

Experimental Study of Flue Gas Desulfurization Wastewater Zero Discharge from Coal-fired Power Plant

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Abstract. In order to ensure the FGD (Flue Gas Desulfurization) system security and reliability, part of the wastewater should be discharge from the FGD system. Desulfurization wastewater with high salinity, high corrosion and other characteristics will lead to water pollution and waste of resources, and it is necessary to take a security and stability method to treat high concentration saline wastewater. The zero discharge treatment technology of desulfurization wastewater was proposed, and a coal-fired power plant desulfurization wastewater as the research object, designed the system process, carried out experimental study of pretreatment combined with evaporation crystallization of wastewater. In the pretreatment stage, sodium sulfate was added to the water, and then the effluent was pumped into the evaporation crystallization unit, based on the method of gypsum crystal, the high purity sodium chloride was prepared. Pilot experimental results show that the system treatment technology for power plant desulfurization wastewater zero discharge is feasible, which can realize the crystallization salt resource; Sodium chloride salt crystals after purification for more than 99.10% purity, satisfy the standard of industrial salt optimal level, and can be utilized as industrial raw material.

Introduction

At present, the limestone-gypsum wet method is the most widely used in coal-fired power plant for Flue Gas Desulfurization system^[1]. In order to ensure the FGD (Flue Gas Desulfurization) system security and reliability, Flue Gas Desulfurization system allowed discharging part of the wastewater^[2-3]. Impurities mainly from flue gas desulfurization wastewater and the desulfurization agent, which the former is derived from the combustion of coal, which the others is derived from the limestone dissolution and reactions. Therefore, desulfurization wastewater mainly contains suspended solids, sulfate, supersaturated sulfite and heavy metals and other impurities^[4]. Due to calcium and magnesium ion and sulfate ion concentration is high, desulfurization wastewater easy to form scale in the heating process^[5], the concentration of sulfate ion is 4000 mg/L, calcium ion is 1500-5000 mg/L, magnesium ion is 3000-6000mg/L, and calcium sulfate in the supersaturated state. Material corrosion protection requirements for equipment and pipe is very high^[6], because the desulfurization wastewater with high salinity, especially high content of chloride ion, and strong acidic (pH of 4-6.5), as well as strong corrosive.

The FGD wastewater treatment process are mainly chemical treatment method, which can be roughly divided into wastewater treatment system and sludge treatment system, and the wastewater treatment system can be divided into the neutralization, sedimentation, flocculation and concentration process.etc^[7-8]. However, even after the traditional processing, the FGD wastewater still has such characters as high salt content, high corrosive, whether direct emissions or incorporated into the municipal sewage plant will harm the environment. The wastewater zero discharge process will be the main direction of the FGD wastewater treatment in the future^[9]. Existing coal-fired power plant

wastewater zero discharge process mainly is multi-effect evaporation technology, such as mechanical vapor recompression evaporation technology^[10].

This trial for the FGD wastewater of a certain power plant was in Hebei province of China, chemical method was adopted to improve the pretreatment, removing all kinds of heavy metals, suspended solids, sulfide and fluoride, etc., adopting evaporation crystallization technology and recycling condensed water, realizing zero discharge of the desulfurization wastewater.

Wastewater quality

The FGD wastewater analysis results is shown in Table.1 and indicate that calcium magnesium concentration is very high, these ions can cause scaling phenomenon. So pretreatment of dosing softener cost is very big. Chlorine ion, sulfuric acid root ion, sodium ion, calcium ion, magnesium ion, TDS and other content is still very high, So as to the desulfurization wastewater zero discharge is necessary. Zero discharge is considered the most flexible solution because it can treat FGD wastewater from any type of coal. No matter what changes, the system will be built to handle variability.

