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Advanced treatment technology for FGD wastewater in coal-fired power plants: current situation and future prospects

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ABSTRACT

At present, the desulfurization wastewater produced from flue gas desulfurization (FGD) has complex compositions, discharging of FGD wastewater results not only consumption of large quantities of water resources but also destruction of the environment. With the implementation of "The Action Plan for Prevention and Treatment of Water Pollution" in China, the discharging requirements for FGD wastewater from coal-fired power plants are increasingly stringent. Besides, the traditional chemical precipitation method can no longer meet the needs of the current "zero discharge" policy. Thus, advanced treatment of desulphurization wastewater has become an inevitable trend. It is necessary to analyze the existing advanced treatment technologies for desulfurization wastewater and find out the difficulties and problems existing in these technologies. Then, the rationalizations of these technologies will be proposed, and improvable system will be designed as well as the goal of "zero discharge" achieved gradually. This paper will discuss the characteristics of desulphurization wastewater and introduce the current status of existing wastewater treatment techniques by comparing their advantages and disadvantages. In the end, combined with technologic development and the analytic results above, a new concept of "thermal membrane hybrid method" is being proposed.

Keywords: Desulfurization wastewater; Zero emission; Advanced treatment technology; Thermal membrane hybrid method

1. Introduction

With the rapid development of industry and economy in China, the population expansions and coal-based energy consumption are aggravated increasingly. Coal-fired power generation is the dominated way to solve the demand for electricity in China, but a large amount of sulfur dioxide will be produced in the process of coal-fired power generation. As a toxic gas, SO_2 is not only harmful to human body and plants, but also it can damage the ecological environment. SO_2 is the main precursor for acid rain. The limestone-gypsum wet desulfurization process is a common way to achieve flue gas desulfurization, which has been used for Chinese coal-fired power plants [1–3]. In order to guarantee the stability of the desulfurization system and the quality of the gypsum product, it is required that the concentration of Cl in the desulfurization slurry should not be too high, generally controlled below 20,000 mg/L. Therefore, some

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wastewater is discharged from the desulfurization system, which becomes the source of desulfurization wastewater [4]. The desulfurization wastewater contains many heavy metals and suspended solids. If not processed in depth or just discharged by conventional treatment, inevitable severe damage to the environment will be caused. How to treat desulfurization wastewater in depth and effectively, even achieve zero emissions in the industry have been becoming the focus of widespread attention.

There is an industry index can be followed in water quality for desulfurization wastewater, named "Limestone-Gypsum Wet Desulfurization Wastewater Quality Control Index" (DL/T997-2006) [5], which stipulates the monitoring items and the maximum permissible discharging concentration of pollutants for the outlet of desulfurization wastewater treatment system. As the increase of environmental problems, the government has paid more attention to sewage discharge. In April 2015, the State Council promulgated the "Water Pollution Prevention and Control Plan" (also known as "Water Ten") [6], claiming that, the national water environment quality should be improved. The serious pollution of water bodies should be greatly reduced, to comprehensively improve the ecological environment and achieve a virtuous cycle of ecological system. On May 21, 2017, the "Guidelines for Feasible Technical Guidelines for Pollution Prevention and Control of Thermal Power Plants" [7] was officially implemented, which clearly defined the specific treatment methods for desulfurization wastewater. It also emphasized that, except for the desulfurization wastewater, all kinds of wastewater can basically achieve "multi-purpose water, use step by step" and non-effluent discharge in wastewater near-zero emission technology. Therefore, zero liquid discharge of desulfurization wastewater is the key to solve the problems.

Based on the current conventional triplet tank treatment technology, is a higher level advanced treatment technology for desulfurization wastewater, to meet the needs of near zero emissions of future desulfurization wastewater. At present, the analysis and evaluation of advanced treatment technology is still relatively lacking. Therefore, various advanced treatment technologies will be discussed in this paper, which is based on the analysis of existing treatment technologies and the characteristics of desulfurization wastewater, so as to provide beneficial reference for the development of the industry.

2. Characteristics of desulphurization wastewater

2.1. Source of desulphurization wastewater

The desulfurization wastewater has large amount of water as well as complex composition. Some of it comes from the limestone-gypsum slurry wastewater. In the absorption tower, the slurry has a high moisture content, which was produced by the reaction of flue gas and limestone slurry. In order to recycle gypsum, the slurry must be dehydrated by a vacuum belt dewatering machine. This process will generate a certain amount of wastewater; another part of wastewater is generated by the flushing equipment. In the process of desulfurization, the high concentration of limestone slurry in the slurry tank and gypsum slurry in the absorption tower was easy to produce scaling and blockage. Therefore, washing the equipment continuously during the operation is indispensable. In addition, boiler flushing water, reverse osmosis (RO) concentrated water, resin regeneration wastewater in chemical workshop; circular drainage and cooling water of unit also belong to desulfurization wastewater [8].

2.2. Water quality component of desulfurization wastewater

Desulfurization wastewater has a broad variety of pollutants because of its wide sources, and its water quality is related to the type of coal quality and desulfurization absorbent. The desulfurization wastewater mainly contains a large amount of supersaturated nitrite, sulfite, suspended solids, heavy metal ions, F^- and Cl^-. The composition of the desulfurization wastewater is showed in Table 1. The source of the pollutants is shown in Fig. 1.

