金属羟基化合物在锡石表面吸附与糊精作用机理的研究

李 晔 许 时 张宏泉
(武汉工业大学)

摘 要 糊精在锡石表面吸附最佳 pH值为 7.6左右,而矿浆中锡石表面吸附 H^+ 和 OH^- 离子等吸附点 pH值为 5.4 糊精主要是与锡石表面的 $Sn(OH)_4$ 组分发生作用而吸附。与锡石相比,赤铁矿表面吸附的糊精量明显较高,其最佳吸附 pH值为 6.6,展示了糊精对二者作用的选择性。

关键词 锡石 糊精 吸附 定位离子 赤铁矿

1 前 言

糊精是淀粉在酸性条件下部分水解的产物,它与淀粉的基本差异主要是它的分子量较小(800~ 70000)、支链少,淀粉的分子量高达几百万,既有支链也有直链结构。

糊精在矿物浮选中主要作为浮选抑制剂使用。人们已研究了糊精对煤、辉钼矿的抑制作用及糊精在铜铅混合硫化矿、黄铜矿和方铅矿、辉铜矿和镍黄铁矿等的浮选分离中的抑制作用,提出了糊精与矿物表面的疏水键作用和化学作用两种作用机理。然而,作者研究结果表明[1,2]:糊精在金红石、赤铁矿、方解石和重晶石表面吸附为化学吸附,在萤石表面吸附为物理吸附,更可能是氢键作用。本研究的主要目的是为了深入揭示糊精与锡石表面的作用本质,同时探查糊精对锡石和赤铁矿作用的差异。赤铁矿等氧化矿物在工业浮选中常是污染锡石浮选精矿的主要杂质。

2 试验原料、药剂和方法

2.1 试验原料和药剂

锡石由中南工业大学提供(采自平桂矿务局),原矿经锤细、研磨、筛分成 -38μm粒级,再用 4M HCl浸泡 24h,然后用蒸馏水反复冲洗,直至洗液 pH值和电导率与蒸馏水

g,添加在洗涤剂中可直接消除 Ca^{2+} 对表面活性剂的有害作用,提高洗涤剂的去污能力。沸石的洗涤助剂效能表现在与 Ca^{2+} 的交换作用、对有机酸的吸附作用、微细粒子悬浮特性以及洗衣粉的防固化作用。此外,沸石还是一种高容量的洗涤助剂,其表面吸附能力为三聚磷酸钠的五倍,允许洗涤剂配方中表面活性剂的大剂量使用。在高效浓缩型洗涤剂中,沸石的配入量可达 30%。

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接近为止。再低温烘干备用。锡石经 X-射线衍射分析表明,除锡石峰外,其它杂质峰都很微弱,其比表面为 0.45m^2/g,化学分析结果见表 1。赤铁矿参看文献[1]。糊精由新泽西·菲利普斯堡 J·K·巴克化学公司提供的,其分子量为 7900;杂质含量为(%):N < 0.087, P < 0.05, S < 0.05;经 X-射线光电子能谱测试表明糊精纯度很高。

表 1 锡石矿样化学分析结果(%)

项目	Sn	Mn	As	Fe_2O_3	WO_3
含量	77.4	0.095	0.024	0.74	0.26

其它试剂均为分析纯,试验用水为一次蒸馏水。

2.2 试验方法

2.2.1 吸附试验 称取 1.0g(-0.038mm)矿样到锥形瓶中,加入 50ml 0.01M NaCl,调节溶液 pH,在固体完全分散后,加入相同 pH值、已知浓度的糊精液 50ml,摇匀,把盛有矿浆的锥形瓶放到恒温 25℃的回转摇荡槽中摇动 90min,使吸附达平衡,重新记录平衡 pH,把上层清液以 8000r/min离心 3min。离心液用苯酚浓硫酸比色法分析残余的糊精浓度,即取 4ml离心液,加入 1.5ml 5%苯酚,摇匀,然后快速加入 10ml浓硫酸,冷却后在 488.0nm处测定吸光率,根据标准曲线计算残余的糊精浓度。

