厦门大学

博　士　学　位　论　文

低金硫比高砷金精矿生物搅拌预氧化-提金

和堆浸选择性脱砷的研究

Research on stirred-biooxidation as pretreatment for
extracting gold and selectively heapbioleaching arsenic from
a low Au/S ratio but high-arsenic pyrite concentrate

胡　杰　华

指导教师姓名：龙敏南　教授
专　业　名　称：环　境　工　程
论文提交日期：**2017 年 11 月**
论文答辩时间：**2017 年 12 月**

2017年12月

厦门大学学位论文原创性声明

本人呈交的学位论文是本人在导师指导下, 独立完成的研究成果。本人在论文写作中参考其他个人或集体已经发表的研究成果, 均在文中以适当方式明确标明, 并符合法律规范和《厦门大学研究生学术活动规范（试行）》。

另外, 该学位论文为（   ）课题（组）的研究成果, 获得（   ）课题（组）经费或实验室的资助, 在（   ）实验室完成。（请在以上括号内填写课题或课题组负责人或实验室名称, 未有此项声明内容的, 可以不作特别声明。）

本人声明该学位论文不存在剽窃、抄袭等学术不端行为, 并愿意承担因学术不端行为所带来的一切后果和法律责任。

声明人　（签名）:
指导教师（签名）:

年　　月　　日

厦门大学学位论文著作权使用声明

　　本人同意厦门大学根据《中华人民共和国学位条例暂行实施办法》等规定保留和使用此学位论文，并向主管部门或其指定机构送交学位论文（包括纸质版和电子版），允许学位论文进入厦门大学图书馆及其数据库被查阅、借阅。本人同意厦门大学将学位论文加入全国博士、硕士学位论文共建单位数据库进行检索，将学位论文的标题和摘要汇编出版，采用影印、缩印或者其它方式合理复制学位论文。

　　本学位论文属于：

　　（　　　　）1.经厦门大学保密委员会审查核定的保密学位论文，于　　年　　月　　日解密，解密后适用上述授权。

　　（　　　　）2.不保密，适用上述授权。

　　（请在以上相应括号内打"√"或填上相应内容。保密学位论文应是已经厦门大学保密委员会审定过的学位论文，未经厦门大学保密委员会审定的学位论文均为公开学位论文。此声明栏不填写的，默认为公开学位论文，均适用上述授权。）

　　　　　　　　　　　　　　　　声明人（签名）：

　　　　　　　　　　　　　　　　　　　年　　月　　日

摘　要

本文针对低 Au/S 比、高硫、高砷难处理金精矿，围绕生物搅拌预氧化-氰化提金和生物柱浸降砷两条技术路线开展工作，重点研究了生物搅拌预氧化间歇单槽试验与连续试验氧化效果、差异及其机理；生物柱浸氧化富硫层的生成、消替以及砷选择性优先浸出的机理。在实验研究的基础上，考察了它们的应用前景并进行初步技术经济评价。

试验金精矿为低 Au/S 比、高硫、高砷难处理金精矿。其中 GS 金精矿 Au、S、As 含量分别为 18.43 $g \cdot t^{-1}$、40.57%、2.37%，Au/S 比 0.45，73.49%的金为硫化物包裹金，98.85%的 S 为硫化物中的硫。DS 金精矿 Au、S、As 含量分别为 20.62 $g \cdot t^{-1}$、35.01%、2.13%，Au/S 比 0.59，57.74%的金为硫化物包裹金，99.01%的 S 为硫化物中的硫。主要金属矿物是黄铁矿、雌黄铁矿、毒砂；主要脉石是石英、绢云母、长石。

5 L 的间歇单槽烧杯搅拌实验优化生物氧化条件为：DS 金精矿，不磨矿，反应温度 40℃，矿浆浓度 15%，氧化过程 pH 控制在 1.3 左右。20 L 的间歇单槽试验说明金浸出率随氧化时间延长而提高，DS 金精矿，氧化 7 d，金的平均浸出率为 90.28%，氧化程度越高，金浸出率越稳定，平行试验间的误差越小。

模拟连续试验，GS 金精矿，停留时间 6 d，反应温度控制在 45℃左右，不返液，尾渣品位降至 2.15 $g \cdot t^{-1}$，金浸出率达到 90%以上；停留时间 8 d，反应温度控制在 40℃左右，返液 25%，尾渣金品位降至 3 $g \cdot t^{-1}$ 以下，金浸出率 90%以上；缩短停留时间为 6 d，反应温度控制在 40℃左右，返液 25%，体系恶化。模拟连续试验说明提高温度，有利于加速氧化进行且砷更多溶出，而铁、硫酸根则更易形成钒类物质留在渣中。10 L 连续氧化体系过小，取样误差导致渣计氧化脱除率波动较大。

