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# 银的湿法提取技术研究进展

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**摘要:** 银作为兼具重要金融与工业价值的战略金属, 其高效、环保的提取技术对保障资源可持续利用意义重大。当前银资源主要来源于三大渠道: 一是原生矿产, 其中65%为伴生矿, 20%为独立银矿; 二是二次资源回收, 占比约25%且呈增长趋势, 主要来自电子废弃物、感光材料等高含银的“城市矿山”; 三是, 少量银资源来自各国政府的战略储备与民间收藏库存。在环保法规日益严格的背景下, 原生矿产开发成本显著增加, 二次资源回收的经济与环境价值日益凸显。本文系统综述了各类银提取方法, 包括传统及新兴技术的技术原理、应用现状与研究进展, 旨在为相关技术升级与产业化应用提供科学参考。

**关键词:** 银; 银矿; 提取; 回收

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银是一种在地壳中丰度较低的过渡金属元素。自然界中虽有单质银, 但更常以化合物形式存在于矿石中。银单质呈银白色金属光泽, 粉末态则为暗黑色, 常温常压下银的化学性质稳定<sup>[1-2]</sup>。银在化合物中呈一价形态存在, 能形成多种化合物。提取工艺中最常见的化合物为硝酸银、氯化银、硫酸银和氰化银等<sup>[3]</sup>。银具有良好的导电性、导热性、光波反射性能和延展性, 被广泛应用于多个领域, 在航空航天装备以及电子电气行业中的应用尤为广泛<sup>[4-5]</sup>。银是制造计算机、电视、通讯设备、制冷装置及雷达系统中各类精密导线和电接触元件的优选材料<sup>[6]</sup>。银对碱性环境的出色耐受性使其在化工领域备受青睐, 例如用作生产苛性钠的反应釜(碱锅)材料, 以及实验室中熔融强碱(如氢氧化钠、氢氧化钾)的专用坩埚材料。银在光学领域、保温容器和医药行业也有广泛应用<sup>[7-8]</sup>。银粉

可作为实验室电器设备的防腐涂层; 其微粒形态展现出显著的抗菌效应, 不仅用于伤口处理, 还在航天器水循环系统中充当净化剂。溴化银凭借其快速感光特性和强大的成像能力, 是制造照相胶片等感光材料的核心原料。

银资源主要来源于三个方面: 一是自然矿产资源, 其中约65%为铅锌铜等金属矿的伴生副产物(品位较低), 约20%来自以银为主的独立银矿床(品位较高); 二是二次资源回收(占比约25%且持续上升), 其核心为电子废弃物(如电路板、光伏银浆等, 含银量远超矿石)、工业催化剂、感光材料及各类含银废料等; 三是少量的政府和民间储备库存。当前趋势显示, 随着原生矿石品位下降和环保要求提升, 从电子废弃物等“城市矿山”中高效回收银已成为保障银资源可持续供应的关键路径。

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本文系统综述了各类银提取方法的技术原理、应用现状与研究进展,包括从独立银矿中提取银、从有色金属矿伴生银矿中提取银、从“城市矿产”中提取银等,为相关技术升级与产业化应用提供科学参考。

### 1 从独立银矿中提取银

根据银的品位及其在经济价值中的重要性,含银矿石分为三类:一是独立银矿,指银品位足够高,一般银含量高于150 g/t,是唯一或占绝对主导地位的经济开采目标;二是共生银矿,指银品位虽略低于独立矿,通常为100~150 g/t,但仍具有重要的独立经济价值,与铅、锌等主要价金属在经济上同等重要或作

为不可或缺的联合产品,必须通过综合回收工艺专门提取;三是伴生银矿,指银品位较低,通常银含量小于50 g/t,但实际小于100 g/t的银矿我们都称为伴生银矿,不构成主要开采目标或不具有独立经济价值,主要作为开采铜、金、铅、锌等主金属时的副产品,其价值贡献较小且回收依赖于主金属的生产流程<sup>[9]</sup>。