2.2.2 滴定试验 把预先调好 pH值为 11.15的蒸馏水取出同等两份。其中一份蒸馏水用 0.1604M HCl在 ZD-3型自动电位滴定仪滴定,滴定速度控制在 0.13244ml/min;另一份加入 -0.038mm锡石 5g搅拌 30min后读取初始矿浆 pH值,以后以同样滴定速度,直到两滴定曲线相交,且溶液呈强酸性,整个滴定过程控制在 25±1℃。

3 试验结果与分析

糊精在锡石和赤铁矿表面吸附曲线与 pH关系如图 1。由图可知,锡石吸附曲线峰值在 pH为 7.6左右,在两个不同日期测试的锡石吸附曲线形状十分相似,证明试验结果重现性较好。而糊精在赤铁矿的吸附峰值在 pH为 6.6左右,且赤铁矿吸附糊精密度最大值为 1.53mg/m^2,比锡石表面吸附峰值 0.77mg/m^2大,这表明糊精在赤铁矿表面作用比锡石强,且两峰值所在 pH区间不同,通过控制矿浆 pH值和糊精在这两种矿物表面作用强弱,可以把锡石从赤铁矿中分离出来。

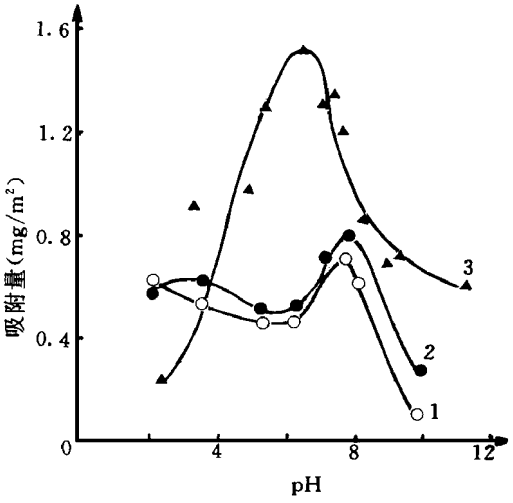

图 1 糊精在锡石和赤铁矿表面吸附量与矿浆 pH关系

初始糊精浓度 50mg/l,温度 25±1℃。1-锡石,试验日期 1995-10-17;2-锡石,试验日期 1995-10-20;3-赤铁矿。

由于锡石是氧化矿,H^+或 OH^-是锡石表面定位离子,锡石表面吸附 H^+或 OH^-对糊精吸附将会产生一定影响,为了揭示锡石表面吸附 H^+或 OH^-与糊精吸附作用的关系,作者通过滴定试验确锡石表面 H^+和 OH^-的等吸附点,试验结果如图 2所示。

由图 2可知,两曲线交点 pH值为 5.4,此时锡石表面吸附 H^+和 OH^-离子量相等,所以 pH值为 5.4是锡石等吸附点。根据图 1可知,糊精在锡石表面吸附量最大值在 pH 7.6左右,由于锡石等电点为 6.9,H^+、OH^-和 Sn^{4+}及 Sn^{4+}的各种羟基化合物都是锡石定位离子,H^+或 OH^-在锡石表面等吸附点

