doi:10.3969/j.issn.1007-7545.2021.07.006

拜耳法铝酸钠溶液中有机物脱除研究进展及化学氧化法应用展望

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摘要:拜耳法铝酸钠溶液中的有机物将影响氧化铝产品质量、生产顺行,而如何经济、高效地对拜耳法铝酸钠溶液中有机物进行脱除至今仍是亟待解决的行业难题。综述了拜耳法铝酸钠中有机物的来源、积累、危害及其脱除的研究进展,重点分析了工艺简单、清洁环保的化学氧化技术用于拜耳法铝酸钠溶液中有机物脱除的研究现状,并对光—化学催化氧化技术在铝酸钠溶液中有机物的脱除进行了展望。

关键词:拜耳法;铝酸钠溶液;有机物脱除;化学氧化法

中图分类号:TF821　　**文献标志码**:A　　**文章编号**:1007-7545(2021)07-0027-07

Research Progresses and Outlook of Chemical Oxidation Method for Organics Removal in Bayer Sodium Aluminate Solution

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Abstract: Organic compounds in sodium aluminate solution will affect quality of alumina products and production in Bayer process. However, how to economically and efficiently remove organic compounds from sodium aluminate solution of Bayer process is still an industry problem to be solved. Origin, accumulation, hazard, and removal process of organic matters in Bayer were summarized. Application of simple and environment friendly technique of chemical oxidization in organic compounds degradation in Bayer process were discussed. Photochemical oxidization method was proposed to be a potential technique for organic compounds decomposition in Bayer process.

Key words: Bayer process; sodium aluminate solution; organics removal; chemical oxidation

2018 年我国氧化铝产量已达 7 000 万 t[1],位居全球第一。拜耳法是氧化铝生产的主要方法[2],铝土矿中有机物及生产过程中添加的有机药剂会在拜耳法铝酸钠溶液中不断累积,对氧化铝产品质量和生产过程产生不利影响[3-7]。国内外学者对拜耳法铝酸钠溶液中有机物脱除开展了很多研究,目前主要有生物法、物理法、化学法等,但各类方法或存在成本能耗高,或处理有机物种类单一,或处于实验室

收稿日期:2021-03-07

基金项目:国家自然科学基金青年基金资助项目(51804088);贵州省科学技术基金项目(黔科合基础[2020]1Y219 号、[2019]1082 号);贵州省科技计划项目(黔科合平台人才[2018]5781 号)

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研究阶段。迄今，拜耳法铝酸钠溶液中有机物的经济、高效脱除仍是拜耳法生产氧化铝行业的一大难题。在众多方法中，化学氧化法因具有工艺简单、清洁环保等优势而备受青睐。因此，本文综述了拜耳法铝酸钠溶液中有机物脱除的研究现状，重点对化学氧化法进行了分析与讨论，对具有潜力的有机物复合脱除方法进行了展望。

1 拜耳法铝酸钠溶液中有机物的来源与累积

拜耳法铝酸钠溶液中有机物的来源主要包括铝土矿中有机物及氧化铝生产环节引入的有机药剂等[8]。我国铝土矿资源相对匮乏[9]，进口铝土矿中有机物含量较高，约为0.1%～0.28%[4]。来自矿物中的有机物约占铝酸钠溶液中有机物总量的96%[10-11]，且矿物中腐殖酸更容易在铝酸钠溶液中积累[12]；氧化铝生产、矿物浮选过程中添加的有机试剂约占4%[10]。铝土矿中有机物主要以腐殖酸为主，其中约40%随赤泥排出，40%转换为非草酸盐，10%转换为草酸盐，剩余10%转换为碳酸盐[13]。陈文汨等[8]通过试验得出矿石中约20%～30%有机碳进入到溶液。拜耳法铝酸钠溶液中有机物种类繁多，不同原料和工艺对有机物种类与组成有较大影响[14-16]。目前铝酸钠溶液有机物中含未降解的腐殖酸等约占溶液中总有机碳25%；脂肪族有机物如甲酸、乙酸、草酸、琥珀酸、丙二酸、戊二酸、己二酸、庚二酸、乳酸、苹果酸、酒石酸等约占总有机碳44%；芳香族有机物包括4-羟基苯酸、邻苯二甲酸、对苯二甲酸、没食子酸、香豆酸、水杨酸等[17]。低分子量有机物以简单的有机盐形式存在，较为稳定的有甲酸盐、乙酸盐和草酸盐等[18-19]。有研究表明草酸钠为主要的最终产物之一[20]。

