# Technical analysis of increasing the concentration ratio and sewage reuse of circulating cooling water in power plants

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#### ABSTRACT

Reducing water consumption by circulating cooling systems is the key to achieving energy conservation, reducing emissions from the power plant and ultimately realizing the goal of zero liquid discharge. In this paper, two aspects of power plant cooling water researches are reviewed, that is, improving the concentration ratio and desalinating from the circulating cooling sewage. Thus, some primary existing methods for improving the concentration ratio of cooling water and technologies for desalination and reuse of wastewater are reviewed in this paper, the existing problems, as well as potential solutions and innovative technologies for improving their performances, are described. The processes of related experimental researches and results have been made clear and the technological application in the engineering have been recounted also, which devoted to observe the development direction of these technologies and to find what should be focused on in the future. Based on the above analysis, this paper concludes that the focus of improving the utilization of cooling water is how to develop more green water treatment agents, cleaner means for dealing with sewage to reduce secondary pollution. Desalination and reuse of sewage using electrochemical technology with anti-pollution, larger flux, excellent membrane materials will be the dominant trend. In further studies, how to achieve the most optimized combinations of different technologies is an important research breaking point in water conservation and emission reduction for circulating cooling water systems in power plants.

Keywords: Circulating cooling water; Concentration ratio; Power plant; Desalination

# 1. Introduction

The power industry is an important national economic entity for any nation, but is also the main consumer of fossil fuels and water resources, making the issues of energy saving, water saving and emissions reduction in the power industry particularly urgent. In particular, a series of policies and regulations in China such as the Action Plan for Water

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Pollution Prevention and Control (referred to as "Water Ten") [1] was promulgated by the State Council in April 2015, the "Thirteen Five" Total Water Consumption and Intensity of Dual Control Action Program was enacted in July 2016, and the National Water Saving Action Plan was put forward in October 2016, had been issued with a view to water saving, emissions reduction, and water pollution control. Many countries have further intensified efforts in industrial water-saving and drainage control, and the issue of water resources is the primary problem that must be addressed

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by industrial enterprises. This is the driving force to explore measures to reduce water use and the amount of sewage discharge.

The power plant is one of the biggest water consumers. The supplementary water used by its cooling water system accounts for 60% to 80% of the entire plant's consumption [2] and sewage accounts for 15% to 17%. When the concentration ratio is less than 2, the proportion of wastewater to the total amount of supplementary water is up to 60% to 80%. The concentration ratio of circulating cooling water in power plants is generally only about 2 to 3 times. The large water consumption and low recycling rate of the circulating cooling system are the primary reasons for the low water reuse rate. Therefore, reducing the amount of make-up water used and sewage generated by increasing the concentration ratio is a good approach. However, to avoid a concentration ratio too high in the circulating cooling system, part of the sewage needs to discharge while a certain amount of clean water is replenished. The discharged water is referred to as the circulation cooling water sewage and has the characteristics of being a large volume of water with high salinity [3]. If the produced water obtained by the desalination of sewage can be used as supplementary water for the circulating cooling system, the amount of freshwater and the discharge of sewage can be greatly reduced. In terms of circulating cooling water of power plants, the discharge zero liquid should be achieved on the principle of "multi-use, reuse by step, recycle use".

As early as the 1970s, researchers from abroad began to research and develop technologies for zero discharge of circulating cooling water. These days the concentrating ratio of circulating cooling water systems in the developed world was generally in the range of 6–8, for individual systems that achieve zero discharge [4]. In contrast, the circulating water concentration ratio of most power plants in China was only 2–3 times. Chinese thermal power plants need to exert the utmost effort to improve the concentration ratio of circulating cooling water and desalination reuse of the sewage to achieve an improved water treatment program [5]. In summary, the research progress of techniques for increasing the concentration ratio of circulating cooling water and desalting of drain water is reviewed in this paper. Based on the above two aspects, a zero discharge technology roadmap for the circulating cooling system of the power plant is summarized in Fig. 1.

# 2. Water quality analysis of circulating cooling water

To verify and evaluate the possible use of treated wastewater, we should first discuss the quality of water and fouling criteria of circulating cooling water in the power plant in detail. Table 1 gives the water quality standard for circulating cooling water according to the "Quality of circulating cooling water used in power plant" (DB37/T1575-2010) issued by China's Shandong Bureau of Quality and Technical Supervision in 2010. Due to differences in the operating conditions of different power plants, the design of water replenishment systems of the circulating cooling water for each plant will be slightly different. Most domestic power plants were initially designed to use treated surface water or groundwater as supplementary water. Now, to conserve water, most power plants use reclaimed sewage as supplementary water. Therefore, there are two corresponding water quality standards comparative with the different replenishment water sources of circulating cooling systems in the power plant. The water quality standard of reclaimed sewage as a make-up water supply source for the power plant circulating cooling system is shown in Table 2 [6].

