Technology Research of Desulfurization Wastewater Zero Emissions

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Abstract. This paper investigates the operation process and operating costs of Heyuan Power Plant and Hengyi Power Plant wastewater by on-site inspection. It is considered that in areas with high environmental protection requirements, the highly reliable pretreatment + evaporation crystallization process should be considered first. In combination with the situation of the power plant, a reverse osmosis system is added after the pretreatment device to increase the processing capacity of the equipment and reduce the running cost.

1. Introduction
With the strict requirements of the country for environmental protection, almost all coal-fired power stations have installed desulphurization facilities. With the long-term operation of the desulfurization equipment, a certain amount of desulfurization wastewater must be periodically discharged. Desulfurization wastewater is different from general wastewater. Its density is low and it is weakly acidic. The chemical oxygen demand is inorganic ions with reducing properties. The content of suspended solids is high. The soluble salt content is about 40,000 mg/l, mainly Cl-, followed by Ca$^{2+}$ and SO$_4^{2-}$. In addition, the desulfurization wastewater also contains a certain amount of heavy metals, generally mercury, arsenic, chromium, copper, lead and other substances. Under normal circumstances, the amount of desulfurization wastewater generated is 15-20 kg/MW·h. The amount of desulfurization wastewater of 300,000 kW unit is about 5 m$^3$/h without considering the water balance control [1, 2].

In the conventional desulfurization water treatment method, in the neutralization tank, Ca(OH)$_2$ is added to adjust the pH value to 8.5-9.0 to precipitate most heavy metals; in the sedimentation tank, organic sulfur (TMT) is added to make the remaining heavy metals precipitation in the form of sulfide; if the water quality COD exceeds the standard, it is necessary to add an oxidant or aeration treatment in the neutralization tank. After that, the solid in the waste water is made into a mud cake by flocculation and clarification, and is transported out by the automobile, and the pH value of the remaining clear liquid is adjusted to 6.9-9.0 and discharged. Since the high concentration of Cl- cannot be removed in the process, the waste water is dehydrated. Introduce an advanced treatment process by discharging [3, 4].

2. Introduction of two mature advanced treatment processes
At present, the zero-emission treatment process of desulfurization wastewater is relatively advanced, and the actual operation conditions are Guangdong Heyuan Power Plant and Sanshui Hengyi Power Plant. Therefore, these two technologies are selected for on-site investigation and comparative analysis.
2.1. Pretreatment + evaporation crystallization process

Heyuan Power Plant is a 600MW ultra-supercritical unit, close to Dongjiang Reservoir, which is one of the important water sources in Shenzhen and Hong Kong. Therefore, the Ministry of Environmental Protection requires the plant to have no wastewater discharge port and implement zero discharge of wastewater. The pretreatment process of the desulfurization wastewater of the plant is designed and supplied by Xi’an Thermal Engineering Institute Co., Ltd., and the evaporation crystallization part is designed and supplied by Shenneng Environmental Protection.

2.1.1. Pretreatment process. The pretreatment process adopted by the power plant adopts a two-stage sedimentation treatment process, the first-stage coagulation sedimentation achieves the purpose of reaching the standard discharge, and the second-stage coagulation sedimentation meets the requirements of the water inlet index of the evaporation system.

Process: The desulfurization wastewater enters the reaction tank 1 uniformly, and the lime is added to the pool to adjust the pH value to about 10-10.5. Most of the heavy metals, Mg$^{2+}$, and F-, sulfate and the like react with the lime to form a precipitate, and the mixture enters. In the reaction cell 2, an organic sulfur solution is added to the reaction cell 2 to remove residual heavy metal ions, and then an iron-based coagulant and an organic polymer flocculant are added to complete solid-liquid separation in the mechanically stirred clarification tank 1.

A part of the sludge generated in the clarification tank 1 is returned to the reaction tank 1, and the supersaturated gypsum is removed by the principle of the gypsum seed crystal method, and the other part is sent to the sludge concentration tank for sludge concentration, and the supernatant in the concentration tank is partially returned to the sludge. The reaction tank 1 is reprocessed, and the concentrated sludge is subjected to solid-liquid separation by a chamber filter press, and the pressure filtrate is also refluxed into the reaction tank 1 for reprocessing, and the mud cake formed by the pressure filtration is transported.

