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Case study-fluoride wastewater from photovoltaic industry recycled

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ABSTRACT

Tianwei Yingli New Energy Resources Co., Ltd., located in China, mainly engaged in silicon solar cell production and sales. Fluoride wastewater mainly came from cell production. Original facilities discharged fluoride wastewater, through Chemical precipitation process. Discharged fluoride wastewater could be up to standard. But the cost of wastewater treatment was high, especially in the low concentration wastewater. To save the water resources and reduce the cost, the classified collection was implemented, then used double pass RO to treat low concentration fluoride wastewater. Before wastewater into RO system, adjusted the pH value and passed activated carbon filter. RO product water instead of tap water entered the pure water preparation system to reuse. The project total investment was about 6.7 million Yuan, treating wastewater was 4320 m^3/d. Net income of 3.06 million Yuan/a, and static payback period is 2.2 years. The economic benefit was remarkable.

Key words: Reverse osmosis; Fluoride wastewater; Photovoltaic industry; Wastewater reuse

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INTRODUCTION

Reverse osmosis has high desalination rate, and is conducive to environmental protection. In recent decades, it has been widely used in water reuse, industrial water supply, and wastewater treatment, etc[1].

Photovoltaic industry in China has developed rapidly; photovoltaic wastewater treatment attracts more and more attention [2]. The main wastewater from photovoltaic industry is fluoride wastewater. Most companies discharge the fluoride waste water, after simple processing [3]. With the increasingly water resources scarce, fluoride wastewater reuse has become the inevitable trend.

Tianwei Yingli New Energy Resources Co., Ltd., located in China, mainly engaged in silicon solar cell production and sales. Fluoride wastewater mainly came from cell production. Original facilities discharged fluoride wastewater, through Chemical precipitation process. Discharged fluoride wastewater could be up to standard. But the cost of wastewater treatment was high, especially in the low concentration wastewater. To save the water resources and reduce the cost, the classified collection was implemented, then used double pass RO to treat low concentration fluoride wastewater. The system ran stably, and the effect was very good.

INTRODUCTION OF WASTEWATER

The fluoride wastewater mainly came from the silicon solar cell workshop. Silicon wafer cleaning includes pure water cleaning, alkaline (NaOH) cleaning, acid (HF) cleaning and mixed acid cleaning. High concentration fluoride wastewater was from acid cleaning and mixed acid cleaning, and the low was from pure water cleaning and alkaline cleaning. Fluoride wastewater was unstable. The amount and pH value often changed. At the same time, the wastewater was poor in biodegradability.

RO method was more suitable for the processing of low concentration wastewater than the high, so the high concentration wastewater entered the treatment system of high fluoride wastewater, and this project treated the low fluoride wastewater. Source of wastewater was shown in Figure