间歇试验与连续试验氧化效率对比说明生物氧化连续试验效果优于间歇试验。间歇单槽实验前 10 d，Fe、S 的平均脱除速率分别为 0.0972 $mol \cdot L^{-1} \cdot d^{-1}$ 和 0.0593 $mol \cdot L^{-1} \cdot d^{-1}$，As 前 5 d 的脱除速率为 0.00653 $mol \cdot L^{-1} \cdot d^{-1}$。随反应进行，间歇试验脱除速率不断下降。而连续扩大实验全程硫、铁、砷的算术平均脱除速率分别为

$0.208 \text{ mol·L}^{-1} \text{ d}^{-1}$，$0.120 \text{ mol·L}^{-1} \text{ d}^{-1}$ 和 $0.00731 \text{ mol·L}^{-1} \text{ d}^{-1}$。Fe、S、As 脱除速率提高，有利于缩短停留时间或减小反应器容积，降低生产成本，为低 Au/S、高硫、高砷金精矿搅拌生物预氧化-氰化提金工艺提供了可能。

连续试验效果优于间歇试验主要机理：较间歇单槽实验，连续生物氧化过程各级反应槽中的 pH、Eh 更加稳定，且浸出液中总铁、硫酸根离子、砷酸根离子浓度增长慢，各槽离子浓度更稳定，稳定的反应条件有利于构建稳定的菌群结构。微生物菌群结构研究表明，连续试验各特定槽有各自专有的，与相应反应条件匹配的菌群结构，细菌活性更高，氧化效率更高。

柱浸生物氧化生成大量的单质硫。电镜和能谱分析表明生成的单质硫等包覆在矿石表面。延长氧化时间该富硫层可继续被氧化。柱浸生物氧化中细菌多样性不高，各种菌数量差异不大，活性不高，富硫层难以快速氧化为硫酸根，给选择性优先溶解砷带来可能。

采用室温和控温微生物柱浸氧化，研究硫元素在各形态间的转化规律。不同温度条件下，氧化渣总硫量（TS）和硫化物中硫（$S-S^{2-}$）含量基本都随柱浸时间延长逐步降低，单质硫（S^0）含量先提高后降低，硫酸盐中硫（$S-SO_4^{2-}$）含量先增加到后期变化趋势不明显。比较不同温度下 TS、$S-S^{2-}$ 日平均脱除率及 S^0、$S-SO_4^{2-}$ 日平均生成率发现，提高柱浸温度可加快破坏硫化物晶格结构而且硫化物更倾向于生成 S^0。

考察柱浸液总铁、硫酸根和砷浓度随浸出时间变化差异，发现浸出液中砷最先达到溶出平衡，证实了毒砂中的砷优先被氧化溶出。45℃砷的溶出平衡发生在 42 d 内，砷脱除率大于 85%；42 d 内 TS 的脱除率仅为 57.3%。硫砷脱除率差异优于搅拌浸出，说明柱浸氧化中砷和硫的脱除速率差异可以被强化放大。

氧化渣氰化浸出实验优化氰化条件为：液固比 2，氰化钠浓度 1‰，氰化时间 24 h。总碱耗试验发现 GS 金精矿，在总停留时间 8 d，氧化温度 40℃，氧化后液返回 25%工艺中，若全部采用氧化钙中和，吨金精矿总碱耗为 497kg 石灰；总停留时间 6 d，温度 45℃，氧化后液不返回，若全部采用氧化钙中和，吨金精矿总碱耗为 415kg 石灰。固体废弃物毒性鉴定试验证明了生物氧化的中和渣和氰化渣均为一般工业固体废物。

生物搅拌预氧化-氰化提金工艺的研究，为低金硫比、高砷、高硫金精矿的开发，提供了除焙烧工艺外的选择。按生产规模 100 t d^{-1}，生产原料为 DS 金精

矿，不磨矿，不返液，矿浆浓度 15%，预氧化 6 d，预氧化温度 45℃，不包括尾矿工程，仅主体工程及设备总投资约为 6000 万元。每吨金精矿生物搅拌-预氧化-氰化的生产处理成本为 819.2 元，计算出每克黄金生产成本为 45.5 元。