独立银矿的主流工艺是浮选富集—精矿氰化—锌粉置换或者直接氰化法。WANG等<sup>[10]</sup>对云南某铜伴生银矿进行研究,浮选工艺如图1所示<sup>[11]</sup>,该矿石含银479.5 g/t,铜含量为0.54%,选矿工艺处理后精矿具有优异的指标,银品位为4 787.31 g/t,银回收率为87.97%。

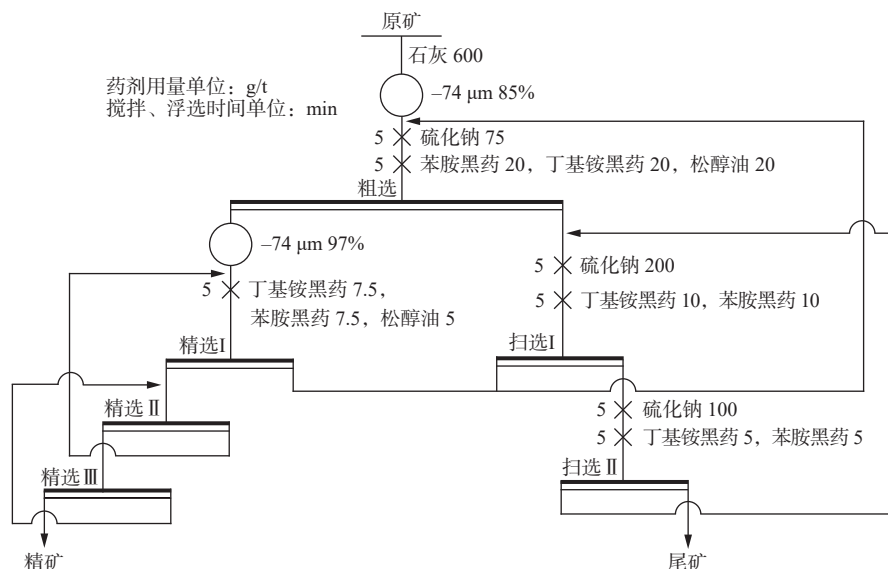
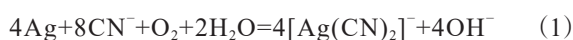


图1 浮选工艺流程<sup>[11]</sup>

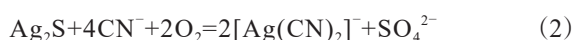
Fig. 1 Flotation process flow diagram<sup>[11]</sup>

氰化法基本原理是利用氰化物(如NaCN、KCN)在氧化剂(通常是空气中的氧气)存在下,与矿石中的银单质或银的化合物反应,生成可溶于水的稳定银氰配合物,再通过还原反应将银从配合物溶液中提取出来,实现银与脉石(矿石中的无用杂质)的分离,其反应方程式<sup>[12-14]</sup>如下。

游离银单质的浸出反应式:



硫化银常见银矿物的浸出反应式:



银的还原析出反应式:



白成庆等<sup>[15]</sup>考察了氧压预处理对某浮选尾矿后续氰化浸出金银效果的影响。结果表明,在预处理氧

压为1.5~1.8 MPa、温度180~200 °C、反应时间1.0 h、液固比3:1的优化条件下,氰化浸出阶段金的浸出率达到81.77%,而银的浸出率则为33.29%。靳冉公等<sup>[16]</sup>对湖南难处理含硫银精矿的研究表明,经焙烧预处理(400 °C, 2 h, 5%添加剂)后,在吨矿氰化钠用量20 kg、液固比3:1、浸出时间48 h的条件下,可获得80.66%的银浸出率。段东平等<sup>[17]</sup>针对银为主的多金属精矿,通过采用氨浸—氰化或氨浸—酸脱铅—氰化工艺,在85~100 °C、0.2 MPa氧压条件下完成氨性浸出后,实施常规氰化处理,可使银的氰化浸出率达到99%。王明等<sup>[18]</sup>针对锰银矿中的银,采用添加剂焙烧—氰化浸出工艺进行中试处理。回转窑连续运行80 h,物料焙烧时间为(30±5) min,所得焙砂产率为85.54%,其中银含量为237.73 g/t,银回收率达到

99.19%。该焙砂在500 L反应釜中直接进行氰化浸出,液固比控制在2:1~2.2:1,浸出时间为6~15 h,每吨原矿氰化钠用量为700 g,最终银浸出率为86.5%。