2.3. Water quality characteristics of desulphurization wastewater

- With the pH value(4.5–6.5), the wastewater has a high concentration of Cl^- and strong corrosiveness, which means the corrosion resistant equipment materials are needed [9];
- The suspended solid content is high, and the mass concentration is generally above 6,000 mg/L. The main components are gypsum particles, silica, iron and

Table 1
Composition of desulphurization wastewater

Water quality index	Average value
K^+, mg/L	73.6
Na^+, mg/L	271
Ca^{2+}, mg/L	1,417.4
Mg^{2+}, mg/L	2,592.4
Fe, mg/L	4.8
Al^{3+}, mg/L	18.6
NH_4^+, mg/L	9.39
Ba^{2+}, mg/L	0.09
Sr^{2+}, mg/L	4.23
Cl^-, mg/L	5,635
SO_4^{2-}, mmol/L	7,123
HCO_3^-, mmol/L	1.437
Total hardness	284.05
pH	5.98
Ammonia nitrogen, mg/L	10.15
COD_{Mn}, mg/L	24.56
COD_{Cr}, mg/L	325.15
BOD_5, mg/L	151.23
TOC, mg/L	7.64
SS, mg/L	19,209
CO_3^{2-}, mmol/L	0
NO_3^-, mg/L	226.2
NO_2^-, mg/L	12
OH^-, mmol/L	0

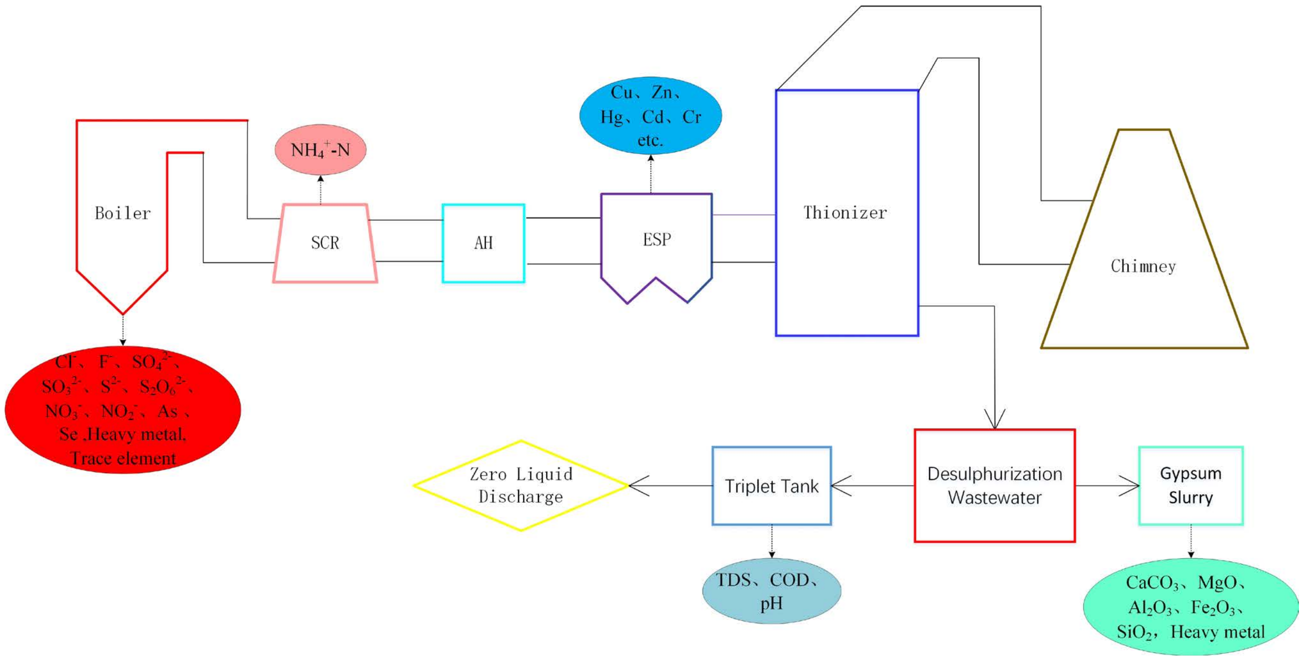

Fig. 1. Sources of pollutants in desulphurization wastewater.

aluminum hydroxides. It is easy to cause fouling of the membrane filtration device due to the large particle size of the suspended solids.

- Desulphurization wastewater has high salinity, and the inlet total dissolved solids (TDS) is 33,500–64,000 mg/L;
- The main cations are hardness ions in wastewater, such as calcium and magnesium. The Ca^{2+} content is generally 1,500–6,000 mg/L, and the Mg^{2+} content is generally above 4,000 mg/L. The content of iron and aluminum is also relatively high. The anions mainly have Cl^-, SO_3^{2-}, F^-, etc. These ions are mainly derived from coal. A high concentration of SO_4^{2-} will lead to a high supersaturation of $CaSO_4$. If the wastewater goes through the process of membrane concentration and reduction, it will be easy to cause fouling in the membrane system while difficult to recover after cleaning.
- There are many types of heavy metal ions in desulfurization wastewater, such as mercury, cadmium, lead and copper. Most of them are the first class pollutants, which are strictly controlled in national environmental protection standards. Although the concentration is not very high, it is far above the emission standard.
- There is a certain chemical oxygen demand (COD) in the wastewater. The main substance is reduced inorganic substance, such as sulfite. Besides, it contains reducing inorganic ions;
- The hardness of the wastewater is relatively high (5,000–12,000 mg/L), which has a certain influence on the subsequent treatment unit.

2.4. Hazard of desulfurization wastewater

2.4.1. Desulfurization systems impact

The desulfurization wastewater contains abundant suspended particulate matter, which is prone to scaling thus causes blockage of pipelines. The solubility of limestone will reduce, affecting the desulfurization efficiency due to the mixing of F^- and Al^- in the desulfurization wastewater. When the content of Cl^- is higher, the pH of the slurry will decrease the pH of slurry and the desulfurization rate decrease while the possibility of scaling will increase. Furthermore, the quality of gypsum by-product will also be affected.