生物堆浸氧化处理高砷精矿工艺的研究，为高砷低金硫比的开发利用提供一条全新的出路。45℃生物堆浸 30 d 条件下，可得到砷含量 0.41%，氧化渣率 84.38%，金品位 24g t^{-1} 以上的氧化渣金精粉，此类金精粉计价系数在 75%以上。按日处理量 500t 金精矿，初步估算总投资成本约在 5000 万左右，吨矿处理成本将低于 150 元。

本文的研究解决了试验金精矿销售困难的局面，将为低金硫比、高砷、高硫金精矿的开发利用提供理论和技术上的指导。堆浸选择性降砷为高砷低金硫比金精矿的开发模式提供新的思路，经济效益明显。

关键词： 低金硫比高砷金精矿；搅拌预氧化；堆浸选择性降砷；菌群结构；初步经济评价

Abstract

The stirred-biooxidation pretreatment is paid the increasing attention due to the reduction of easy-to-treating ores. Though it has been studied so much, there are still some issues hard to resolve, such as narrow application range and the unclear relationship between bacterial and the condition. Focusing on those problems, three different-scaled stirred-biooxidation experiments had been conducted to evaluate whether the "stirred biooxidation-cyanidation" process was fit for the low Au/S ratio but high arsenic-contained gold arsenopyrite/pyrite concentrates. Then a new process was designed to reduce arsenic content for it through heap bioleaching.

Two kinds of mineral concentrates were used in this study. One is called as GS gold concentrate (GS), and the other is DS gold concentrate (DS). GS and DS contained 18.43 g Au/tonne, 40.57% S, and 2.37 As or 20.62g Au/tonne, 35.01% S, and 2.13 As, respectively. The gold and sulphur phase analysis results showed that gold was mainly held in a sulfide lattice, and the sulfide was the dominant form of S in the sample. Pyrite and arsenopyrite are the main metallic minerals of the concentrate. According to its chemical and mineralogical compositions, this concentrate was assigned to the pyrite-arsenopyrite type.

Both 5 L and 20 L batch tests were conducted to optimize the biooxidation condition. The optimal experiment conditions was established as that: 15% DS pulp density was oxidized at 40℃ with no grinding and the pulp pH was controlled at about 1.3. The results of 20 L batch tests showed that gold extraction increased with the time and the gold extraction reached up to 90.28% after 7 day's oxidation.

The results of simulated continuous experiments showed that the gold reached a 90-plus percent extration for 6 oxidation days spent at 45℃,with no leach liquid return; and it needed 8 days at 40℃,with 25% leach liquid return.

Compared to the maximum removal rate of the batch tests （in the initial 10 days）, the arithmetic average release rate of total iron in the continuous tests is nearly twice as high. The removal rates of sulfur and iron can be calculated as 0.0972 mol L^{-1} d^{-1} and 0.0593 mol L^{-1} d^{-1} in the initial 10 days, respectively. And then their removal rates reduced to almost half in the following days. The arithmetic average

removal rates of S,Fe, As in the entire oxidation process of the continuous tests are $0.208 \text{ mol L}^{-1}.d^{-1}$, $0.120 \text{ mol L}^{-1}.d^{-1}$ and $0.00731 \text{ mol L}^{-1}.d^{-1}$. Rapid and efficient iron, arsenic and sulfur removals will shorten the biooxidation time, which may significantly reduce the cost of operation and equipment investment.

Compared to the batch tests, the continuous tests have shown the better oxidation effect results due to the more diversity and more stable bacterial community structure, and the slower ion accumulation. Nutrient was added and bacterial metabolites was discharged continually to kept a relatively balanced and stable environment in the continuous experiments. The microbial community structure in each tank of stirred biooxdation test was stable an d unique, and the sulphide was converted to sulphate promptly. The leach liquor in the last tank of continuous test will be discharged from the circuit as well; however, the leach liquor of the batch test cannot be drained. The ion concentration remained stable in every reactor of the continuous test, while it kept on increasing in batch test. The dissolution behaviors of Fe, S and As showed that a sudden changing experiment condition had a negative effect on the biooxidation rate, which always occurred to the batch test. And the growth of bacteria was restricted by the higher ions concentration in the batch tests.

The biooxidation of sulfide minerals was limited due to poor gas transportation in biological column tests. Elemental sulphur was more likely to be one of the main product in column leaching tests. Though the S^0 was unstable and not tight, it also needed more time to convert it into sulphate. It made selectively leaching arsenic firstly possible. Only three bacterias in heap bioleaching lixivium at room temperature were sequenced. *They were Acidithiobacillus callus, Leptospirillum ferriphillum, Sulfobacillus thermosulfidooxidans*. Due to the poor bacterial activity in bioheapleching process, the S^0 passivation was grown to cover the ore surface and then limited the sulphide biooxdation rate.