## 2 从有色金属矿伴生银矿中提取银

### 2.1 从阳极泥中提取银

伴生银矿是指银并非作为主要开采目标,而是以副产品形式存在于其他主金属矿床(如铜、铅、锌或金矿)中的矿产类型。银通常以微量赋存于主金属矿物晶格(如方铅矿中的银置换铅)或分散的独立矿物中,其回收完全依赖主金属的选矿和冶炼流程,通常是从重金属冶炼过程产生的阳极泥中回收。阳极泥是电解过程中在阳极底部沉积的富含贵金属和杂质的不溶性残留物。从阳极泥中提取银是一个复杂的冶金过程,主要涉及从铜、铅等金属电解精炼过程中产生的阳极泥中回收贵金属<sup>[19]</sup>,处理流程如图2所示<sup>[20]</sup>。

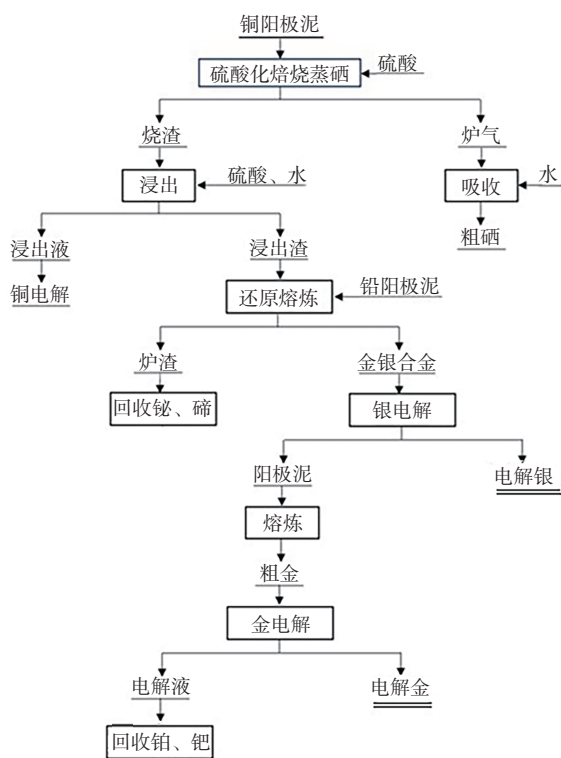


图2 铜、铅阳极泥处理流程图

Fig. 2 Treatment flow sheet of copper and lead anode slimes

#### 2.1.1 从铅阳极泥中提取银

曲胜利等<sup>[21]</sup>以铅阳极泥熔炼所得锑渣为对象,通过浮选与重选对比试验发现,重选工艺较优,可有效分离回收渣中的金、银等贵金属,从而提升铅阳极泥中贵金属的整体回收率,其中银回收率达到

72.42%。YI等<sup>[22]</sup>采用氧化—真空挥发—碳还原工艺从铅阳极泥中分离富集金和银。在真空挥发之前,对铅阳极泥进行选择性氧化。然后,采用真空挥发和真空还原法富集金和银。研究了温度和时间对真空挥发分离和还原富集的影响。试验结果表明,所得富集产物中Ag含量高达67.58%,铅阳极泥中银的回收效率为99.25%。苏莎等<sup>[23]</sup>通过盐酸浸出法富集铅阳极泥中的金、银,重点考察了盐酸浓度、反应温度、液固比及反应时间对铜、铋、铊、金、银浸出行为的影响。研究结果显示,在盐酸浓度3 mol/L、液固比8:1、温度85 °C、时间4 h的优化条件下,铜、铋、铊的浸出率分别达到98%、99.5%和99.6%;经此浸出处理后,铅阳极泥中的金、银含量较浸出前显著富集,增幅达到2倍以上。黄海飞等<sup>[24-25]</sup>采用侧吹富氧熔池还原熔炼系统升级银生产线,对铅阳极泥实施直接还原熔炼。这项技术升级使得有价金属的综合回收率较传统工艺获得显著提升,银、金、铅、铋、铜、铊的回收率均超过99.5%,尤为突出的是,主金属银、铋、铊的直收率分别达到了94%、90%和85%。

