

# 含氟废水处理工艺改造

邹东雷 杨忠平 原文双 林旭峰

(吉林大学环境与资源学院, 吉林 长春 130026)

**摘要** 针对氢氟酸洗沙废水 pH 低、氟含量高等特殊性, 提出一套完整的治理工艺。该处理工艺操作简单、运行稳定, 在进水氟含量达 1 560 mg/L 时, 出水仍能达标排放, 氟的去除率达 99% 以上。

**关键词** 化学沉淀 含氟废水 工艺改造

## 0 引言

某砂矿生产精砂过程采用氢氟酸洗沙工艺, 导致洗沙过程产生的废水含氟量较高、pH 偏低。扩大生产后, 洗沙废水水量增大、氟含量增加, 而原有沉淀法处理工艺不能满足国家排放标准, 无法进行正常的生产, 因此必须对原有处理工艺进行改造。

### 1 设计水质、水量及排放标准

该项目生产中产生的废水主要来自洗沙段, 通过类比调查及物料衡算, 确定该矿废水水量及污染物浓度见表 1。废水排放执行《污水综合排放标准》(GB8978-1996) 一级标准。

表 1 设计水质、水量及排放标准

项目	pH	氟浓度 (mg·L <sup>-1</sup> )	水量 (t·h <sup>-1</sup> )
生产废水	2~3	800	35~110
排放标准	6~9	10	

### 2 处理工艺流程

该工艺设计本着可靠、节能的原则, 在保证处理效率的前提下, 尽可能使建设投资节省合理、符合国家的有关政策, 工艺流程见图 1。

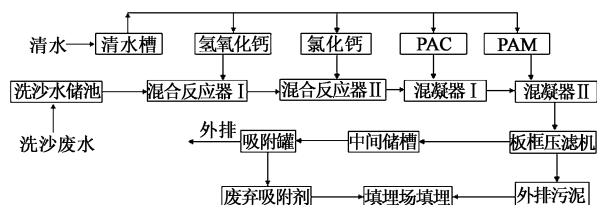


图 1 改造后处理工艺流程

### 3 设计思路及工艺参数

原废水处理工艺主要为传统的单纯投加  $\text{Ca}(\text{OH})_2$  化学沉淀法, 出水由于氟浓度偏高、pH 较大而无法达到排放标准。因此本工艺采用化学沉淀、混凝吸附的改进处理方法。

由于  $\text{CaF}_2$  与水中的  $\text{Ca}(\text{OH})_2$  可产生共溶现象,

故即使投加过量的  $\text{Ca}(\text{OH})_2$  也不可能使氟含量达到理论计算值。但过量的  $\text{Ca}^{2+}$  是保证  $\text{CaF}_2$  的沉淀达到最佳量的必要条件。而投加过量  $\text{Ca}(\text{OH})_2$  又会导致出水的 pH 偏高, 无法达到排放标准, 因此采用共同投加  $\text{Ca}(\text{OH})_2$  和  $\text{CaCl}_2$  的改进方法。  $\text{Ca}(\text{OH})_2$  的投加量根据出水的 pH 达到排放标准来确定, 而  $\text{CaCl}_2$  的投加量则根据废水中氟的含量和投药成本来共同确定。

废水中悬浮的  $\text{CaF}_2$  与  $\text{Ca}(\text{OH})_2$  的共溶颗粒, 是导致水中的氟浓度偏高的主要原因, 通过试验得出, 向废水中投 PAC 和 PAM 可以使共溶颗粒形成较大的絮凝体沉淀, 从而使废水中氟含量降低。故本工艺在原有工艺的基础上又增加了 PAC 和 PAM 的投加。

在投加药剂方面, 由于投加溶液与投加固体药剂相比, 具有反应充分、投加量容易控制、反应时间短等优点, 故设置  $\text{Ca}(\text{OH})_2$  配制罐 16 m<sup>3</sup>,  $\text{CaCl}_2$ 、PAC、PAM 配制罐各 5.5 m<sup>3</sup> 来预先将固体药剂配制成溶液。由于 PAM 的溶解问题, 故在配制罐前添设 PAM 溶解罐 11 m<sup>3</sup>。配制药剂质量分数见表 2。

表 2 药剂配制质量分数 %

$\text{Ca}(\text{OH})_2$	$\text{CaCl}_2$	PAC	PAM
10	10	5	0.2

由于  $\text{CaF}_2$  及絮凝体与洗沙废水中的废砂的共同沉淀作用使原沉淀池中的沉淀物含水量较小并且黏稠度高而导致不易清理。而板框压滤机却具有滤渣易清理、过滤时间短等优点。故本设计采用 4 台 8 m<sup>3</sup> 的板框压滤机代替原有的沉淀池。在板框压滤机后又添设了由 8 个 2.2 m<sup>3</sup> 的密闭罐分别串联成 2 组而成的吸附罐, 其中添加由石灰等物质混合烧结而成的改性陶粒, 以用于深度处理废水。

