wirbelschicht erfolgt.

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Doctor(a)
GUSTAVO HOLLMANN RESTREPO.
Apoderado(a)

Oficio N° 04942

ASUNTO:	Radicación N°	04-33866
	Solicitud internacional	PCT/DE02/03394
	Fecha inicio fase nacional	14/04/2004
	Trámite	011
	Evento	379
	Actuación	416
	Folios	001

Como resultado del examen de forma, realizado con fundamento en el artículo 38 de la Decisión 486 de la Comisión de la Comunidad Andina, artículo 27 del Tratado de Cooperación en Materia de Patentes (PCT), regla 51 bis del Reglamento y Circular Única de la Superintendencia de Industria y Comercio, se le comunica que:

- -La solicitud no contiene copia del documento en que consta la cesión del derecho de patente del inventor al solicitante o a su causante (Art. 26-k) Decisión 486).
- La solicitud no contiene el poder debidamente otorgado, con el lleno de requisitos exigidos por los artículos 63 y subsiguientes del Código de Procedimiento Civil. Adicionalmente deberá presentar el documento que acredita la existencia y representación legal de la sociedad solicitante, cuando éste fuere una persona jurídica.

En cumplimiento de lo dispuesto por el artículo 39 de la Decisión 486, se le requiere para que dentro del término de dos meses siguientes a la fecha de notificación del presente oficio, complete los requisitos anteriormente enunciados. En caso de no dar cumplimiento al presente requerimiento, la solicitud se considerará abandonada y perderá su prelación.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única N° 10 de 2001.


ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe de la División de Nuevas Creaciones.

31 4 MAYO 2004

El anterior requerimiento fue notificado por fijación en lista de fecha, _____
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