#### 2.1.2 从铜阳极泥中提取银

WEN等<sup>[26]</sup>通过碳热还原和超重力分离从铜阳极泥中回收银、铜和铅。在预处理过程中,硫酸化焙烧后的铜阳极泥中去除了99.9%的硒,铅、铜和银等有价金属通过碳热还原浓缩为铅-银-铜多相络合物。研究了温度对还原效率的影响,并以热力学分析为依据。在超重力分离系数 $G=600$ 、温度1 423 K、时间5 min的最佳超重力分离条件下,得到了过滤后的铅-银-铜多相络合物和残余相。结果表明,过滤后的Pb-Ag-Cu相收率约为83%,其中银的回收效率达到96%。XU等<sup>[27]</sup>利用硫代硫酸盐从含高Sn、Pb、Sb的铜阳极泥中浸出Au、Ag、Pb,其中银的浸出率高达93.4%。KHANLARIAN等<sup>[28]</sup>采用较低温度的硫酸化焙烧—浸出工艺,最佳条件下得到银的回收率为96.48%。DONG等<sup>[29]</sup>开发出一种清洁的湿法冶金工艺,可以高效、经济地从铜阳极泥中回收硒、铜、金、银等有价元素,先后采用 $\text{Na}_2\text{SO}_3$ 还原和铁粉沉淀法从浸出液中回收硒和铜。选择 $\text{NaClO}_3\text{-H}_2\text{SO}_4\text{-NaCl}$ 溶液选择性浸出金,通过 $\text{H}_2\text{C}_2\text{O}_4$ 还原回收溶解的金。采用 $\text{Na}_2\text{SO}_3$ 用密封反应器浸出银,通过 $\text{Na}_2\text{S}_2\text{O}_4$ 还原回收浸出的银。在最佳条件下,银的回收率达到99.4%,获得的金属银的纯度为96.5%。LI等<sup>[30]</sup>采用一种绿色高效的去除铜阳极泥中砷、铅和铋的方法,

采用一步真空碳热还原工艺。残渣中回收的银含量从10.64%增加到15.61%，回收率为99.76%。

## 2.2 从冶炼渣中提取银

### 2.2.1 从有色冶炼渣中提取银

周兴等<sup>[31]</sup>针对云南某湿法炼锌厂氧压浸出工艺产生的高含银锌硫渣,开展了硫脲法浸银研究。系统优化了相关工艺参数。研究发现,硫脲浸银具有显著的化学驱动力,硫脲在银表面的结合能为83.9 kJ/mol。在液固比8:1、硫脲浓度10 g/L、浸出时间2 h、温度50 °C、pH为1.5、Fe<sup>3+</sup>浓度0.3 mol/L的条件下,银浸出率可以达到85.71%。高丽霞等<sup>[32]</sup>基于“NaCl+H<sub>2</sub>SO<sub>4</sub>+NaClO<sub>3</sub>”体系开展了处理高硫酸钙锌冶炼渣的研究,在氯化钠浓度300 g/L、氯酸钠用量3 g、硫酸用量6 g、液固比5:1、温度90 °C的优化参数组合条件下,浸取50 g酸浸渣3 h,银浸出率可达约97%。李国栋等<sup>[33]</sup>针对某锌冶炼渣(金品位1.78 g/t、银品位202.40 g/t)开展研究。该渣中银矿物主要呈硫化银和金属银形态。基于此矿石特性,研究采用了重选—浮选联合工艺回收金银。在优化条件下(磨矿细度-0.074 mm占75%,给矿速度2 kg/min,流态化水流量3.5 L/min,离心力70倍重力加速度,给矿浓度45%)进行尼尔森重选,获得的金精矿品位为204.20 g/t,金回收率为69.77%。随后对尼尔森尾矿实施浮选(一粗两精一扫闭路流程),最终获得银精矿品位为825.50 g/t,银回收率77.82%。YANG等<sup>[34]</sup>提出了一种基于硫氰酸铵的湿法冶金工艺,用于从经脱锰预处理后的锰银硫化精矿中高效回收银。该工艺在加压氧气气氛下进行,利用硫氰酸铵溶液作为浸出剂。相较于传统的氰化法和氯化法,硫氰酸铵体系展现出显著的优越性:浸出效率更高、环境毒性显著降低,并兼具优异的选择性和工艺稳定性。在优化的浸出参数(如温度、NH<sub>4</sub>SCN浓度、氧压、pH、时间等)条件下,经4次循环浸出后,银的浸出率可以达到88%。

