

从冶锌工业废渣中综合回收镓、铟、锗的研究

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Studies on the Crystallization Purification Technology of Puerarin Induced by Electromagnetic Field

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本文对稀土金属元素镓、铟、锗的分布、在高科技领域的主要应用作了扼要的介绍, 分析比较了国内外从锌渣中回收镓、铟、锗的方法、工艺及研究进展。针对冶锌工业废渣中回收镓、铟、锗的具体困难: 全萃法有机相有毒、易燃、损失较大, 生产成本较高, 单宁沉淀锗回收率低, 其颜色影响锌、镉的利用等不足。提出了一种从锌渣中综合回收镓、铟、锗的新技术与新工艺, 能够低成本、高效率地从锌渣中回收稀土金属镓、铟、锗, 且不影响七水硫酸锌的产品质量。 本文解决了从锌渣酸浸液中萃取铟的两个重要技术难题, 一是萃取铟时, 不影响镓与锗的回收, 二是在锌渣浸取液中有铁、镉、铜等金属离子存在的条件下, 不干扰铟的萃取。在镓与锗共存条件下, 利用不同的萃取和反萃取条件, 用P\_(204)萃取剂从镓、铟、锗共存液中来分离和提取铟。研究了在锌渣浸取液中使用P\_(204)萃取剂对铟的萃取的各种影响因素: 如酸度, 时间, Fe~(3+)浓度, 对铟的萃取率和反萃取率的影响, 有效地消除了共存元素的干扰, 铟的回收率达到95%。然后, 应用单宁-栲胶提取锌渣浸取液中的锗与镓。研究发现在一定的实验条件下, 单宁和镓生成有色的单宁-镓络合物, 此络合物稳定, 可以被活性炭等固体吸附剂吸附。提出了用单宁与镓形成络合物、活性炭吸附回收镓的新方法, 突破了从锌渣中用萃取法、多次中和法等回收镓的传统方法的约束。首次实现了用单宁从锌渣酸浸液中的分离、富集和提取镓, 回收率达到91%以上。其次, 对传统的单宁-栲胶法沉淀锗进行了系统的研究, 发现了单宁沉淀锗的本质是形成不溶于水的络合物, 找到了影响锗回收率的关键因素是酸度, 通过对酸度的控制将锗回收率从60%提高到86%。在对镓与锗个别提取方法研究的基础上, 利用单宁-栲胶来从锌渣酸浸液中提取和分离镓与锗。单宁与锗生成不溶于水的沉淀, 过滤得到含锗沉淀; 单宁-镓络合物可溶于水, 能被活性炭吸附。在络合理论及吸附理论的指导下, 利用两种络合物的性质差异来分离和提取镓与锗, 镓回收率达到91%, 锗回收率达到86%。通过对镓、铟、锗个别提取方法的研究, 以及镓、铟、锗共存时对其中某一种元素提取的研究, 提出了一种从锌渣中综合回收镓、铟、锗的新工艺流程。新工艺流程除铟的回收采取萃取法外, 回收锗与镓均采用无毒、污染小的单宁络合法, 分离锗以后的溶液中剩余的单宁可以继续用来分离镓, 各金属元素分离程度高, 摘要精简了工序, 有利于实现绿色生产。采用活性炭将单宁的颜色吸附, 消除了对后续工艺的影响, 生产的七水硫酸锌达到国家二、三级工业产品技术指标。将冶锌工业废渣的排放量减少80%以上, 需要无害化处理的残渣(主要是泥砂)仅占原锌渣的7%, 显著地降低了企业用于环境治理费用。

The distributing of gallium, indium and germanium and their main application in the high-tech field were briefly narrated in the paper. The method, technics and evolvment of recovering gallium, indium and germanium from zinc residues were compared. The shortage, for example poison, flammability, high losing rates and high production cost to use full extraction, low recovery rates to deposit germanium using tannin and its color affecting on using of zinc and cadmium, existed in present technics of recovering gallium, indium and germanium from zinc residues. A new technology of recovery and new process flow, which can efficiently recover gallium, indium and germanium from zinc residues and don't affect the quality of seven water zinc sulfate, were advanced. In this paper, two key technical problem of extracting indium from acid lixivium of zinc residues were resolved. One problem was not to affect recovery of gallium and germanium when indium was extracted, another was not to disturb extraction of indium when the metallic ion, for example iron, cadmium, copper et al, existed in the lixivium of zinc residues. The separation and extraction of indium were performed from the concomitant solution of gallium, indium and germanium by different conditions of extraction and anti-extraction using p204 as extractant. The affect of different factor, for example acidity, time and thickness of Fe<sup>3+</sup> on indium's extraction rate and anti-extraction rate by using p204 was researched. The disturbance of concomitant element was effectively eliminated and the recovery rate of indium was over 95%. Then, the germanium and gallium were extracted by using tannin-kaojiao from lixivium of zinc residues. On some condition, tannin and gallium can form chelate complex, which is stable and can be adsorbed by solid sorbent, e.g. active carbon. The new method, which broke through extraction, multi-neutralization to recover gallium from zinc residues, was advanced to recover gallium by tannin and active carbon. The separation, enrichment and recovery of gallium were first performed from acid lixivium of zinc residues and the recovery rate was over 91%. Secondly, the traditional method of depositing germanium by using tannin and kaojiaowas fully researched in this paper. The essence of depositing germanium by using tannin is that the anti-soluble chelate complex was formed. The key factor of affecting germanium's recovery rate is acidity. The germanium's recovery rate was increased from 60% to 86%. The germanium and gallium were recovered and separated from acid lixivium of zinc residues by using tannin and kaojiao on the base of individual extraction of germanium and gallium. The tannin and germanium formed anti-soluble deposit, which was filtrated to get germanium. But the tannin and gallium formed soluble chelate complex, which can be adsorbed by active carbon. According to different character of two chelate complex, germanium and gallium were recovered and separated. The recovery rate of gallium is over 91% and the recovery rate of germanium is over 86%. Through the study on individual recovery of gallium, indium and germanium, a new process flow of general recovery of gallium, indium and germanium was advanced. In the new process flow, gallium and germanium were recovered by chelation using innocuous tannin except that indium was recovered by extraction. After the germanium was separated, the surplus tannin can be used to separate gallium. Every metallic element was effectively separated. Working procedure was simplified and was propitious to realize clean production. The color of tannin was adsorbed by using active carbon in order to avoid effect on back technics. The quality of seven water zinc sulfate reached the standard II of industrial product. The quantity of residual residues was decreased over 93% and the remainder, which is only 7% of original zinc residues, was mostly mud and sand which need be innocuously disposed. So the disposal cost of environment was evidently reduced.

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