To realize the desalination and reuse of the circulating cooling water of the power plant, the water quality of the discharge water needs to be understood first to guide the subsequent desalination research of sewage. The water quality of the circulating cooling water from five different power plants is summarized in Table 3. As can be seen from Table 3, the pH of the wastewater from the circulating cooling water is mostly alkaline. The temperature ranges from 25°C to 40°C. The Ca<sup>2+</sup> concentration is generally below 500 mg/L, the cl<sup>-</sup> concentration is 300–500 mg/L, SO<sub>4</sub><sup>2-</sup> is generally around

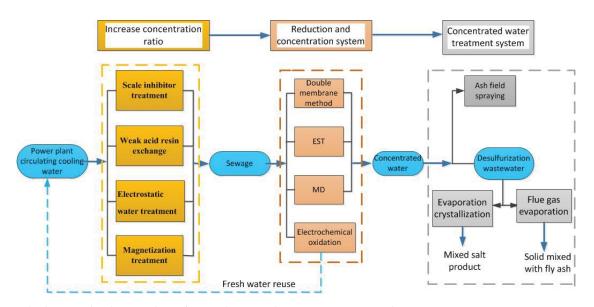


Fig. 1. Zero discharge technology roadmap for circulating cooling water in a power plant.

Project	Conditions of use	Allowable value
Turbidity/NTU	Determined by the production process requirements	≤20
	Heat exchange equipment for the plate, fin tube	≤10
pH	-	6.8–9.5
Calcium hardness + Methyl	$CaCO_3$ stability index RSI $\geq$ 3.3	≤1,100
orange hardness/mg L <sup>-1</sup>	Heat transfer surface water sidewall temperature	Calcium hardness < 200
Total iron/mg L <sup>-1</sup>	-	≤1.0
$SO_4^{2-}/mg L^{-1}$	-	≤2,500
Silicic acid (with SiO <sub>2</sub> )/mg L <sup>-1</sup>	-	≤175
$Mg^{2+}$ and $SiO_2$ (with CaCO <sub>2</sub> )/mg L <sup>-1</sup>	pH ≤ 8.5	≤50,000
COD <sub>c</sub> /mg L <sup>-1</sup>	_	≤100
Free chlorine/mg L <sup>-1</sup>	Loop back to the water explorer	0.2–1.0

Table 1 Circulating cooling system water quality standards (GB50050-2007)

Table 2

Water quality requirement of reclaimed water as circulating cooling water

Project	Water quality requirement of reclaimed water as cir-
	culating cooling water
pH (25°C)	7.0-8.5
Total iron/mg L <sup>-1</sup>	≤0.30
Suspended matter	≤10
Hardness/mg L <sup>-1</sup>	$\leq$ 2.50 × 10 <sup>2</sup> (Calcium car-
	bonate)
Alkalinity/mg L <sup>-1</sup>	≤2.0 × 10² (Methyl orange
	alkalinity, based on cal-
	cium carbonate)
BOD <sub>5</sub> /mg L <sup>-1</sup>	≤5.0
COD <sub>Cr</sub> /mg L <sup>-1</sup>	≤30.0
Na⁺/mg L⁻¹	-
Cu <sup>2+</sup> /mg L <sup>-1</sup>	≤0.050
$Ca^{2+}/mg L^{-1}$	30–200
Cl⁻/mg L⁻¹	≤2.50 × 102
SO <sub>4</sub> <sup>2-</sup> + Cl <sup>-</sup> /mg L <sup>-1</sup>	-
$Mg^{2+} \times SO_4^{2-}/mg L^{-1}$	-
Silicic acid (SiO <sub>2</sub> )/mg L <sup>-1</sup>	-
Free chlorine/mg L <sup>-1</sup>	0.1–0.2 (at the end)
$NH_{3}^{-}N_{4}^{3}/mg L^{-1}$	<5.0
Oil/mg L <sup>-1</sup>	<3.0
Total phosphorus (PO <sub>4</sub> <sup>3-</sup> )/mg L <sup>-1</sup>	≤2.0
Dissolved solid matter/mg L <sup>-1</sup>	<1.0 × 103
TDS/mg L <sup>-1</sup>	_
Total number of bacteria/mL <sup>-1</sup>	<1.00 × 103
Biological slime ml/m <sup>3</sup>	-

500 mg/L, although in some power plants  $SO_4^{2-}$  can be more than 1,000 mg/L. The concentrations of all these ions limit the increase of circulating ratio. The synergistic action of different ions, such as deposition and scaling and accelerated corrosion, also have a big impact on cooling water systems.