The supernatant of the clarification tank 1 enters the reaction tank 3, and Na$_2$CO$_3$ is added to the tank to remove Ca$^{2+}$ ions which are likely to cause scaling in the subsequent deep evaporation treatment system, and the effluent from the reaction tank 3 enters the mechanical stirring clarification tank 2 for solid-liquid separation and sedimentation sludge It contains a large amount of CaCO$_3$, which can be returned to the desulfurization treatment system for reuse. The supernatant of the clarification tank 2 enters the intermediate pool. At this time, the pH of the effluent is 10-10.5, the Ca$^{2+}$ concentration is reduced to 1000 mg/l, and a part of the water is used for the preparation of the lime slurry. The remaining water was passed through a pH recovery tank, and the pH was adjusted to 8.5-9.0 with hydrochloric acid to be used as an evaporation system.

After the above treatment process, the wastewater pollution index can meet the discharge requirement in addition to the pH. Therefore, when the evaporation system is shut down, the water in the clarification tank can be directly discharged after adding the acid and alkali to adjust the pH to the standard.

2.1.2. Evaporation crystallization process. The process draws on multi-effect evaporation and forced circulation crystallization technology in evaporation salt production. This system uses four-effect evaporation method for evaporation and concentration, and forced circulation to carry out crystallization. After crystallization, the concentrated water returns to the inlet for reuse, and the power plant is used to assist the steam. As a heat source, the steam parameter is about 0.2-0.3 MPa, 165 °C, and the steam consumption is about 6-7 tons / hour. After the condensed water is collected, it is taken to the intermediate pool for use, and the crystallized salt is dried and then bagged for shipment.

2.2. Evaporation and concentration + forced circulation crystallization

Hengyi Power Plant is two 600,000 kW supercritical coal-fired generating units. The power plant site is adjacent to the water source protection site, so the control of sewage discharge indicators is stricter. The project selected the desulfurization wastewater crystallization technology of Foshan Dejia Electric
Environmental Protection Technology Development Co., Ltd. to achieve zero discharge of wastewater. After the project was put into operation, Foshan Dejia Company undertook the operation and maintenance of the desulfurization wastewater system.

The desulfurization wastewater process is not designed with a pretreatment system. The desulfurization wastewater and other industrial wastewaters are mixed and directly passed into the evaporation concentration crystallization process by evaporation. The evaporation concentration is carried out by MVC evaporation concentration + forced circulation crystallization. The treated crystal salt is entrusted to the local solid waste treatment company. Packed out.

3. Comparison of the two schemes
The Heyuan Power Plant project covers an area of about 2,000 m² and uses a 4-effect evaporator treatment process. The overall system cost is about 70 million yuan, and the total cost of running and depreciating is about 15 million yuan/year.

The technology of this scheme is relatively advanced and the parameters are high. The desulfurization wastewater has achieved zero discharge after treatment, but the cost and operation cost of the system equipment are high and the economy is slightly insufficient.

From the on-site field research, the system is running well, the backwashing and descaling period of the equipment is about once a month, the maintenance amount and the operation amount are less; the site is clean and tidy, the crystal salt is white in color, and the visual sense is good after bagging; The mud cake has a low water content and is condensed into pieces for easy transportation.

The equipment of Hengyi Power Plant covers an area of about 600 m², the overall system cost is about 55 million yuan, and the operating depreciation cost is about 14 million yuan / year (depreciation 15 years) or 16 million yuan / year (depreciation 10 years).

Among them, key equipment such as compressors are all imported equipment, and a large amount of titanium alloy and other materials are used inside the evaporator. Because the system does not have pre-treatment equipment, the system has high water inlet hardness, and the internal fouling speed of the evaporator is very fast. Descaling is required every 3-5 days, and the equipment reliability is poor. The crystalline salt was yellowish and the specific ingredients were not detected.

The device has a simple structure and low equipment cost, but the pretreatment system does not cause frequent system fouling, large maintenance, low equipment reliability, and the salt is not pure due to the presence of a large amount of calcium and magnesium salt mixture in the crystalline salt. Can not be recycled and reused.

In summary, due to the existence of the pretreatment system, the Heyuan Power Plant makes the pretreatment + evaporation crystallization process superior to direct evaporation concentration + forced circulation crystallization in terms of both technical and reliability. In terms of economy, the mechanical compression process of Hengyi Power Plant is more dominant, but it needs to be further calculated according to the cost of steam.

4. Program design
Since the desulfurization process water of the plant adopts desalinated water and the initial chloride ion content is low, the salt content and hardness of the desulfurization wastewater are much lower than other plants. The chloride ion content of the desulfurization wastewater is only 1/3 of that of Heyuan Power Plant, and 1/2 of Sanshui Hengyi, and the total hardness is also the same. Therefore, it is conceivable to add a reverse osmosis system after the pretreatment process to double the brine entering the evaporation crystallization system, so that the treatment amount of the evaporation crystallization system is doubled, which not only reduces the equipment cost but also reduces the operation cost.

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