### 2.2.2 从黄金行业氰渣中提取银

氰渣是金、银等贵金属矿石经氰化钠浸出提金后产生的固体废渣,含有残留的游离氰化物、金属氰络合物(如铁氰化物)及砷、铅等重金属,具有高毒性、难降解性和环境持久性,属于危险废物。其中残留少量金、银、铜等贵金属,需通过二次回收技术进一步提取。

秦贞军等<sup>[35]</sup>以青海某金矿氰化车间产生的氰化尾渣为原料,该尾渣含有金、银、铅、锌等有价值元素,其中银品位28.76 g/t,具有较高的回收利用价值。利

用浮选工艺,在高氰高碱度介质中,在对氰化尾渣进行擦洗性磨矿,破坏金属矿物被氧化的矿物表面后,采用一次粗选、两次扫选、两次精选的浮选流程,最终获得了银品位332.84 g/t的浮选精矿,同时氰化尾渣中的砷被抑制,精矿中的砷品位仅为0.35%,实现了资源的综合回收。张耀军等<sup>[36]</sup>采用一粗两扫两精的混合浮选流程,选用ATTA药剂作为活化剂,丁基黄药+乙硫氮为捕收剂,获得了银回收率为67.15%,品位为877.26 g/t的混合精矿。刘明杰等<sup>[37]</sup>以浮选金精矿氰化浸出后置换金泥精炼提纯过程产出的高银冶炼渣为研究对象,开发了铅原位捕集富集—真空蒸馏分离的贵金属综合回收工艺。通过调节氧化铅用量及真空蒸馏温度等参数,优化了回收效果。该工艺能有效富集渣中贵金属,最终蒸馏产物合质金的金银含量高于90%。

## 3 从“城市矿产”中提取银

在科技日新月异的今天,电子产品的更新换代速度前所未有,随之产生的电子废弃物也正以前所未有的速度增长。电子废弃物中银含量远高于原生矿,废弃感光材料的银含量为0.5%~2%(约原生银矿品位的50~200倍)、电路板触点的银含量为0.1%~0.5%(约原生银矿品位的10~50倍)<sup>[38]</sup>。妥善处理这些电子废弃物,进行高效的资源回收,从废弃电子设备中提取银的核心优势在于实现资源高效循环与绿色转型。该过程通过物理富集与环保湿法工艺的结合,显著降低对原生矿产的依赖,推动电子废弃物中贵金属的可持续利用<sup>[39]</sup>。同时避免了传统冶金的高污染风险,以绿色技术路线减少环境负荷,并依托协同回收机制同步提取多种高值金属,兼具经济可行性与生态效益,为资源循环提供闭环解决方案<sup>[40]</sup>。

### 3.1 从废旧电路板中提取银

废弃电路板中银主要存在于电路板的触点、连接器、某些开关和部分芯片封装中。其主要工序为:拆解/粉碎、预处理(去除有机物/贱金属)、浸出(硝酸或氰化物)、置换/沉淀回收银、精炼<sup>[41]</sup>。

WACHTER等<sup>[42]</sup>从电子继电器中提取银,通过继电器拆卸、贱金属去除、硝酸浸出、沉淀、转化氧化银和熔化。得到银的纯度为94.9%,最终银回收率为原料的0.44%。在试验的第二阶段,使用混合类型的电子继电器来比较产量,混合电子继电器的最终收率达到0.54%的Ag,纯度超过95%。ORABY等<sup>[43]</sup>使用甘氨酸或甘氨酸盐,用于从切碎和研磨的印刷