#### 3. Increasing the concentration ratio

Increasing the concentration ratio of circulating cooling water is a method frequently used to improve the utilization rate of cooling water in thermal power plants to save water resources and reduce sewage discharge. However, a high concentration ratio will exacerbate the scaling and corrosion of the circulating cooling equipment, which may cause a number of problems for the safe operation of the thermal equipment [11].

The concentration ratio refers to the ratio of the salinity of the recycled water to the makeup water [12], which is an important technical and economic indicator to determine the recycling rate of water used in the cooling system in the operation of an industrial circulating cooling water system. A higher concentration ratio enables a greater number of recycling of cooling water. The volume of water will be reduced accordingly not only for fresh added but also for sewage. Increasing the concentration ratio of cooling water can save water resources with obvious economic and social benefits. Therefore, technologies that increase the concentration ratio of circulating cooling water are the primary methods for saving industrial water.

The main limitations of increasing the concentration of circulating cooling water are: when the concentration ratio increases, the salinity increases, leading to corrosion and scaling of the condenser; and the impact on the quality of the supplementary water in the circulating water system [13]. To counteract these effects, current methods adopted by power plants include adding acid, putting scale inhibitors, softening the supplementary water, and using weak acid ion exchange resin treatment. All these approaches can improve the concentration ratio of circulating cooling water, reduce the amount of discharge from the circulating cooling water system, and lessen the loss of sewage [14]. Several typical ways of improving the concentration ratio are given below.

### 3.1. Traditional circulating water treatment technologies

Adding acid to circulating water can reduce the alkalinity and significantly increase the concentration ratio of circulating water. When the alkalinity of circulating water is decreased, the corresponding saturated calcium

Test items	Power plant1	Power plant2	Power plant3	Power plant4	Power plant5
рН (25°С)	8.9	7.82	8.72	8.5	8.35
Conductivity/(25°C)	2,425	3,312	2,817	2,255	_
Total hardness/mg L <sup>-1</sup>	581.2	832.4	953.5	834	_
Total alkalinity/mg L <sup>-1</sup>	415.2	403.2	400	_	_
COD/mg L <sup>-1</sup>	35.2(Cr)	30.55(Cr)	80.0(Cr)	4.9(Cr)	12.8(Mn)
$CO_{3}^{2-}/mg L^{-1}$	59.5	_	_	75	_
HCO <sup>-</sup> <sub>3</sub> /mg L <sup>-1</sup>	499.4	_	488.2	372	105
Suspended matter/mg L <sup>-1</sup>	31	5.5	-	8.2	150.5
$SO_4^{2-}/mg L^{-1}$	504.6	484.6	948.9	503	1,420
Cl <sup>-</sup> /mg L <sup>-1</sup>	308.8	419.0	256.8	315	389
$PO_4^{3-}/mg L^{-1}$	0.39	0.33	1.01	1.32	_
$Ca^{2+}/mgL^{-1}$	306.5	487.5	360.7	313.2	365
Mg <sup>2+</sup> /mg L <sup>-1</sup>	90.6	344.9	110.2	100.2	75
Fe <sup>3+</sup> /mg L <sup>-1</sup>	0.13	0.71	-	_	_

Table 3 Water quality of circulating cooling sewage (Zheng and Yu [7]; Liu et al. [8]; Yin and Guan [9]; Yan [10])

ion concentration can be greatly increased. The concentration ratio is also improved while the water quality remains unchanged. The reduction of alkalinity of the circulating water is closely related to pH value. Circulating water must be kept within an operating pH range. In recent years, this technology is employed by most domestic power plants operating at high concentration ratios [15]. The concentration ratio of circulating cooling water in a power plant in Luoyang, Henan province is 1.5 to 2. To reduce the amount of replenishment needed for the circulating water system, an activated acid treatment was carried out in the plant in February 2004. The pH of the circulating water is guaranteed to be within the specified limits with the acid addition system. After one week's operation, the concentration ratio of the circulating water grew to 3.3. The requirement of freshwater for replenishment declined from 200 to 160 t/h, leading to an average monthly saving of 71,520 t [16]. This method requires less investment in equipment, but operating conditions must be strictly managed since excessive acid will cause system corrosion.