根据试验结果得出, 当  $\text{Ca}(\text{OH})_2$  与废水完全混

合反应后再投加  $\text{CaCl}_2$  处理效果最佳,故设置 2 台  $15\text{ m}^3$  的机械搅拌式混合反应器,分别进行混合反应,其停留时间  $15\text{ min}$ 。废水首先由洗沙水储池进入混合反应器 I 与  $\text{Ca}(\text{OH})_2$  配制罐、经泵输出部分溶液混合,部分回流到配制罐,人工控制方法添加药剂。此阶段主要保证废水 pH 为  $8\sim 9$ ,有利于后续混凝处理并保证  $\text{Ca}^{2+}$  与  $\text{F}^-$  反应达到了平衡状态,有利于投入  $\text{CaCl}_2$  后反应更快地向正方向进行,以使废水中氟含量达到利于后续处理的最优值。在反应完全后废水以重力自流的方式进入混合反应器 II,以上述同样的方式添加  $\text{CaCl}_2$  溶液。

经充分搅拌反应后混合反应器 II 出水依次流过 凝器 I、II 进行凝絮反应。由于 PAC 和 PAM 的用量相对较少,为减少设备和占地面积,通过计量泵计量后采用静态混合器在管道中混合。凝器 II 出水通过板框压滤机将  $\text{CaF}_2$  过滤去除,在经过改性陶粒吸附后达标外排。

4 试运行操作参数及监测数据

进水采用连续运行的方式进行。4 台板框压滤机,运行状态为半连续式,交替运行,其中 1 台达到预定压力后,切换进水阀,使废水进入另 3 台板框压滤机,同时清理停止运行的板框压滤机中的滤渣并清洗滤布。当另 1 台达到预定压力后,重复上面的操作步骤。清理周期为  $8\text{ h}$ 。

试运行期间,定时监测进水及出水水质,水质情况见表 3。由表 3 可知,在试运行 1 个月时间内,出水水质并未因为多次重新配制新药剂溶液和清理板框压滤机中的滤渣及清洗滤布而出现显著的波动,出水氟含量和 pH 保持相对稳定,氟的去除率始终保持在  $99\%$  以上。因此该工艺设计合理并可以正式投入运行。

5 结论

(1) 该工艺运行稳定,出水氟  $< 10\text{ mg/L}$ ,达国家一级排放标准。

表 3 水质监测数据

日期	原水氟离子 浓度/( $\text{mg}\cdot\text{L}^{-1}$ )	板框出水 $\text{F}^-$ 浓度/( $\text{mg}\cdot\text{L}^{-1}$ )	吸附后 $\text{F}^-$ 浓度/( $\text{mg}\cdot\text{L}^{-1}$ )	去除率/ %	出水 pH
08-28	1 155.08	10.11	8.13	99.30	7.84
08-29	1 155.08	9.01	8.75	99.24	7.95
08-30	1 505.71	10.13	7.34	99.51	7.54
08-31	1 565.45	11.84	7.02	99.55	7.45
09-01	1 507.74	11.38	7.37	99.51	7.76
09-05	1 300.67	14.56	8.13	99.37	7.92
09-10	1 288.67	12.30	8.75	99.32	8.04
09-20	1 146.67	10.95	7.37	99.35	7.95
09-30	1 083.25	10.53	8.13	99.25	8.11

(2) 采用联合投加  $\text{Ca}(\text{OH})_2$  和  $\text{CaCl}_2$  混凝的处理方法,沉淀效果好,出水 pH 约为 8,优于传统单独投加  $\text{Ca}(\text{OH})_2$  的方法。

(3) 板框压滤机的过滤时间远小于传统的沉淀时间,用于清理滤渣的工作量小于清理原沉淀池中沉淀物的工作量,每台板框压滤机运行其清理周期为  $8\text{ h}$ 。

参考文献

[ 1 ] 张焕祯,王振川,赵韵琪,等.石灰- $\text{CaCl}_2$  絮凝法处理酸性高氟废水的试验研究.环境工程,1995,13( 1 ): 8-10

[ 2 ] 周钰明,余春香.吸附法处理含氟废水的研究进展.离子交换与吸附,2001,17( 5 )

[ 3 ] 李雪玲,刘俊峰,李培元.石灰沉淀法除氟的应用.水处理技术,2000,26( 6 ): 359-361

[ 4 ] 张希祥,王煤,段德智.氧化钙粉末处理高浓度含氟废水的实验研究.四川大学学报,2001,33( 6 ): 111-113

[ 5 ] 乔芸雯,唐为亮.光纤废水处理工程设计.环境工程,2003,21( 2 ): 26-28

作者通信处 邹东雷 130026 吉林长春市西民主大街 938 号 吉林大学环境与资源学院  
电话 ( 0431 ) 8499792  
E-mail zoudl@jlu.edu.cn

2007- 11- 26 收稿

环保热词汇

无车日: 根据建设部测算,开展“无车日”活动 1 天,仅民用轿车即可节省燃油  $3.3\times 10^7\text{L}$ ,减少城市污染排放总量约  $90\%$ 。这说明了一个浅显的事实,保护环境是每个人力所能及的事。同时,需要强调的是,保护环境无法毕其功于一役,因此,这样的活动,应该成为常态;这样的行为,应成为每个人的习惯。

摘自“中国环境报”

**Abstract** Combining with the existing smelting conditions, it was carried out that checks on relevant parameters of the primary dedusting systems for the converters of Panzhihua Iron and Steel Group Company; it was also analyzed the existing problems of the systems according to the parameters of the original design. The measures for improving the dedusting systems were proposed and implemented, after which the dedusting systems could meet the demands on treating pollution.