Table 1. Main characteristics of raw wastewater

Element	Mass concentration/(mg·L ⁻¹)	Element	Mass concentration/(mg·L ⁻¹)
pH	6~7*	SiO ₂	10~20
Chromaticity (method of dilution multiple)	30~50*	Na ⁺	1500~4500
SS	≤500	Ca ²⁺	1000~2000
COD	≤150	Mg ²⁺	3000~6000
NH ₄ ⁺	15~30	Fe	10~20
S ²⁻	≤1.0	Cu	≤0.5
F ⁻	≤15	Hg	≤0.05
Cl ⁻	≤12000	Cd	≤0.1
SO ₄ ²⁻	1000~2000	TDS	15000~25000

Technological process and principles

Crystallizer is generally in the form of forced circulation and flash vessels^[11-12]. In recent years, vertical tube falling film evaporators and mechanical vapor recompression (MVR) forced circulation salt crystallization have been widely used in desalination industries^[13]. A schematic diagram of the experimental system is shown in Fig. 1. Using the calcium sulfate seed combine MVR evaporation crystallization process. In the pretreatment section of main additive lime and sodium sulfate, remove most of the hardness and heavy metal, and then into the evaporation crystallization system. A certain amount of calcium sulfate crystal seed was added in the evaporation crystallization system at the beginning. The seeded slurry evaporator process has proven to be the most reliable and efficient evaporator design to concentrate salt-laden wastewater prone to scaling from calcium sulfate, calcium fluoride, calcium phosphate, and silica. In the seeded slurry process, low solubility salts precipitate preferentially on calcium sulfate seed crystals suspended in the circulating brine in the evaporator, rather than precipitating as scale on the heat transfer surfaces. Condensate in the system can directly reuse and the produced sodium chloride salt crystals can reach more than the secondary standard of industrial salt .

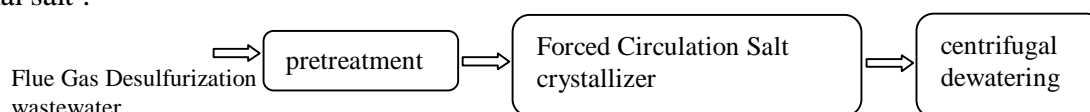


Fig.1. Schematic diagram of experimental system

Handling capacity of pretreatment device was 0.8m³·L⁻¹, and evaporation crystallization evaporation capacity of 500 kg·h⁻¹.

Results and discussion

Preprocessing performances.

Pretreatment period of drug dosing amount is shown in the Table 2.

Table 2. The operating condition

Parameters	lime	Sodium sulfate	Hydrochloric acid	TMT	flocculant	PAM
	$\text{g}\cdot\text{L}^{-1}$	$\text{g}\cdot\text{L}^{-1}$	$\text{mL}\cdot\text{L}^{-1}$	$\text{mg}\cdot\text{L}^{-1}$	$\text{mg}\cdot\text{L}^{-1}$	$\text{mg}\cdot\text{L}^{-1}$
value	13	24	5	20	200	5

Analytical curve of COD, calcium and magnesium ions, sulfuric acid root ion and chloride ion in the raw water and effluent as shown in the Fig.2-6. Pretreatment effluent magnesium ions content reduced from $3529 \text{ mg}\cdot\text{L}^{-1}$ to $90 \text{ mg}\cdot\text{L}^{-1}$.

As seen from the data curve, calcium ions content decreased in a certain degree, down from $1753 \text{ mg}\cdot\text{L}^{-1}$ to $1635 \text{ mg}\cdot\text{L}^{-1}$, sulfuric acid root changed from $3812 \text{ mg}\cdot\text{L}^{-1}$ to $3927 \text{ mg}\cdot\text{L}^{-1}$. Through adjusting the desulfurization wastewater pretreatment, Ca^{2+} and SO_4^{2-} content is higher, maintain ion ratio 1:2.4 levels, accordance with the requirements of the crystal kinds of water quality.