电路板中回收贱金属与贵金属。碱性甘氨酸溶液选择性地溶解铜、锌和铅,然后在随后的浸出步骤中使用甘氨酸和少量氰化物回收金和银。浸出系统在两个加工阶段都保持碱性。在两阶段甘氨酸浸出体系中,银的回收率为85.3%。王治科等<sup>[44]</sup>研究了硫氰酸盐-双氧水( $H_2O_2$ )体系浸出废电路板中金银的工艺。系统考察了硫氰酸盐浓度、 $H_2O_2$ 浓度、溶液pH、固液比、温度及搅拌速度对浸出效果的影响。优化条件为: $H_2O_2$ 浓度0.05 mol/L、 $SCN^-$ 浓度0.4 mol/L、固液比1:250、搅拌速度200 r/min、室温、浸出时间8 h。在此条件下,金浸出率超过90%,银浸出率达到79%以上。陈淑敏等<sup>[45-46]</sup>采用旋转圆筒阴极耦合可溶性阳极的二级电解工艺,实现了电子废弃物中镀银层的高效选择性回收。该技术以镀银废件为阳极,采用 $AgNO_3-HNO_3-Cu-KNO_3$ 电解体系,在阴极电位0.8 V、阴极旋转速率0.5~2.0 L/min、温度46 °C及电流密度200~500 A/m<sup>2</sup>的条件下,实现了86%的银回收率以及99.8%的纯度。

### 3.2 从含银胶片中提取银

从含银胶片(如废弃X光片、电影胶片、印刷胶片)中回收银是一项成熟的工业技术,核心在于高效剥离银层并提纯。杨健等<sup>[47]</sup>分析了废弃光盘中各金属含量,采用NaClO提取废弃光盘中银的方法,使反射层和盘基分离,再以锌粒还原,提取出单质银,实现了盘基及银的回收利用。

李晓艳等<sup>[48]</sup>研究了处理废感光胶片中银及片基的方法,采用10%的稀硝酸在最佳温度70~90 °C的条件下将废感光胶片所附的银化合物溶解成银离子,达到脱银目的,用电解方法从含银溶液提取纯银,方法操作简便,无污染,母液可重复使用,银纯度高达99%。ABDEL-AAL等<sup>[49]</sup>系统研究了硝酸提取废旧胶片中银的工艺优化。研究通过控制变量试验确立关键工艺条件:胶片尺寸需破碎至小于8 mm以增大反应界面,在90 °C高温及50 min反应时长下,采用6%硝酸浓度实现银的高效氧化溶解。试验数据表明,此参数组合下卤化银浸出率达到98%。后续通过锌粉置换法回收浸出液中的银离子,近乎达到100%的银回收率。熊道陵等<sup>[50]</sup>采用硝酸浸出工艺从废胶片中回收银,首先使用10%的硝酸溶液对胶片进行3次浸出,随后向浸出液中加入碳酸钠沉淀剂,经沉淀、水洗去杂、熔炼后可得到纯度为99.5%的银。

### 3.3 从废旧光伏组件中提取银

通过热解—选择性浸出等工艺可以实现废旧光

伏组件中银的高效回收,兼具显著的资源、环境与经济三重效益。汪启飞等<sup>[51]</sup>提出了一种高效回收光伏组件的方法,通过液氮冷冻(-196 °C)与120 °C加热两种方式快速分离背板与玻璃,获得胶封硅片。随后,在液氮预处理10 min后,采用550 W功率的机械剪切法,可在160 s内高效粉碎胶封硅片,实现汇流带、晶硅料和EVA胶膜的分离。为进一步提纯晶硅料,需在600 °C下保温15 min以去除残留EVA。相较于传统回收工艺(即未分离背板玻璃即整体粉碎),该方法显著降低了后续分选难度和整体成本,尤其适合现场快速分离与各组分高效回收。他们针对回收的晶硅料粉末,研究了硝酸浸出提银工艺,重点考察了硝酸浓度、浸出温度、液固比及浸出时间对银浸出率的影响,在尽可能减少硝酸用量的条件下,银的提取率高达99.12%。