**Keywords** converter dedust flue gas venturi tube throat

## THE CHARACTERISTICS AND MEASUREMENT OF NOISE FROM PIPELINE OF PIPE GALLERY OXYGEN AREAS IN LARGE IRON AND STEEL PLANTS .....

Yu Wuzhou Zeng Huaxiu Li Minna et al( 68 )

**Abstract** Portable sound insulation/ noise abatement tube method is presented to make efficient pipe noise measurement and identification of pipelines of pipe gallery in oxygen area for a large iron & steel plant, and the characteristics of pipe noise are analyzed. The results show that this method is effective and reliable. What's more, pipe noise changes along pipe length due to the effect of valves and bendings, and different pipes emit noise with different levels and spectral characteristics. It is suggested in this paper that proper pipe lagging structures should be applied to pipe gallery with different pipelines according to their noise contributions.

**Keywords** noise measurement pipe noise

## IMPROVEMENT ON DECOLORIZATION PROCESS OF ACTIVATED CHAR .....

Zhang Mengcan( 71 )

**Abstract** According to the problems of the traditional decolorization process of activated char, their causes were analyzed and a feeder of venturi tube was developed, which fundamentally solved the pollution of adding activated charcoal, the bump and the fusion speed. The decolorization time was decreased and the production efficiency was also raised.

**Keywords** activated charcoal decolorization venturi tube feeder

## PILOT-SCALE TEST ON NITROTOLUENE WASTEWATER TREATMENT WITH MICRO-ELECTROLYSIS AND I-BAF .....

Ye Zhengfang Wang Zhongyou Mou Jinghai et al( 73 )

**Abstract** Pilot scale test was made on the treatment of nitrotoluene wastewater by using micro-electrolysis and immobilized microorganism-biological aerated filter (I-BAF) process. The results indicate that the process has high efficiency and low cost (0.23 Yuan/t wastewater) and it also has characteristics of steady running and powerful resistance to impact load. When total hydraulic retention time is 28 h, the removal rates of nitrotoluene (MNT, DNT and TNT), aniline and COD are 99%, 85.1% and 72.8%, respectively.

**Keywords** immobilized microorganisms biological aerated filter micro-electrolysis nitrotoluene wastewater

## CHARACTERISTIC STUDY ON NEW BIOREACTOR SHORT-RANGE NITRIFICATION DENITRIFICATION .....

Song Yinghao Yang Shasha Zhao Zongsheng et al( 76 )

**Abstract** Some studies on nitrite accumulation in nitrification process by using air lift reactor were performed. Treatment effect of combined process of nitrification-denitrification was also studied by combining air lift reactor with upflow sludge bed after it had been operating for six months. The results show that when concentration of influent ammonia was more than 98 mg/L and free ammonia reached 1.07 mg/L, concentration of effluent nitrite started to rise and over 50% of nitrification rate ( $\text{NO}_2^-/\text{N}$  or  $\text{NO}_3^-/\text{N}$ ) could be achieved. When ammonia sludge loading was close to 0.53 kg/(kg·d), ammonia removal rate was quite high and nitrification rate was maximum. But when sludge loading reached 0.85 kg/(kg·d), ammonia removal rate fell. There was obvious particulate sludge in upflow sludge bed reactor. Treatment effect of ultimate effluent turned good obviously when carbon source was enough.

**Keywords** air lift reactor short-range nitrification-denitrification upflow sludge bed reactor particulate sludge

## TREATMENT PROCESS OF OILY WASTEWATER DURING ROLLING PROCESS .....

Wang Jiang Li Zhengyao Han Jingtao( 79 )

**Abstract** The process of demulsification-flocculation-activated carbon adsorption is used in the treatment of the oily wastewater from a rolling mill. During the treatment, W25 is used as demulsifier and PAC as flocculant, then the water is filtered by activated carbon, whose effluent can reach the second-order emission standard.

**Keywords** demulsifier wastewater treatment physicochemical methods

## INNOVATION OF TREATMENT PROCESS OF WASTEWATER CONTAINING FLUORINE .....

Zou Donglei Yang Zhongping Yuan Wenshuang et al( 81 )

**Abstract** A complete set of wastewater treatment process is proposed according to the fact that there is a lower pH and a higher  $\text{F}^-$  in the wastewater from the process of washing sand by hydrofluoric acid. The treatment process features simple operation and stable running, therefore, the effluent still can meet the emission standard when the fluorine content of the influent is 1560 mg/L, and the removal rate of F is over 99%.

**Keywords** chemical precipitation wastewater containing fluoride technological innovation