2.4.2. Ecosystem impact

There are two aspects that mainly influence ecosystems. On the one hand, SO_4^{2-} will affect soil and the balance of water in the desulfurization wastewater, and it will produce toxic substances such as H_2S, $S_2O_3^{2-}$ and $S_4O_6^{2-}$ under the reaction of reducing bacteria, which leads to soil structure destruction and affects the normal growth of plants. The resulting sulfate is well soluble in water and difficult to be removed by water self-purification, inhibiting the growth of aquatic organisms. On the other hand, desulfurization wastewater contains many heavy metal pollutants such as manganese, selenium, chromium, copper, mercury, zinc, nickel, lead and so on. If they enter into the soil and water, not only the organisms will be poisoned, but also human health will be affected.

3. Desulphurization wastewater treatment technologies

3.1. Traditional desulphurization wastewater treatment technologies

The traditional treatment technologies of desulfurization wastewater include chemical precipitation, filtration, electrodialysis (ED), ion exchanging and ultrafiltration (UF) [10]. The chemical precipitation (also known as triplet tank technology) is commonly used methods in traditional treatment technologies for desulfurization wastewater [11]. The process of technology is shown in Fig. 2.

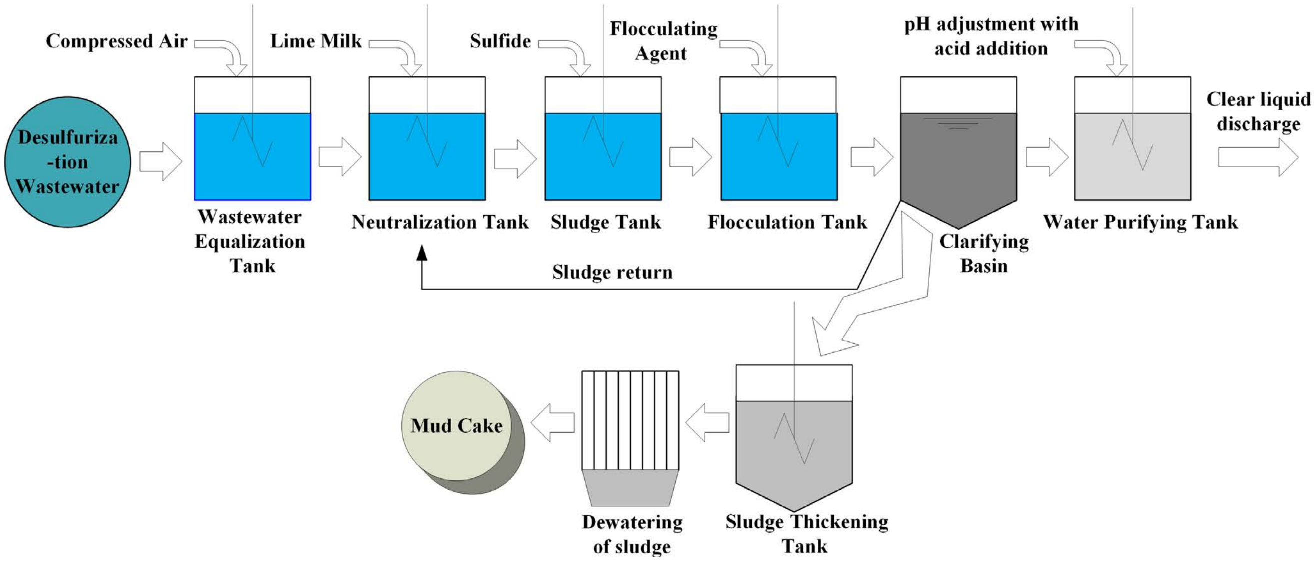

Fig. 2. The process flow chart of chemical precipitation technology.

At present, stages such as, neutralization → precipitation → flocculation → clarification are used in domestic coal-fired power plants to treat desulfurization wastewater. The system is mainly composed of three parts: wastewater treatment, triplet tank dosing (neutralization tank, settling tank, flocculation tank) and sludge dewatering. To adjust the pH value of wastewater, alkaline neutralizer is often added to the neutralization pond, such as NaOH, $Ca(OH)_2$ and $CaCO_3$. Organic sulfur (such as TMT-15 or S^{2-}) is added to the sedimentation tank to remove heavy metal ions such as Pb^{2+} and Hg^{2+}. In the consequence, the precipitates generated by the reaction are removed. The role of the flocculation tank which is usually relatively small and dispersed is mainly aimed at the removal of suspended particulate matter. Due to the sedimentation performance, it is difficult to be captured only by the action of gravity. Therefore, flocculant (such as $FeClSO_4$) shall be added to the flocculation tank. In order to enhance the flocculation effect, it is usually essential to add a coagulant polyacrylamide (PAM) to the flocculation tank. After the above three steps, wastewater is discharged to clarification tank, and separated by gravity. The separated liquid is alkaline and needs to be acidified to neutrality. A small portion of the separated sludge is refluxed to the neutralization tank, and the other is filtrated into a mud cake after being concentrated and dehydrated.

There are many disadvantages in the chemical precipitation method for removing desulfurization wastewater [12]: (1) Huge investment. It requires a large amount of chemical agents in the process of separating the chemical batching system; (2) It requires expensive maintenance costs due to the large scale of system; (3) It is difficult to be recycled. At present, there is no method for effectively removing F^- and Cl^- in desulfurization wastewater, and Cl^- is strongly corrosive under acidic conditions. Therefore, it is hard to be recovered after treatment; (4) it is difficult to remove the harmful substances thoroughly. With the introduction of increasingly stringent environmental standards, COD and some other hazardous substances, such as selenium, also needs to be completely removed.