2 有机物对拜耳法生产氧化铝的主要危害

有机物对拜耳法生产氧化铝的危害主要包括对铝酸钠溶液物化性能、氧化铝溶出性能、氢氧化铝析出、赤泥沉降及对设备等的影响[21-22]。有机物会改变铝酸钠溶液物理性质[23-26]，导致溶液密度、沸点、比热容增加，黏度升高，界面张力降低，产生大量泡沫占居有效容积，严重影响生产顺行[10,20]。有机物与碱反应生成有机钠盐如草酸钠、碳酸钠等，将造成碱损失[20]。铝土矿溶出过程中，有机物包裹在铝土矿表面可能会导致其溶出性能降低[25]。有机物，特别是草酸钠会使氢氧化铝粒度变细，过饱和草酸钠以极细的针状结晶析出，并作为二次晶核促进氢氧化铝结晶，吸附在氢氧化铝晶种活性位点上的草酸钠还能降低晶种活性、细化氢氧化铝粒度、降低晶种分解率并导致晶体呈片状生长[20,25,27]。当氢氧化铝中含有大量草酸钠时，可使氧化铝含碱量增加[20]。腐殖酸类有机物还会导致氧化铝晶体白度降低[28-29]、影响赤泥沉降与过滤分离过程[10,17,30-31]。有机物还将加剧设备结疤[32]，而结疤会导致使传热效率降低，能耗升高[33]。并且，有机物在高温条件下还可能部分分解成为气体(如甲烷等)，恶化生产环境[10]。

3 铝酸钠溶液有机物的脱除方法

拜耳法铝酸钠溶液有机物脱除的策略有：1)源头处理，如铝土矿焙烧法；2)从溶液中脱除有机物，如母液煅烧、吸附、沉淀，或将有机物进行氧化分解[16]。具体方法可分为生物法、物理法和化学法。

3.1 生物法

采用微生物通过生物化学法降解拜耳溶液中有机物[34-35]，具有较好前景，但需进一步研究强碱条件的适用性，且主要针对草酸盐降解，目前处于研究阶段。

3.2 铝土矿焙烧法

采用铝土矿焙烧法，可高效将有机物分解为二氧化碳等，刘艳艳[36]发现，在450 ℃焙烧，矿石中有机物含量可降低至0.03%，且氧化铝的溶出性能不受影响，脱除效率高，但能耗、成本较高[10]。

3.3 母液焙烧法

高温条件下对循环母液进行焙烧，可有效将溶液中有机物转换成二氧化碳，可较为彻底地脱除有机物，且溶液不需要苛化。通过焙烧使铝酸钠溶液溶出温度低、速度快[10]，国外有工业应用案例[11,37]，但该方法仍然存在能耗、成本高等不足。

3.4 离子交换法

铝酸钠溶液流过离子交换树脂时，有机分子被交换到树脂上而实现脱除分离，具有耗能低、污染少等特点，但树脂机械强度易降低、功能团易失活，且再生困难[10]。

3.5 结晶法

通过蒸发浓缩、添加晶种等使铝酸钠溶液有机钠盐结晶析出，可降低有机物浓度[10,38]，具有操作简单、草酸钠去除效果较好的特点。国内外针对结晶法开展了大量研究[39-40]，但该方法仅针对草酸

盐,对其他有机物脱除效果较差且会导致部分铝、碱损耗[41]。

3.6 沉淀法

向拜耳母液添加沉淀剂,如石灰、钡盐等,使之与有机物形成沉淀物实现分离[10,42]。沉淀法不足之处与结晶法类似[43]。

4 化学法脱除铝酸钠溶液中有机物研究进展

化学氧化法是将拜耳法铝酸钠溶液中的有机物通过氧化分解的方式进行脱除[44],分解产物主要为二氧化碳和水[45-46],高级氧化技术因其可产生强氧化性、无选择性、操作简单、清洁环保等优势受到广大科研人员的青睐[42,47-49],主要包括了氧气/臭氧氧化、双氧水氧化、化学催化氧化和光催化氧化等。