## 4 结束语

本文系统梳理了从各类银资源中提取银的主要方法,涵盖传统的伴生/独立银矿开采模式与新兴的二次含银资源(如电子废弃物、感光材料等)的湿法回收工艺。分析表明,相较于原生矿产,二次含银资源凭借其超高品位、显著的资源再生效率及突出的环境友好特性,正迅速崛起成为保障国家资源供应安全的关键支柱,有效缓解了对原生矿产的过度依赖。面向未来,银资源的可持续获取面临战略金属供应紧张与全球生态转型的双重压力。为应对挑战,研究与发展将重点聚焦于以下绿色前沿方向:一是开发环境风险更低的无氰浸出体系,彻底革新传统提银工艺的环境足迹;二是构建银二次资源的绿色高效回收技术体系,有针对性地回收利用快速增长的含银城市矿产资源。创新技术的突破应以协同推进资源高效循环、工艺低碳化转型与产品高值化利用为主要目标。通过整合优化原生与二次资源开发路径,构建一个环境友好、经济可行、供应稳定的银资源可持续供应链体系,从而应对银矿资源的逐渐贫化并提供潜在解决方案。

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## Research Progress on Wet Extraction Technology of Silver

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**Abstract:** Silver, a precious metal possessing significant financial attributes and extensive industrial applications, plays a crucial role in the global economy. Ensuring its sustainable supply necessitates continuous advancements in extraction technologies that prioritize both efficiency and environmental responsibility. This paper examines the evolving landscape of silver resource supply and the corresponding technological imperatives for sustainable extraction. Current global silver supply is structured around three primary channels. Natural mineral resources

constitute the dominant source, accounting for approximately 85% of total supply. Within this category, associated silver extracted as a by-product from polymetallic deposits—particularly lead-zinc-copper ores—is paramount, contributing roughly 65% of global silver output. In contrast, primary silver mines, dedicated to silver extraction, provide only about 20% of supply. This sector faces mounting challenges, including a persistent decline in average ore grades globally, escalating extraction costs due to deeper mining operations, and the impending depletion of economically viable reserves in several key regions. Secondary resource recycling represents an increasingly vital and rapidly expanding supply stream, currently constituting approximately 25% of total silver supply and exhibiting a clear upward trajectory. This "urban mining" approach focuses on recovering silver from diverse waste streams, primarily electronic waste (e-waste) such as discarded printed circuit boards (PCBs) and end-of-life smartphones, which collectively generate over 50 million tons annually due to accelerated technological obsolescence. Additional significant sources include spent industrial catalysts and obsolete photosensitive materials like medical X-ray films and photographic films. Critically, these secondary resources often contain silver concentrations substantially higher than those found in average primary ores. Beyond their economic value, efficient recovery from these sources offers substantial environmental benefits by diverting hazardous waste from landfills and reducing the need for virgin resource extraction, thereby positioning urban mining as a cornerstone of the circular economy for silver. A small portion of silver resources comes from government strategic reserves and private collections, primarily used to regulate market supply and demand and address sudden resource crises. Discernible industry trends underscore a pivotal shift. Stringent and expanding global environmental regulations are significantly increasing compliance costs and operational complexities for primary silver mining operations. Concurrently, the economic viability and ecological advantages of recovering silver from secondary resources, particularly the vast and growing stream of e-waste, are becoming increasingly pronounced. Consequently, the development and optimization of tailored extraction technologies suitable for the distinct characteristics of various silver-bearing resources—especially high-yield, low-impact processes for complex secondary materials—have emerged as a critical pathway. This technological focus is essential not only for securing long-term silver supply stability but also for aligning with global sustainability objectives, notably the "Dual Carbon" goals of carbon peak and carbon neutrality. This review systematically synthesizes the current state of silver extraction methodologies. It analyzes the technological principles, practical applications, and recent innovations across different techniques, categorized according to the specific occurrence forms and matrices of silver in both primary ores (polymetallic and independent deposits) and key secondary resources (e-waste, catalysts, photosensitive materials). By providing a comprehensive assessment of advancements in hydrometallurgical, pyrometallurgical, and emerging bio-hydrometallurgical approaches, this paper aims to serve as a foundational reference for technological upgrades within the industry, fostering more sustainable and efficient practices throughout the silver value chain.

**Key words:** silver; silver mine; extraction; recycling

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