3.2. Zero discharge of desulphurization wastewater

In January 2017, the Ministry of Environmental Protection in China promulgated the "Technical Policy for Pollution Prevention and Control of Thermal Power Plants" [7], which clearly stated that the desulfurization wastewater should be reused after treatment with lime treatment, coagulation, clarification, neutralization, etc. In order to achieve non-effluent discharge of desulphurization wastewater, using evaporation drying or crystallization is encouraged. The idea of zero discharge of desulfurization wastewater is not about discharging wastewater outside from the power plant. It is more about reusing most of the wastewater and only discharging a small amount of water into the atmosphere in the form of steam. This concept not only greatly reduces the damage to the water environment, but also cuts down the use of clean water sources [13]. After the cascade utilization or concentration reduction of water resources in thermal power' plants, there will be a certain amount of terminal wastewater with water quality inferiority and unable to be directly recycled. It is significant to realizing "zero discharge" of wastewater from the whole plant in the treatment and reuse of wastewater. Fig. 3 is a roadmap for the evolution and development of the advanced treatment technology for desulfurization wastewater.

It can be seen from the above figure that the zero emissions mainly include evaporation pond, concentrated crystallization and flue gas evaporation. As a representative of traditional zero emission, concentrated crystallization can be subdivided into thermal and membrane methods. The technical route generally consists of three parts: wastewater pretreatment, concentration and crystallization, as shown in Fig. 4.

3.2.1. Steam concentration evaporation process

The waste water is concentrated by the steam concentration evaporation technique [14], through which to produce distilled water and concentrated water; the concentrated water is further evaporated by a crystallizer or spray drying

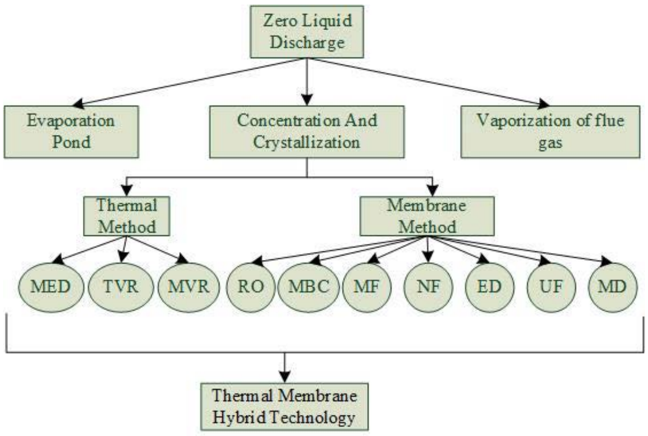

Fig. 3. The evolution and development roadmap of desulphurization wastewater advanced treatment technology.
(1) MED – multi-effect evaporation, (2) TVR – thermal vapor recompression, (3) MVR – mechanical vapor recompression, (4) RO – reverse osmosis, (5) MBC – member brine concentration, (6) MF – microfiltration, (7) NF – nanofiltration, (8) ED – electrodialysis, (9) UF-ultrafiltration, (10) MD – membrane distillation.

to produce distilled water and solid waste. In order to prevent fouling of the evaporator, the wastewater needs to be pretreated so that a large amount of suspended solids and heavy metal ions (such as calcium and magnesium) can be removed. The pretreated wastewater can be treated by low-temperature multi-effect evaporation process (MED), thermal vapor recompression process (TVR) or mechanical vapor recompression process (MVR). Finally, the solid waste is recycled and utilized.

The working principle of MED [15,16] is to connect several evaporators in series and send the preheated raw materials to the evaporation chamber for heat transfer with the steam. The concentrated liquid and the secondary steam are separated in the separator using method of evaporation. Besides, the separated secondary steam is transmitted into the second-effect evaporation chamber, and the concentrated liquid is further concentrated. The equipment of this process covers a large area and consumes a large amount of steam and the equipment investment capital is high, but it can be operated automatically.

The TVR process and the MVR process both belong to the vapor compression distillation technology [17]. Unlike MVR, the TVR process does not use mechanical compressor compression, instead of the supersonic flow of driving air and secondary steam are neutralized in the injector under high pressure and high temperature [18]. Moreover, the discharged compressed steam can be used as a heat source to heat the wastewater. The process equipment has a relatively small footprint, consuming less steam and being operated automatically, although the equipment investment cost is still high.

The MVR process can be generally divided into two types: vertical tube type [19] and horizontal type [20]. The working principle [21] of MVR is that the secondary steam generated by evaporation is compressed, which will cause that mechanical vapor compressor, the pressure, temperature and enthalpy value increase. After the compression, the steam can be used as the second-effect heating and turn into the heating outer tube to heat the solution, thereby replacing the raw steam recycling and achieving the purpose of energy saving. Compared with MED and TVR, the equipment of MVR has a small footprint and can be fully automated. However, the one-time investment is expensive, and the mechanical seal needs to be replaced regularly.

The desulfurization wastewater evaporation and crystallization treatment process system can be divided into three parts: (1) evaporation system; (2) deep concentration/crystallization system (3) crystal drying system. After the