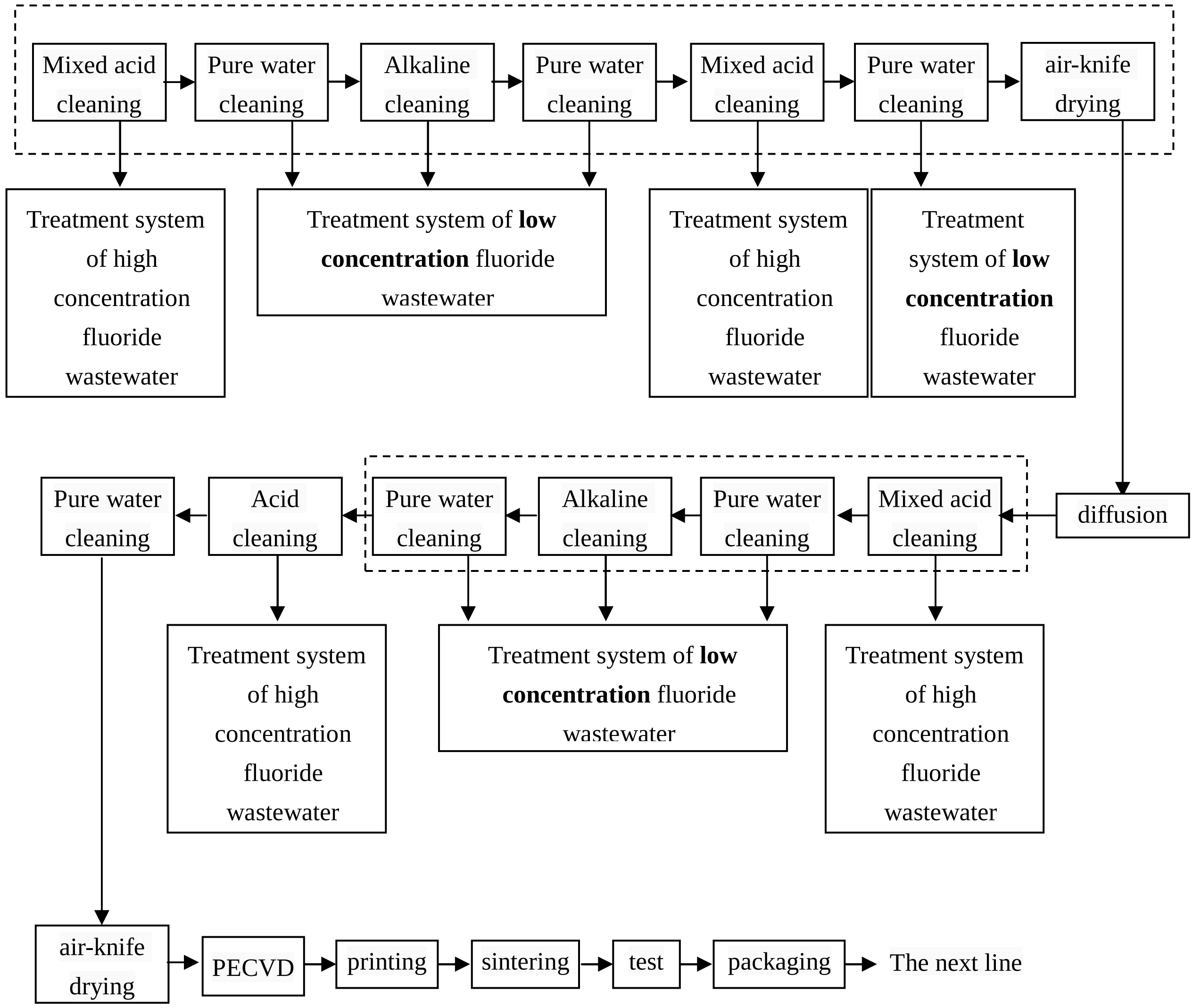

Figure 1 Sources of wastewater

INTRODUCTION OF ORIGINAL FLUORINE FACILITIES

Process of original fluoride wastewater treatment facilities was shown in Figure 2. Through the original treatment facilities, wastewater could meeting the national standard III of Integrated wastewater discharge standard(GB8978－1996).

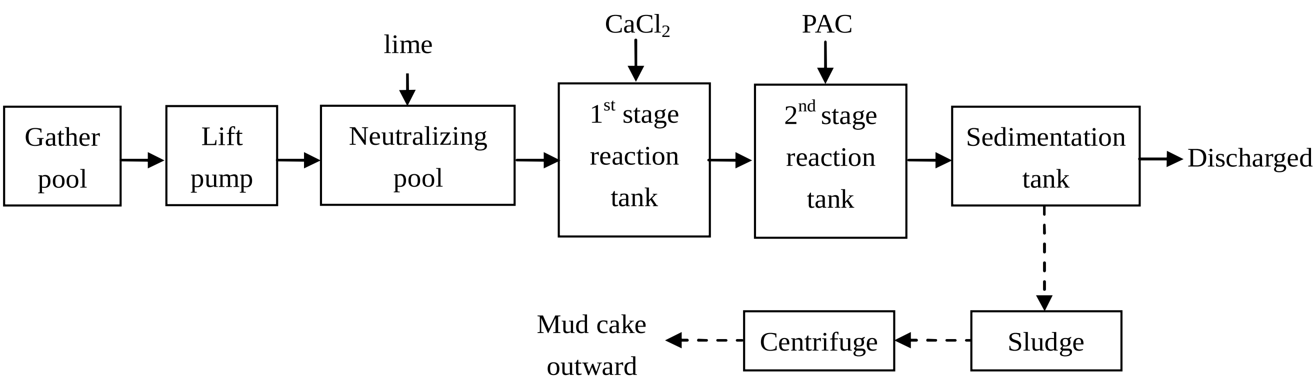

Figure 2 Process of fluoride removal

The process of fluoride removal mainly added lime, calcium chloride and flocculating agent, made the fluoride react with lime and calcium ion in the calcium chloride, and generated CaF_2 precipitation, in order to remove the fluoride in waste water.

The water quality of original fluoride wastewater treatment facilities is shown in Table 1.