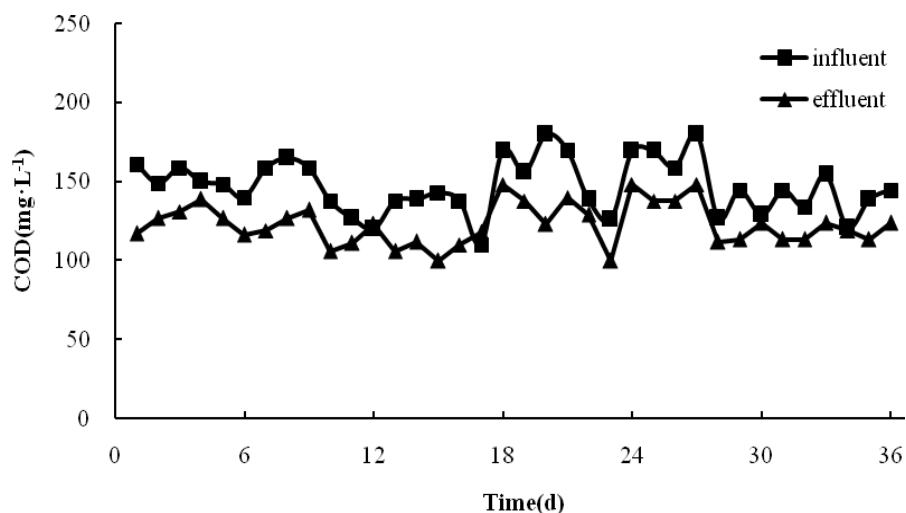


Fig.2. The COD variation in the pretreatment system

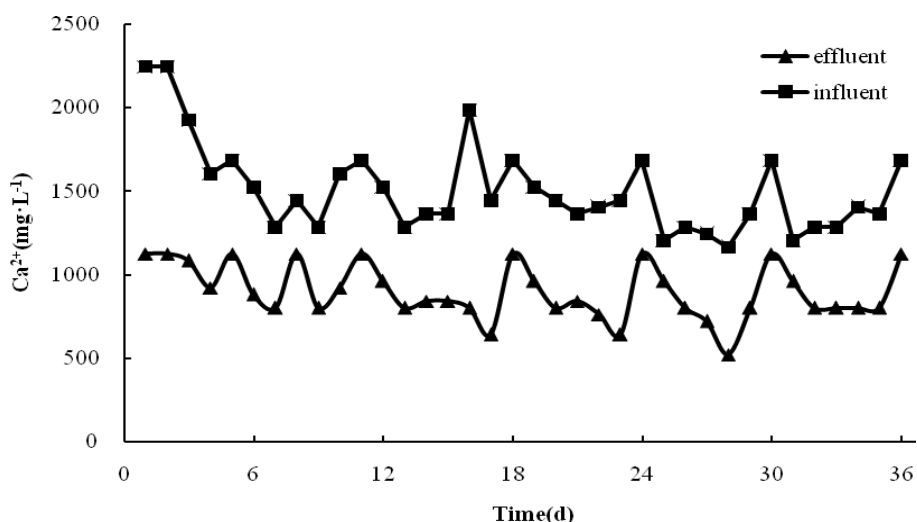


Fig.3. The Ca^{2+} variation in the pretreatment system

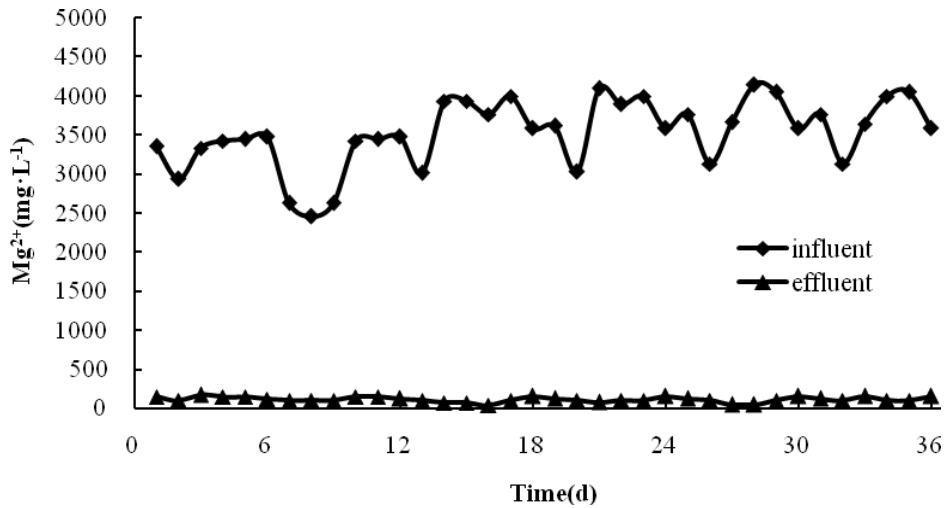


Fig.4. The Mg²⁺ variation in the pretreatment system

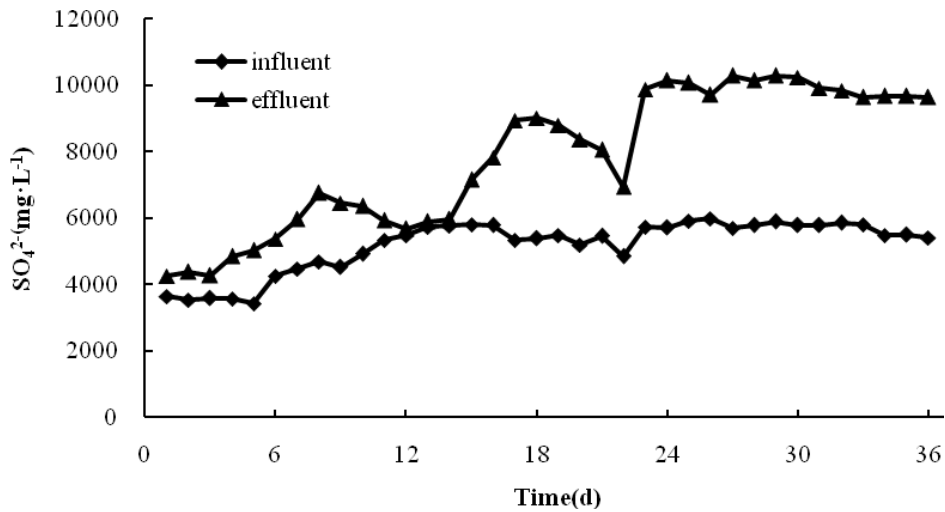


Fig.5. The SO₄²⁻ variation in the pretreatment system

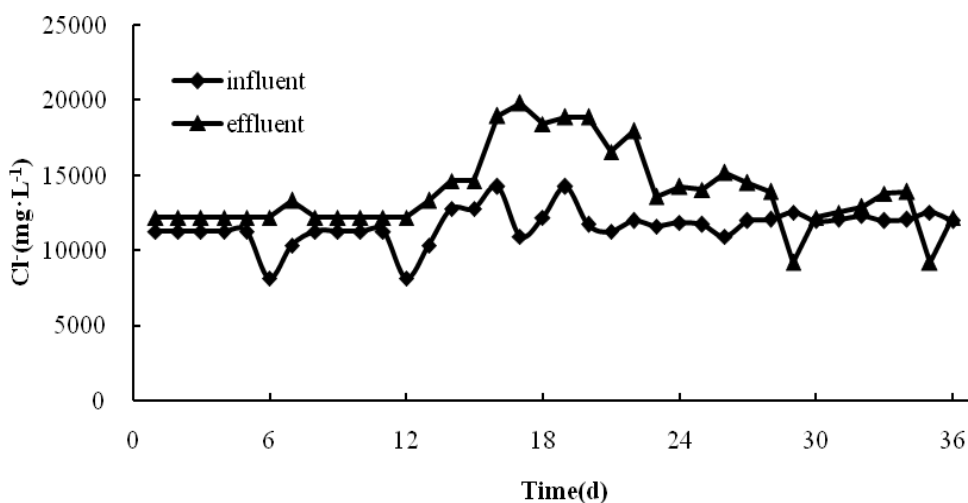


Fig.6. The Cl⁻ variation in the pretreatment system

The evaporation crystallization performances.

Evaporation crystallization pilot plant operation stability, condensed water and salt production quality were analyzed.

As shown in the Fig.7, the total dissolved solids of condensate was less than 20 mg·L⁻¹, consistent with the data of engineering case. In the engineering case, evaporators have been installed to reduce or eliminate the discharge of FGD wastewater, as depicted in Table 3.