The transformation rules of sulphide to other sulfur species was studied in column bioleaching tests at room temperature and 45℃. The content of TS and S-S^{2-} gradually reduced with the column leaching time and the S^0 improved firstly then decreased at both temperatures. It was concluded that the S^0 oxidation rate was promoted and the effect of S^0-rich layer reduced but not eliminated by rising temperature only.

The pitting potential of arsenopyrite was almost 0.1 V lower than pyrite in this experiment. Such differences also made arsenopyrite possible to be preferentially and selectively dissolved. As shown by the concentrations of total iron, sulphate and arsenic with time in the bioleaching lixivium, the arsenic reached in balance fastest. It proved that it was preferential dissolved.

The optimized cyanidation conditions for the bioxidized residue were as follows: cyanide extracting for 24 hours in 1‰ sodium cyanide liquid and 2:1 the ratio of liquid to solid. Per ton GS gold concentrate consumed 497 kg lime, which was oxidized for a retention time of 8 days at 40℃, with 25% liquid return. Per ton DS gold concentrate consumed 415 kg lime, which was oxidized for a retention time of 6 days at 45℃, withno liquid return. The toxicity identification tests for the solid wastes proved that both the neutralization slag and cyanide residue in this process were the general industrial solid waste.

Almost 60 million RMB for previous fixed capital cost was needed to set up a stirred biooxidation as pretreatment for extracting gold with 100 tons ore treatment capacity per day. The operation cost was about 819 RMB per ton concentrate.

Almost 50 million RMB for previous fixed capital cost was needed to set up a heap thin-layer bioleaching plan with 500 tons ore treatment capacity per day. The operation cost was about 150 RMB per ton concentrate. The heap bioleaching technology was useful to remove arsenic selectively.

The research in this paper will provide the theoretical and technical guidance for the stirred-biooxidization and cyanidation process. The column biooxidation leaching to remove arsenic was benefit for its selectivity. It is a new idea for the exploitation utilization of gold concentrate.

Key words：low Au/S ratio but high-arsenic gold concentrate; pre-biooxidation; selectively bioleaching; bacterial structure; techno-economic evaluation

目 录

Table of contents

第一章 绪论

我国金矿类型繁多，已探明的金矿总保有储量 4265 吨[1]，但其中大型、特大型金矿床少，中小型金矿床多，低品位难处理矿石占全国探明储量的比例较大，有大量难处理金矿因矿石含砷、含硫、含炭或因多者皆有而导致矿石难选冶，贵金属得不到有效的开发利用[2, 3]。

冶金技术主要包括火法冶金、湿法冶金以及电冶金[4]。随着矿石品位的不断降低和对环境保护的要求日趋严格，湿法冶金在有色金属、稀有金属及贵金属的冶炼中的地位日益突出[5]，生物冶金是湿法冶金的重要组成部分及发展方向[6]。根据生物作用于目的矿物的过程与结果不同，生物冶金工业通常分为微生物浸出、微生物氧化、微生物吸附与微生物积累[7, 8]。

生物浸出指微生物氧化溶解有价金属，如锌、铜和镍等，氧化后的目的元素以离子形式进入溶液，再通过萃取、电积或沉淀等方式来提取溶液中的金属离子，制备金属原材料的过程[9]。而生物氧化技术[8]是利用浸矿菌（主要包括古菌、细菌和真菌）对包裹目的矿物（或元素）的非目的矿物进行氧化，被氧化后的非目的矿物以离子状态进入液体中，经处理后排放，而目的矿物（或元素）或被解离，或呈裸露状态留存于氧化后的渣中，再将氧化渣中的有价金属溶解到浸出溶剂中。生物氧化与生物浸出并无本质区别，使用的也是同一类微生物，它们尤其适用于低品位复杂矿和硫化精矿中有价金属的提取[10]。生物吸附和生物积累是指通过微生物把水溶液中的金属离子结合到细胞壁或依靠生物体的代谢作用在体内积累金属离子的过程。

生物氧化/浸出技术有如下优点[7, 11, 12]：（1）反应温和，将冶金过程从高温、高压或强酸强碱的条件下变成室温、常压、低酸的反应过程；（2）易操作、生产成本相对较低、产品价值高；（3）无二氧化硫等有害气体排放，溶液循环利用，环境友好；（4）能较经济的处理常规法难以处理的某些低品位矿石，提高资源利用率，适合于开发偏远交通不便的地区。