为 5.4,为了更好地了解它们之间相互关系,锡石矿浆中各种离子组分浓度与 pH关系曲线如图 3所示[3]。

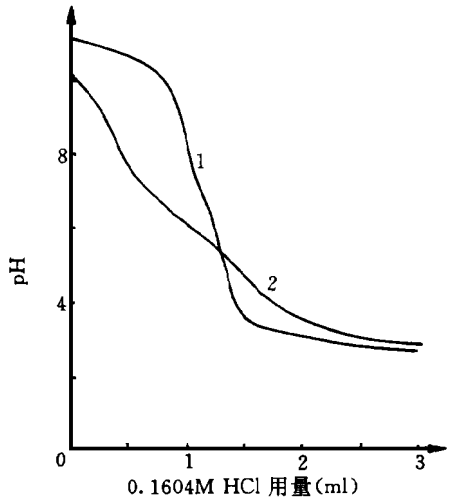

图 2　滴定曲线

蒸馏水初始 pH 为 11.15;1—蒸馏水,2—锡石。

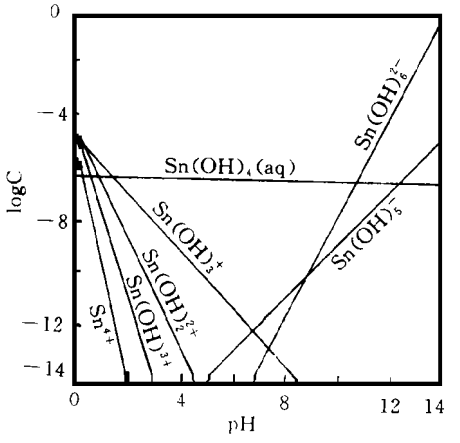

图 3　锡石的溶解组分浓度对数与 pH关系

由图 3可知,在等吸附点 5.4时,矿浆中主要以 $Sn(OH)_4(aq)$、$Sn(OH)_3^+$、$Sn(OH)_5^-$ 为主,并且 $Sn(OH)_4(aq) > Sn(OH)_3^+ > Sn(OH)_5^-$,其浓度依次为 $10^{-6.5}$、10^{-11}、$10^{-13.1}$;当 pH= 7.6时,矿浆中 $Sn(OH)_4(aq) > Sn(OH)_5^- > Sn(OH)_3^+ > Sn(OH)_6^{2-}$,其浓度依次为 $10^{-6.5}$、$10^{-11.6}$、$10^{-12.6}$、$10^{-13.1}$,其中以 $Sn(OH)_4$ 为主,这也说明,在糊精最佳吸附点 $Sn(OH)_4$ 是锡石表面主要定位离子,这表明糊精是与锡石表面 $Sn(OH)_4$ 起作用而吸附,且在糊精最佳吸附点时,锡石表面对 OH^- 的吸附量 Γ_{OH^-} 大于对 H^+ 的吸附量 Γ_{H^+}。

4　结　论

(1)糊精在锡石表面最佳吸附点 pH为 7.6左右;而糊精在赤铁矿表面吸附峰值 pH为 6.6,且糊精在赤铁矿表面吸附最大密度比锡石大得多,通过控制矿浆 pH和糊精在这两种矿物表面吸附密度的差异,可以实现锡石与赤铁矿浮选分离。

(2) H^+ 和 OH^- 在锡石表面等吸附点 pH为 5.4,小于糊精在锡石表面最佳吸附点 pH,且在最佳吸附点锡石表面 $\Gamma_{OH^-} > \Gamma_{H^+}$。

(3)糊精在锡石表面最佳吸附时,锡石主要定位离子组分为 $Sn(OH)_4$、OH^- 和 H^+,这表明糊精主要是与锡石表面 $Sn(OH)_4$ 发生作用而吸附。

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用添加剂提高瓷器白度

白俄罗斯科研人员研究了在日用陶瓷生产坯料(重量含量为高岭土 42%、粘土 7%、伟晶岩 18%、石英砂 25%、氧化铝 2%,另外 6%是二次烧成之后的制品渣)中加入 0.5%~ 2%的添加剂及碳酸钠和水玻璃,以提高瓷器的白度。据报道,当加入三聚磷酸钠时,瓷器白度提高 3%~ 5%;加入 ZrO_2 和 $ZrSiO_4$ 时白度提高 6%~ 8%,其机械强度亦明显提高;当用 $ZrOCl_2$ 水溶液(浓度 10%~ 30%)浸润一次烧成后,瓷器表面白度提高 5%~ 8%。

摘自《建材工业信息》1996,(22)

英文摘要

ENGLISH ABSTRACT

On the Supervision and Management to the "Three Rates" of Mines under the Market Economy

Liu Qinggao

According to the condition of our country and comparing with the foreign laws, the author expounded the necessity and feasibility of supervision and management to the "theree rates" of mines by administrative department. Seven pieces of advice are put forward.