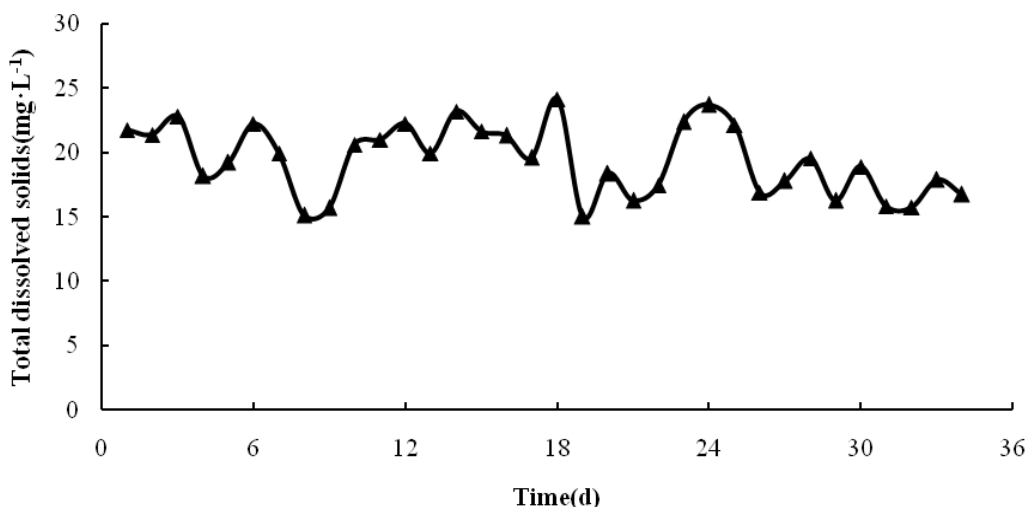


Fig.7. The TDS variation of steam condensate

Table 3. Global engineering case^[14]

project	Project site	Raw wastewater	Raw wastewater characteristics / (mg·L ⁻¹)	processing capacity / (m ³ ·h ⁻¹)	Processing system	value
Monfalcone	Italy	FGD	TDS: 30000, COD: 500	16	Softening + Evaporation +Crystallization	TDS<20mg·L ⁻¹
Duke Energy Indiana	U.S.A.	FGD	TDS: 16000, COD: 181	68		TDS<22mg·L ⁻¹
Energy Resources of Australia (ERA)	Australia	FGD	TDS: 12000, COD: 180	110		TDS<20mg·L ⁻¹

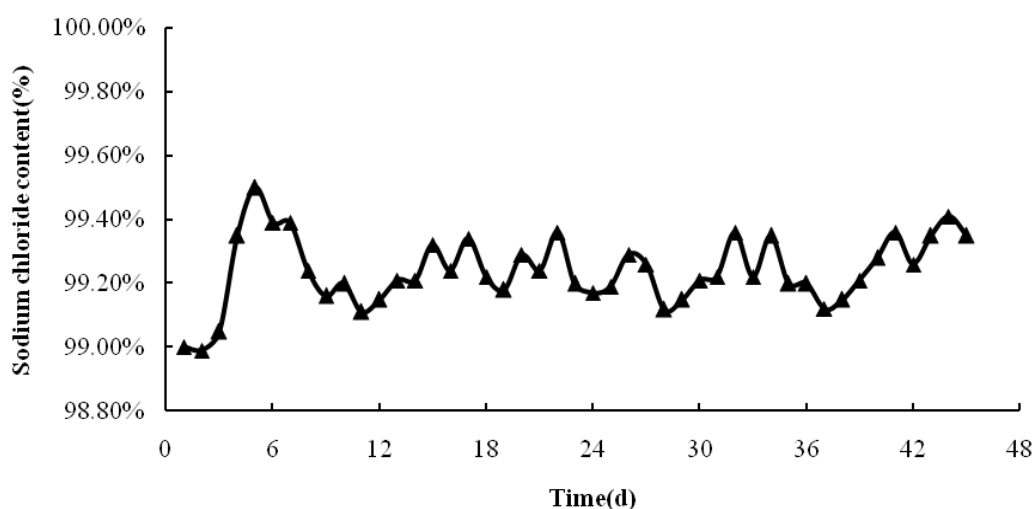


Fig.8. The variation of Sodium chloride salt crystals

Fig.8 shows that sodium chloride salt crystals after purification for more than 99.10% purity, satisfy the standard of industrial salt optimal level, and can be used as industrial raw material.

Conclusions

System pilot experimental results show that the technology for power plant desulfurization wastewater zero discharge treatment technology is feasible, which can realize the crystallization salt resource;

Sodium chloride salt crystals after purification for more than 99.10% purity, satisfy the standard of industrial salt optimal level, and can be utilized as industrial raw material.

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