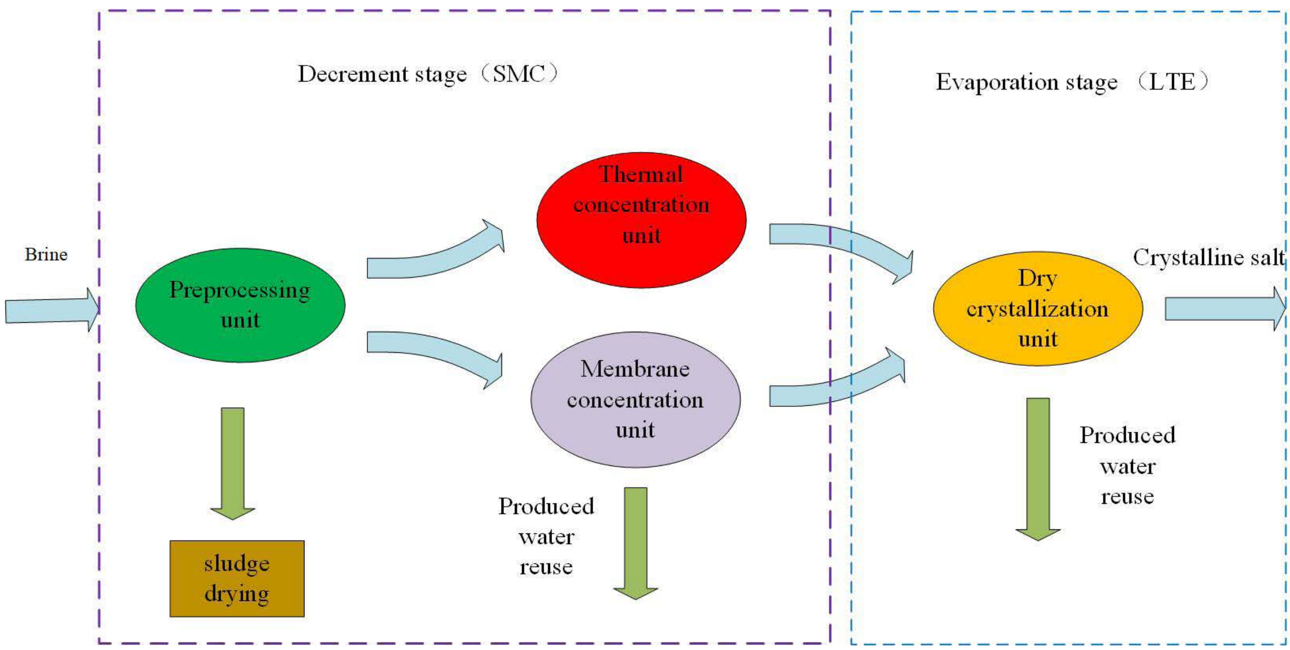

Fig. 4. Concentration crystallization process flow chart.

wastewater enters the evaporation system, the generated steam is cooled to form recycled condensed water; the high concentration wastewater is discharged into the concentration/crystallization system. The concentrate is disposed to form a concentrated liquid that is crystallized to finally form a dry Crystalline salt.

This treatment process has been applied at both domestic and overseas, but the problems cannot be ignored: (1) the largest investment, the highest operating costs, and large area; (2) due to the large amount of salt in the water, it is easy to scale during the system processing, which will affect the treatment efficiency and increase the maintenance cost. (3) The technology has higher requirements on the purity of crystalline salt (the content of NaCl and Na_2SO_4 is not less than 95%, and the water content is not more than 3%), and the desulfurization wastewater needs to be treated in depth. (4) In the actual operation process, the purity and comprehensive utilization of the crystalline salt are the factors that restrict the thermal process. It is difficult to dispose the final product properly because the harmfulness of the evaporated salt is uncertain.

3.2.2. Membrane concentration process

The membrane concentration process is widely used in the water industry, and possesses the characteristics of high efficiency, energy saving, good selectivity and no pollution. The use of this process can not only remove heavy metal salts and sulfides in the desulfurization wastewater [22], but also reduce the amount of evaporation solidification treatment to save energy. After the wastewater is pretreated, it is concentrated and reduced by RO membrane, nanofiltration (NF) membrane and forward osmosis. Finally, the resulting fresh water is recycled and the concentrated water is treated with dry crystallization. Currently methods used in membrane separation processes include: RO, membrane brine concentration (MBC), NF, UF, microfiltration (MF), ED, membrane distillation (MD). The Table 2 compares the parameters of several major membrane separation process technologies.

RO is one of the commonly used techniques in membrane separation [23,24], and RO refers to the phenomenon that a higher pressure (which needs to be higher than the osmotic pressure) is applied in the direction of positive osmosis, which makes the solvent in the high-concentration solution transfer to the low-concentration solution [25]. The RO membrane is a semipermeable membrane with a pore diameter of 0.0001, which is mainly used to filter out solvents and water in the solution, and retains the solute. The materials used for RO membranes are: polyamides, acetates, and aromatic ring polymers. The polyamides are usually used materials [16]. Common wastewater treatment methods are disk-tube reverse osmosis (DTRO) and roll reverse osmosis (YBRO).

Unlike RO, MBC [26] is driven by osmotic pressure difference. Due to the high salinity of the absorbent, it can provide significant osmotic pressure and facilitate water molecules through semi-permeable membranes. The solvent in the waste liquid flows from the high-water chemical potential region to the low-water chemical potential region when it passes through the selective separation membrane, and the solute is blocked on the side of the waste liquid (the high-water chemical potential region). This method has the advantage of low energy consumption and can be operated under low pressure or no pressure. In addition, as high as 98% can be achieved about the salt removal rate, not easy to scale; and the high concentration brine with TDS over 50,000 mg/L can be treated. The disadvantages are poor performance and fewer varieties of positive osmosis membranes, and lack of economical and efficient ways to extract. Meanwhile, it's also hard to find a way that the extract can be re-concentrated.

NF is a pressure-driven membrane separation process between RO and UF. The pore size of the NF membrane is 1~5 nm. The biggest feature of the membrane is that the monovalent and divalent ions can be separated in the wastewater [27]. In the treatment of thermal power plants, UF technology is mainly used to treat large particles, such as organic matter. The MF technology uses pressure as the driving force, mainly for the separation. The particles, bacteria and colloids whose pore size is 0.1–10 μm can be separated through this original solution [28].

The Bipolar Membrane used for ED is a new type of ion-exchange composite membrane. It consists of three parts: a cation exchange layer (*N* type membrane), an interface hydrophilic layer (catalytic layer) and an anion exchange layer (*P* type membrane). When the power is switched on,

Table 2
Comparison of technological parameters of several main membrane processes

Items	RO	ED	MBC
Operating pressure /MPA	7.5~16	Atmospheric pressure	Atmospheric pressure
Kind of energy	Electric	Electric	Electric
Water quality	High salinity	High salinity	High concentration
Concentration ratio	4	2~5	4.5~6
Energy consumption /kWh m^{-3}	2~12.7	7~15	21
Salt removal rate /%	95~97	90	98
Working life	5~8	Shorter	2~3
Fouling resistance	Mid	High	High
Manufacturing procedure	Simple	Simpler	Complex
Maturity	Mature	Relatively mature	Relatively mature

the anions and cations in the water migrates to the anode and the cathode respectively; then, the selective permeability of the anode membrane and the anion membrane are used to form a high concentration region and a low concentration region which are alternately arranged. Finally, the concentration and desalination of the wastewater is attached.