On Administration of "Mining Right" over Private Mines

Liu Zhonghong

Based on expounding development situation and exsisting problems in private mines, Hebei province, the author puts forward that administration of "mining right" over private mines should be strengthened, and suggests that the laws and regulations concerned should be consummated.

On Illegal Mining of State- owned Mine's Resources

Dong Canghai

State- ownship mineral resources experienced seriously illegal mining. This paper discussed and listed typical cases. Such illegal random mining accompanied with waste of resources is forbides but often out of control. The autor suggested several countermeasures.

Utilization of Nonmetallic Minerals in Anqiu County

Zhang Xiuying et. al

The resources´ feature, development and utilization situation, and development trend of nonmetallic minerals in Anqiu County are introduced in this paper.

Phosphate Industry and its Development in Yunnan Province

Huang Zhongquan

Yunnan Province is rich in phosphate resources potential, basis of development and process industry promises a good fufure. At present, improving transportation conditions, adjusting products´ types, and develping deep- processing are important for more economic profits.

Experimental Research on Producing Activated Clay from Bentonite

Cai Shuxia et. al

Activated clay with fine index including decolorizing capability, decolorizing rate, activity number and particle size can be produced from a bentonite ore in Xinjiang by sulfuric acid activation. The processing technology has notable economic profit.

Organosilicon Materials Modify Mineral Surface

Rong kuiyi

In this paper, organosilicon materials which can be used to modify minerals were introduced. The modification mechanism, methods and effect was also explained.

Zeolites Structure, Property and Utilization

Hu Hongjie et. al

The authors expounded the structure and performance of zeolite molecule sieve according to crystal structure theory, and discussed its application in industrial fiedds.

A Study on Mechanism of Dextrin Interaction with Metal Hydroxyl Compound Adsorbed on Cassiterite Surface

Li Ye et. al

It is found that the maximum adsorp-

tion amount of dextrin on cassiterite surface occures at pH 7.6, yet, the equi- adsorption point of H^+ and OH^- on cassiterite surface in pulp is at around pH 5.4. Dextrin is adsorbed on cassiterite surface by action with $Sn(OH)_4$. Dextrin adsorbed on hematite is obviously more than that on cassiterite. The adsorption peak is at pH 6.6. This shows the selectivity of dextrin interaction between the two minerals.

Development of Low- grade Gold Resources

Xue Yingxi

The achievement and new progress in this field at domestic and abroad were reviewed, especially the progress in heap leaching recently.

Concentration of Subsieve Gold by Gravity Separation

Yuan Lingqun

The technology and equipment for recovering subsieve gold by gravity concentration were discussed, test results of washing pan as rougher concentrator were introduced, high- speed shaking table was recommended to be used in cleaning step.

Key Factors in Bacterial Heap Leaching of Gold

Wang Jinxiang

Research and application progress in bacterial heap leaching of gold were reviewed, the technology factors as bacterial kinds, ore properties and implement condition were discussed, and some measures were put forward for improving the process.

Experiment and Production for Reclaiming of Ta and Nb from Taillings Separated by Reverse Magnetic Separation

Qiu Debiao

The "acid leaching process" have been improved on basis of commercial test. In contrasting with the old process, the new one had increased 18.2% in concentrate grade and 59.0% in recovery, and the economic profit had risen greatly.

Recent Behavior in Industrial Minerals Development

Wang Jingliang

Any behavior and questions which are worthy of notice in industrial minerals development were summarized, the rcecnt industrial minerals output and developing matter of each countries were introduced.

Guye Laying Stress on Environmental Protection During Development of Mineral Resources

Li Houcai

Guye District of Tangshan City has hold up rational developing mineral resources according to laws for mang years. They comprehensively harness subsided region on basis of straightening order of mining industry, and receive remarkable economic and social benefits.

Manufacturing Fused Quartz Using Taillings Separated from Kaolin Ore

Liu Shuxing et. al

Quartz concentrate has been sparated from the taillings according to the process mineralogical characteristic of the taillings in Fuzhou, and qualified fused quartz has been manufactured using the concentrate.

翻译: 赵军伟　校对: 冯安生