Table 1 The water quality of original fluoride wastewater treatment facilities

Items	pH	COD_{Cr} ($mg \cdot L^{-1}$)	F^{-} ($mg \cdot L^{-1}$)	Electrical conductivity ($\mu S \cdot cm^{-1}$)	Hardness ($mg \cdot L^{-1}$)
Raw water	2.5~4	8~30	140~300	1600~4000	3~8
Water discharged	6~7	15~80	8~15	3000~6000	800~1400

According to the Table 1, before fluoride removal, quality of fluoride wastewater was relatively clean, just mixed with acid or alkali, and was low concentration of COD and hardness. After adding lime, flocculant and other industrial agent, quality of wastewater was more complicated. COD concentration, conductivity and hardness was higher than before. If joined the excess calcium ion, RO membrane would be easy fouling.

RECYCLING PROCESS DESIGN

According to the characteristics of the fluoride wastewater, selected fluoride wastewater without fluoride removal as recycling object. The wastewater was reused to pure water station, instead of fresh water to produce pure water and supply to production. Concentrated water entered the original fluoride treatment facilities. RO product water needed to meet the quality of < The reuse of urban recycling water –water quality standard for industrial uses> (GB/T 19923-2005).

Considering wastewater characteristics, enterprise production scale, and impact load, the design capacity of wastewater was $180m^3/h$. Product water entered the pure water preparation system for recycling. Process of reuse system is shown in Figure 3.

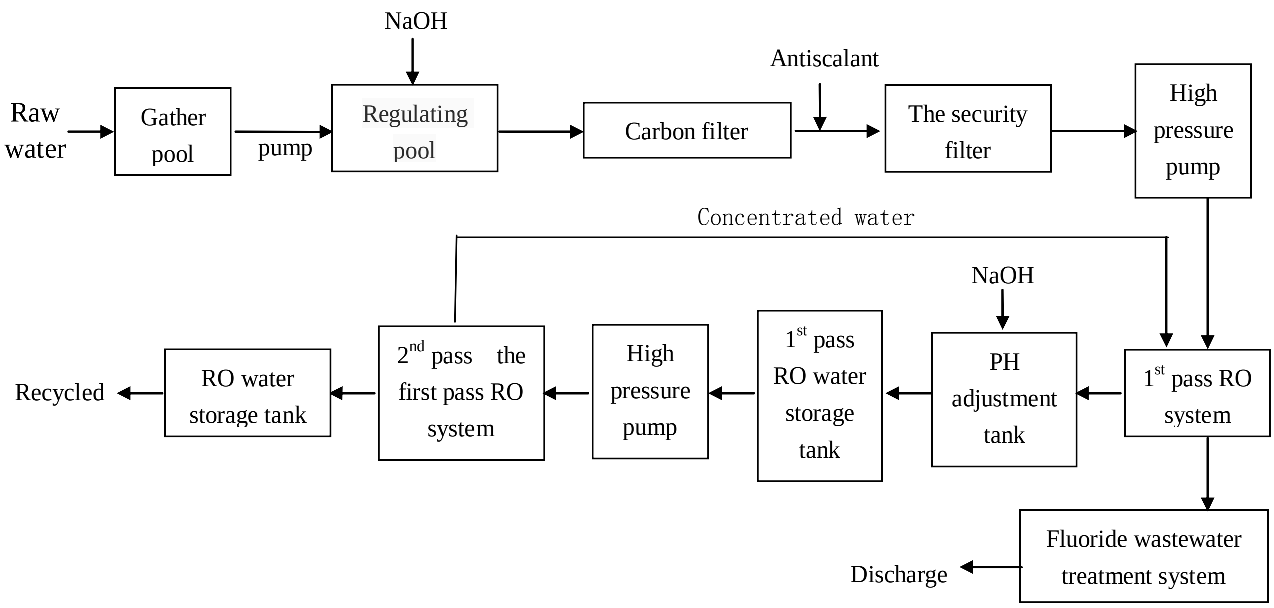

Figure 3 Process of fluoride wastewater reuse system

1. Pretreatment process

The wastewater containing colloidal material such as silicon and silicon dioxide, and pH value was low, so wastewater must to be pretreatment. Pretreatment system includes high pressure pump, pH adjustment pool, Carbon filter, and NaOH dosing device.

Broken silicon particles were small, wastewater was strong corrosive, so did not use a regular grid as interception device. System installed bag filter (filtration precision for 100μm), and avoided broken wafer cutting danger of reverse osmosis membrane.