MD is a separation process that combines membrane separation technology with traditional evaporation technology, in which a microporous hydrophobic membrane to promote the transport of water vapor. The membrane is used to facilitate the transport of water vapor while retain liquid water and hence all non-volatile substances and dissolved salts [29]. The principle of specific working is as follows: the membrane is divided into two sides, a hot side and a cold side. The solution cannot pass through due to the hydrophobicity of the membrane. However, as the temperature of the hot side rises continuously and water vapor is produced, the solution can pass through the hydrophobic membrane. When the water vapor enters the cold side, it is condensed into water, achieving the concentration on the hot side ultimately.

It requires removal of turbidity, fouling materials, and COD to avoid impact on subsequent processing equipment in the membrane concentration portion of the membrane separation process and the subsequent crystallization process. Since the desulfurization wastewater is already oversaturated, it will cause clogging due to the fact that anions and cations may react with the membrane or accumulate in the pores of the membrane. Some of the membrane fouling is irreversible and will affect the effect of interception.

3.2.3. Multistage flash process

Flashing refers to the unsaturated water under certain pressure and temperature conditions, and if the pressure is reduced to the saturation pressure at a certain temperature, vaporization will occur. Furthermore, if the pressure decreases, the vaporization process will continue to strengthen. The multistage flashing process (MSF) [30] is based on the principle of the flashing process, and the wastewater at a high temperature is sequentially passed through a plurality of pressure-decreasing flash chambers to vaporize the wastewater. The obtained steam is condensed and then the eventually recycled water is obtained. The heating process of the MSF is carried out separately from the evaporation process, so that it can make the scale formation less prone. MSF has the advantages of mature technology, good integrity and high operational security. Besides, it is suitable for large or ultra-large desalination devices [31]. The process flow chart is shown in Fig. 5.

At present, MSF is widely used in seawater desalination, but there is no practical application for desulfurization wastewater treatment in thermal power plants. The current difficulties mainly include:

- The complexity of desulphurization wastewater makes it difficult to explore the energy conversion process.
- In the implementation process, the waste water needs to be heated at high temperature, which undoubtedly increases the energy consumption of the process system;
- The final product belongs to a hetero salt, which is more difficult for subsequent treatment.

4. Thermal membrane hybrid method

All the technologies need to be considered to reduce operational and maintenance costs. The steam concentration and evaporation treatment process (thermal method) and the membrane separation process are the main methods of the desulfurization wastewater treatment technology, but both of them have certain problems in some aspects. For example, the thermal process requires a deeper pretreatment before operation, and cooling water is also required to reduce the temperature of the wastewater during operation. The main problem of the membrane method is that the membrane flux is affected by the temperature. The higher the temperature, the larger the membrane flux, which will inevitably increase the salinity rate of treated water. It is not difficult to obtain from the above analysis that there is a certain complementarity between the thermal method and the membrane method. As a new technology concept, thermal membrane hybrid method has the advantages of energy saving and cost reduction, and it combines the high desalination performance of thermal method with the low energy

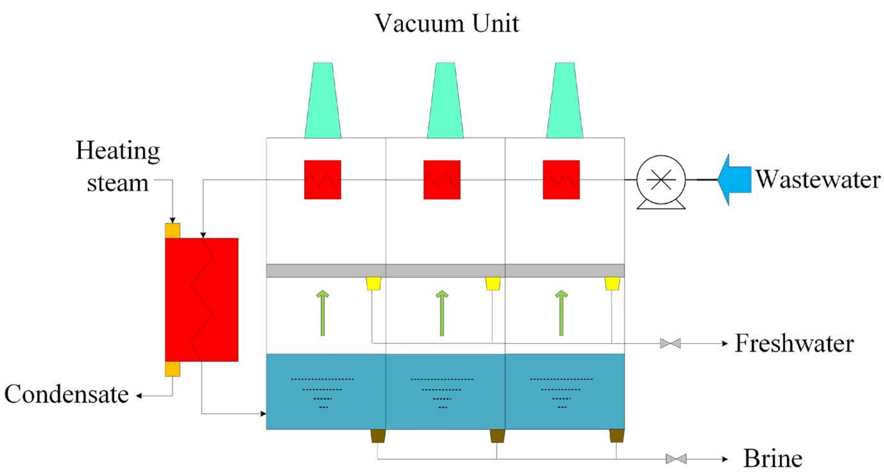

Fig. 5. Multistage flash process flow chart.

consumption of membrane method [32]. So it can make full use of the advantages of the two methods and makes up for their respective deficiencies, leading certain economic benefits and developing potentials.

The thermal membrane hybrid method is mainly used to treat desulphurization wastewater by combining the two waste water treatment methods of thermal method and membrane method. The main processes are MSF-RO and MED-RO. Fig. 6 shows a typical MSF-RO process system.

The thermal membrane hybrid method has many merits' such as, improving the water recovery rate of the thermal method, reducing heat loss, avoiding equipment fouling, and increasing effluent quality and saving energy. At present, the thermal membrane hybrid is still in the preliminary stages of research. It is the essential that makes up for the deficiencies of the thermal and membrane processes, and saves energy consumption, optimizes the operation, reduces costs as well as improves the processing efficiency. The thermal analysis, thermal loss, economy and optimization system of the process have been analyzed and discussed by some literatures [33].