4.1 氧气/臭氧氧化

将氧气、臭氧等氧化性气体吹入铝酸钠溶液中可加速有机物的分解[37]。LIU等[50]研究发现,向260 ℃铝酸钠溶液中通入20 g/L氧气反应90 min后,溶液颜色从蓝黑色变成亮红色,透光度增强。氧气作为氧化剂可加速有机物降解,这种方法耗能、成本低,但效率有待提升。臭氧作为清洁氧化剂,陈映等[51]通过试验发现,臭氧在20 g/h常温下可将种分母液中有机碳从0.68%降低到0.58%,并使溶液脱色。另外,有报道称,偏碱性条件有利于O_3与OH^-反应生成$\cdot O_3^-$与$\cdot OH$[52]。但O_3在水中溶解度低,传质效率低,是限制臭氧化应用的潜在问题[53],且使用O_3作为氧化剂需考虑外泄导致污染问题。

4.2 双氧水氧化

杜振华等[54]对80 ℃苛碱浓度280 g/L铝酸钠溶液反应120 min后发现,草酸钠去除率为65.31%,有机物去除率达60.86%。李军旗等对有机物转变及其湿式氧化进行了系统研究[20,40,54-57],发现双氧水反应速率与有机物浓度遵循一级反应关系,湿式氧化有机物动力学方程[55]为

$$-\frac{\mathrm{d}[c]}{\mathrm{d}t}=3.45\times10^{7}\mathrm{e}^{-\frac{61\,260.63}{RT}}[c][H_2O_2]_0^{1.3}$$

另外,碱性条件下H_2O_2会与OH^-反应生成HO_2^-,减少了羟基自由基产生,会削弱其氧化性能[58]。

4.3 化学催化氧化

化学催化氧化是在化学氧化过程中添加催化剂,以提升有机物的降解效率,主要采用的催化剂为过度金属离子及其氧化物。张浩[59]以氧化铜为催化剂对铝酸钠溶液中有机物进行降解,在260 ℃、氧分压0.1 MPa,草酸钠脱除率高达94.6%。TARDIO等[60]在165 ℃,向铝酸钠溶液通入氧分压为500 kPa气体,对比研究了不同催化剂对有机物的降解能力,发现添加氧化铜时,整体催化能力达61.0%。

4.4 光催化

光催化因有机物降解能力强而备受关注[56,61]。光催化即光催化材料受到光电子激发后,在半导体的价带和导带上分别形成空穴和自由电子,空穴和自由电子与溶液中的H_2O/OH^-或O_2结合形成自由基,进而实现有机物的催化降解[62]。李国庆[63]以自制多孔二氧化钛气凝胶为催化剂,处理铝酸钠液中有机物,6 h光照后有机物去除率达52%。PAREEK等[64-65]也采用二氧化钛作为光催化材料用于拜耳法铝酸钠溶液有机物的光催化脱除,以1.0 g/L二氧化钛为催化剂,液体流速0.2 L/min,初始pH=11.75,反应90 min后,总有机碳转换率达35%。但二氧化钛在拜耳法铝酸钠溶液稳定性较差[66-67]。

4.5 光—化学催化氧化

羟基自由基($\cdot OH$,$E^0=2.8$ V)等具有超强氧化能力的自由基是化学法降解有机物的主要活性物质[68-69]。紫外光(UV)可促进强氧化剂向羟基自由基转变[58,70],而光激发催化剂产生空穴(h^+)与自由电子(e^-)也可转变为自由基或促进强氧化剂向自由基转变[71]。越来越多的研究[72-74]证明,光—化学耦合催化(UV/催化剂/氧化剂),即在UV照射的同时加入催化剂和强氧化剂(包括H_2O_2、O_3等),可通过光子能量($h\upsilon$)促使生成更多的自由基,以强化降解有机物,如$UV/TiO_2/O_3$对除草剂莠去津降解效率从单一光催化的56%提升至93%[73];$UV/Fe\text{-}CeO_2/H_2O_2$脱除四环素效率比单一催化效率提升5.3倍[72];$UV/BiPO_4/O_3/H_2O_2$对硫脲的降解效率为$UV/O_3/H_2O_2$的1.9倍[58]。因此,光—化学催化可作为拜耳法铝酸钠溶液中有机物经济、高效脱除的潜在技术。

5 结语与展望

拜耳法铝酸钠溶液中有机物的经济、高效脱除仍是我国氧化铝行业的一大难题,化学氧化技术因其无选择性、操作简单、清洁环保等优势受到广大科研人员的青睐。但针对高温、高碱且有机物组分复杂、溶液体系复杂的拜耳法铝酸钠溶液,单一的化学

氧化技术难以实现其有机物的高效脱除,复合技术如光—化学催化技术是拜耳法铝酸钠溶液有机物经济、高效脱除的潜在方法,值得科研或工程人员对相关机理、科学及工程问题开展系统研究。

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