When apply NaOH to adjust the pH of waste water, buffer solution would be created in waste water. If directly adjust the wastewater to neutral, the consumption of sodium hydroxide would be substantial. To reduce the cost, pH adjustment could be done in two stages. Adjusted the pH to 5 before proceeding the 1^{st} pass RO. After the treatment of 1^{st} pass RO, remove most of weak acid ions, and adjusted the water pH to neutral before preceding the 2^{nd} pass RO.

Carbon filter could be used to absorb the suspended matter, colloid and a few of organic matter in waste water, thereby ensuring the water requirements of RO system. The back-flushing of carbon filter could be appropriate for cleaning the active carbon, thus improving the lifetime of active carbon.

2. RO system

RO System was the core of wastewater reuse system, which could remove most soluble salt, colloid and microorganism. RO system mainly consisted of the security filter, high pressure pump, two pass RO membrane, membrane cleaning system, antiscalant and reducing agent feeding system. In addition, it was equipped with RO cleaning, automatic control equipment and monitoring facilities and so on.

2.1The security filter

Filtration precision of filter core was 5μm, that could remove pollutants (greater than 5μm), and ensured the normal operation of RO. When import and export filters differential pressure greater than 1 bar, need to change filter core.

2.2High pressure Pump

Install high pressure pumps in front of 1^{st} pass and 2^{nd} pass RO, to provide sufficient water pressure. High pressure pump using variable frequency control could automatically adjust the running pressure, according to different water temperature, thus protected the membrane module.

2.3RO Membrane

The 1^{st} pass RO membrane was made of acidproof polyamide, from HYDECANME, having good ability to resist pollution. It could be applied in low pH water, thus extending the lifetime of membrane. In this model, the length of RO membrane was 1m. Desalination rate of single membrane was 99.6%.The membrane shell was made of 300PSI FRP, especially for RO pressure vessel. The 1^{st} pass RO was designed with two sets of systems: one had 16 pieces of membrane shells, each membrane shell have 6 pieces of membranes. There was 192 in total.

The 2^{nd} pass RO was made of HYDECOULDME CPA-LD RO membrane. Likewise, the membrane shell was made of 300PSI FRP. It was designed with two sets of systems: each has 12 pieces of membrane shells, and each membrane shell had 6 pieces. There were 144 pieces in total.

2.4Antiscalant agent feeding system

In order to avoid any chemical scaling at the concentrated terminal, added antiscalant before the wastewater flows into RO membrane. This system applied high-silicon as antiscalant, effectively preventing the inorganic matter from scaling, and disperse the iron colloid and fine particle that block the microporous membrane.

Feeding system equipped soluble chemical bucket and metering pump, so the addition could be automatically adjusted according to the flow.

2.5Membrane cleaning system

The operating pressure of RO system must be below 2MPa. After a long time, organic matter, inorganic matter and floc from pH value adjusting would be deposited on the membrane surface, cause the membrane pollution. When the performance of RO membrane was degraded and the operating pressure increased, required to clean with chemicals. The cleaning system included clean the chemical bucket, the security filter and pump.

SYSTEM OPERATION

The system had run for a year, operating in good condition. The amount of product water was 90～130m^3/h, the recovery rate was 60%, desalination rate was above 98%.

Product water quality of actual operation was shown in Table 2.

BENEFIT ANALYSIS

The project total investment was about 6.7 million Yuan, treating wastewater was 4320 m^3/d. Wastewater treatment cost was about 3.53 Yuan/t. If 330 days working days, direct operation cost 3.355 million Yuan/a.

The local water fee of was 4.25 Yuan/m3. The project could save fresh water 950 000 m^3/a, and save water fee 4.039

million Yuan/a. In addition, this project ran stability, reduce fluoride density of 11.4 t/a, and cut down the cost of fluoride removal treatment 237.6 million Yuan/a.

So project net income of 3.06 million Yuan/a, and static payback period is 2.2 years. The economic benefit was remarkable.

Table 2 Product water quality

	The quality of product water ($m^3 \cdot h^{-1}$)	pH	Electrical conductivity ($\mu s \cdot cm^{-1}$)	F^- ($mg \cdot L^{-1}$)	recovery rate(%)
5.13	127	7.2	19	2.5	61.2
5.19	98	7.4	9.8	1.8	64.5
5.25	115	7.1	12	2.0	65.7

CONCLUSION

It is feasible, that RO technology is applied to photovoltaic wastewater reuse. Because it can reduce the use of fresh water, at the same time reduced the industrial waste water discharge. It has good economic benefits and social benefits

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