Cardona et al. [34] designed the waste heat from thermal power plants to be supplied to the MSF-RO system. The system could be extended to other energy utilization synergies as well as low costs. For example, A separate RO system can be used due to the mixture can be easily trapped in distilled water with low TDS under ideal salt conditions. MSF and RO can be treated with a common tail treatment unit; the cost of desalination can be reduced without affecting the overall energy saving. Through analysis, it is concluded that it can be improved the overall performance of the system by optimizing the steam turbine extraction pressure (or temperature) and the capacity ratio between MSF and RO. Almulla et al. [35] analyzed in detail the technical and economic aspects of the joint technology of a thermal power plant in the United Arab Emirates, integrating the power generation system with thermal membrane hybrid technology (RO and MSF). The combination of RO and MSF technology can both improve the performance of the MSF and reduce the cost of processing water. In the winter, RO can further reduce the cost of the cogeneration system by using the remaining electrical energy. Iaquaniello et al. [15] used the solar energy combined with MED-RO to use solar energy as a backup system for a gas turbine, and effectively solved the energy shortage during the interval. At the same time, the system can increase temperature and RO membrane flux, as well as a further benefit derives from flexibility of RO system which allows for a better matching of daily and seasonal variation in power and water demand. Moreover, this hybrid system cost of producing water is less than 1 €/m^3. Turek et al. [36] compared the water recovery rate and economy of RO, ED, MD, ED-MSF and NF-RO-MSF systems, and found that the demineralization performance of the thermal membrane hybrid system is better than the single membrane system; the thermal method is more effective than the membrane method in treating high-concentration brine, and the only system which can be comparable to the thermal method is MD. Among the many hybrid methods, the NF-RO-MSF crystalline salt system is the best: high water recovery (77.2%) and low cost ($0.37 per m^3). Sadri et al. [37] established a mathematical model to predict the performance of the MED-TVC-RO coupled system. The

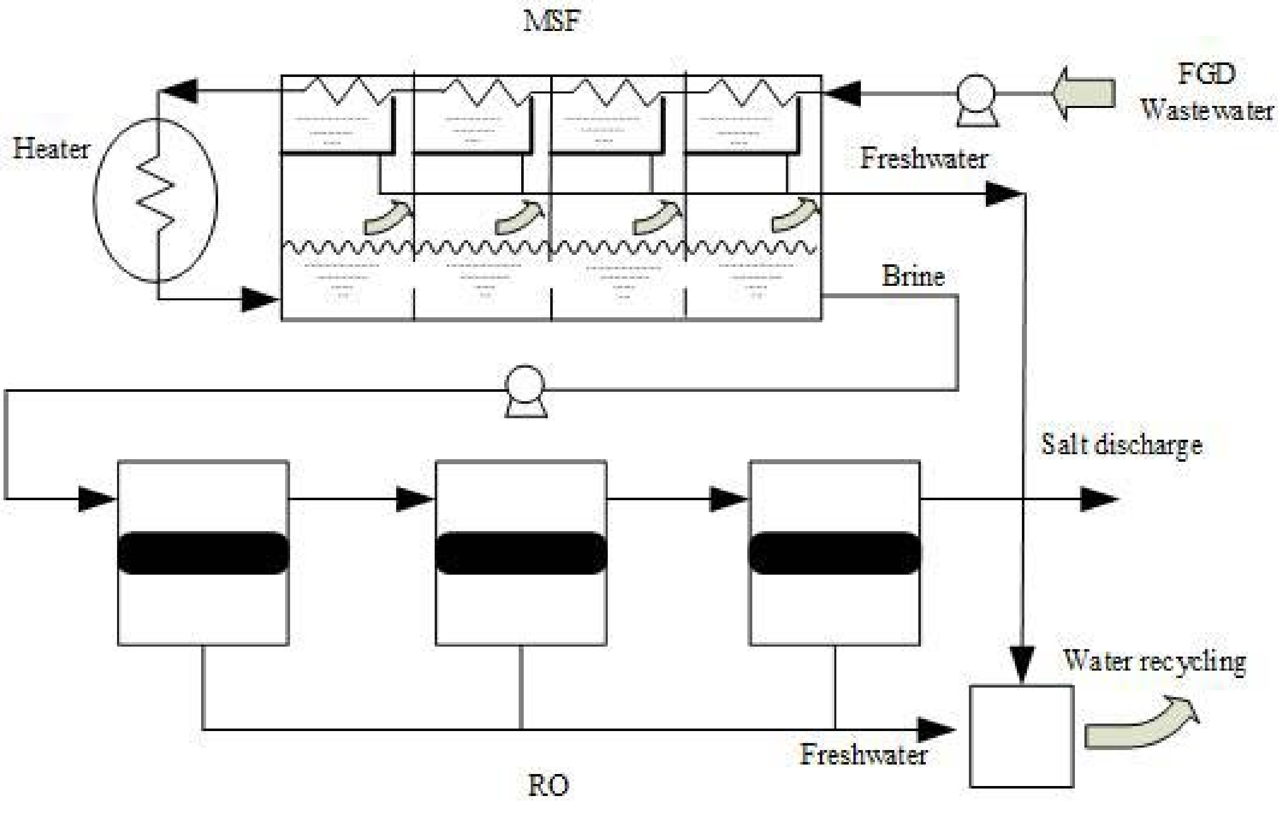

Fig. 6. MSF-RO process flow chart.

system uses RO to remove the salt in the untreated water, and then processes it with the MED system. The genetic algorithm is used to analyze the MED-RO system in different modes. The results show that the energy consumption can be significantly reduced by replacing the single system with the hybrid system. Wu et al. [38] desalinated the salt water by using the MED technology and used chemical precipitation method to remove the hardening treatment. After adding sodium carbonate and sodium hydroxide to desalinated water, calcium and magnesium ions were removed from the water. The produced water is treated with RO to further concentrate the produced water, and the product can be sold as a raw material, which has considerable economic, environmental and social benefits.

The thermal membrane hybrid method can be divided into the following three types according to the process flow:

- The wastewater is first pretreated by thermal method and then treated by membrane method: the water is treated firstly by MSF, and then the brine which is excluded is mixed with the cooling water to serve as the inflow of RO. This method enables the outer drainage of concentrated salt water can be avoided, and the temperature entering the RO system can be raised, so that the membrane flux can greatly increase and the membrane loss is reduced.
- The wastewater is pretreated by the membrane method and then treated by thermal treatment: this method mainly treats the wastewater through RO treatment, which is mainly to remove the easily-scaling ions in the untreated water and limit the maximum salt temperature during operation (TBT). It also avoids fouling of the thermal device, which can improve the water treatment capacity of the thermal device.
- Parallel treatment of thermal method and membrane method: the treated water is divided into two parts, one is treated by thermal method, and another is treated by membrane method. After that, the two parts of water production are coupled. This method can be used to produce water by thermal method and membrane method according to diverse water quality requirements in different places. For example, the thermal method produces a higher salt content. On the contrary, the membrane method produces a lower salt content. So, the salt content of water produced can be balanced by proportional neutralization. Moreover, the membrane method has higher boron content, which can be mixed by thermal water production to reduce the boron content of water production.

Due to the high energy consumption, thermal method generally can be applied to occasions with less amount of water to be processed. The quality of the desulfurization wastewater depends on the requirements for the crystalline salt. If the purity of crystal salt is limited (sodium chloride and sodium sulfate content not less than 95%, the moisture content is not higher than 0.3%), on the depth of the desulfurization wastewater pretreatment will be required. The concentration of chloride ion should not be too high in desulfurization wastewater; otherwise it will destroy the protective layer of metal oxide film of pipeline easily. And the concentration of magnesium ion should not be too high also, because the flocculent colloid is softened by product of magnesium ion, which is difficult to precipitated-filtered and separated. In addition, it will also bring difficulty to process operation. Thermal method faces the problem of heat exchanger fouling frequently. The water recovery rate of the thermal method can reach about 70%, and the recovered water can be used as the system hydration (treatment cost > 100 yuan/ton). A large amount of desulfurization wastewater can be handled by membrane method, and it has high requirements on the quality of the influent water. So, it is necessary to remove suspended solids and scale-prone substances in the desulfurization wastewater to prevent fouling of the membrane. Moreover, the membrane may be reacted with the ions to reduce membrane permeability in the desulfurization wastewater. The membrane water treatment rate is about 50%, and the recovered water can be used for water purification in the desulfurization system, and the power consumption is large (the treatment cost is about 20 yuan/ton). The thermal membrane hybrid method technology combines the advantages of the thermal method and the membrane method, and the applicability and flexibility of process is improved. The process flow of different arrangements can be designed according to the water quality of different desulfurization wastewater. However, the thermal membrane hybrid method technology is still in the preliminary research stage, and more in-depth research are needed from the aspects of process strengthening, process integration, and energy cascade utilization to reduce the investment and operating costs of the technology.

In order to better reflect the advantages of thermal membrane hybrid technology, the analysis and comparison with other advanced treatment technologies are shown in Table 3.

In summary, the thermal membrane hybrid technology combines the advantages of thermal methods and membrane methods. It is superior to a single system in terms of economics and system performances. While giving full play to the advantages of the single system, the defects of the respective systems can also be made up. This method has the following advantages: (1) handling more complex water quality; (2) reducing the energy consumption of treatment and has a high water recovery rate; (3) reducing the film loss effectively and increasing the membrane permeability; (4) the fresh water quality produced is higher than that of independent systems; (5) the thermal method and the membrane method can share the pretreatment system and the post-treatment system, without the need for additional processing facilities, which is of great significance to reduce the cost; (6) lower equipment operation and maintenance costs. The thermal membrane hybrid process has been studied in seawater desalination, but there is still blank in the treatment of desulfurization wastewater in thermal power plants. How to apply the advantages of thermal membrane hybrid technology to deal with the desulfurization wastewater and achieve zero discharge better is the key direction that we need to study and explore in the future.

5. Conclusions

This paper expounds the sources, water quality components, characteristics and harms of the desulphurization

Table 3
Comparison of advanced treatment technologies for desulphurization wastewater

	Membrane concentration	Evaporation concentration and crystallization	Evaporation pond	Thermal membrane hybrid
Water requirements	Water quality is high and scale formation should be considered	Water quality is high and scale formation should be considered	No special requirement	Water quality requirements are relatively low
Produced water quality	Mid	Mid	Low	High
Equipment investment	Low	Low	High	Low
Occupied area	Lower	Low	High	Low
Operating expense	High	Low	Low	Low
Technical key	The system design needs to fully consider the prevention of membrane fouling and pollution, leaving a design margin to adapt to changes in water quality.	It is necessary to consider the scaling problem of the evaporator to improve the reliability of equipment operation	The capacity should be designed to be large enough to ensure the evaporation of wastewater in the season of large evaporation.	When the system is designed, how can the thermal and membrane systems be coupled to produce better water quality, ensure the stable operation of the system, and give full play to the characteristics of the two systems.

wastewater, and discusses the traditional desulphurization wastewater process and the zero liquid discharge process. The advantages and imperfections of the thermal method and membrane method are discussed in detail in the zero-emission process. For example, the thermal method requires large energy consumption, large floor space, and high operating cost. In the membrane method, the membrane is easily contaminated, and the membrane flux can be affected by temperature. At present, zero-emission technology in China is still in the preliminary research stage. The existing technology has the problem of high investment and operating costs and has its own obvious advantages and disadvantages. Therefore, the concept of thermal membrane hybrid technology is proposed in this paper to promote the thermal and membrane methods to compensate for each other, which is of great significance for realizing zero emission of desulfurization wastewater at a low cost and high efficiency, and it is bound to become a hot spot of advanced wastewater treatment technology.

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