In the widely used process of organ phosphorus treatment, a pH value range is controlled between 8.7 and 9.0. The method achieving the goal of zero discharge mainly consists of adding acid to adjust pH and matching with an excellent corrosion and scale inhibitor. Some studies showed that it is a mature method for the treatment of a high concentration ratio, which is reducing the alkalinity of circulating water by adding sulfuric acid and scale and corrosion inhibitors [17].

# 3.2. Modern circulating water treatment technologies

#### 3.2.1. Scale inhibitor treatment

Treatment with scale inhibitors is one of the most commonly used scale inhibition methods for circulating cooling water. In practical applications, scale inhibitors with sustained-release effect are commonly used. A variety of pharmaceutical compounding methods are used to obtain efficient treatment agents for circulating water. Commonly used scale inhibitors include inorganic polymeric phosphate, organic phosphonate, organic low molecular polymers, and compound scale inhibitors. Since environmental laws are getting more stringent, the use of scale inhibitors containing phosphorus will be gradually phased out. The development of green scale-inhibitors is an important research direction [18]. Four 300 MW generating units of a power plant in Northeast China [19] use an all-organic low-phosphorus formula, SQ228, as the scale corrosion inhibitor. The formula consists of organic phosphate, polycarboxylic acid, and related corrosion inhibitors. Using this compound the concentration ratio of the recycled water increased from 2.6 to 8.3. Annual water saving is  $6.084 \times 10^6$  t, while the usage amount of acid and water stabilizing agent decreased by 91.3 and 36.5 t respectively, resulting in a saving of 6.75 million China Yuan a year, which demonstrates obvious economic and social benefits.

Adding stabilizers into the water can increase the solubility of  $CaCO_3$  with ten-fold growth. This method can be applied to alkaline areas with low calcium and magnesium but needs both experimental and theoretical inputs to be managed effectively. It is not appropriate for all water qualities, and zero liquid discharge cannot be achieved in most regions [20].

# 3.2.2. Make-up water softening treatment using lime

This softening method uses lime to react with the calcium and magnesium ions in the water. As early as the 1970s, the idea of softening the circulating water was proposed and was utilized for treating the water in the circulating cooling water bypass system [21]. Typical examples include the high-dose bypass lime softening proposed by Matson and Harris [22], and the ultra-high lime softening (UHLS) side-stream treatment later put forward by Batchelor et al. [23]. Batchelor et al. claimed that UHLS treatment removes the main scale ions and some sulfate, while it also effectively gets rid of SiO<sub>2</sub> in water. Subsequently, in 2003, Abdel-Wahab [24] proposed a super-dose lime and aluminum salt treatment process ultrahigh lime with aluminum (UHLA) that not only removed scale ions but could also partially remove chloride ions from the water, reducing the corrosiveness of water.

Based on existing research, the concentration ratio of circulating cooling water can be increased by softening part, or all, of the make-up water and reducing the concentration of Ca<sup>2+</sup> in the circulating water [25]. By just softening part of the make-up water, reduces softening treatment equipment investment and operating costs, meanwhile, it is beneficial to preserving the circulating water. The specific processing proportions need to be determined by experiment [26]. Also, while the make-up water has been softened, the mixed replenishment mode not only can increase the concentration ratio, reduce the amount of sewage and freshwater, but also cut down the cost of producing water by using a lime and ion exchange treatment for the make-up water high hardness water can be softened. Meanwhile, it can soften the source water, by desalinating through a reverse osmosis membrane, which helps to reach an operating condition with a high concentration ratio of the circulating water. The enterprises in the areas with severe water shortage, that use reclaimed water, seawater, and brackish water for the circulating cooling, is appropriate for this technology [27].

#### 3.2.3. Weak acid resin exchange method

Weak acid exchange resin processing technology [28] is based on ion exchange for improving the concentration ratio. This technology enables to remove most of the circulating water carbonate hardness and reduce the possibility of fouling in the water circulation system, for improving the circulating water, and saving water.

In water the dissociation degree of weak acid resin is low. Only in the media close to neutral or alkaline can weak acid resin dissociate to achieve ion exchange [29]. Since that, these resins have a strong exchange capacity only for carbonate hardness in water. Weak acid cation exchange resins for the selection of various metal ions in water are ordered from strongest to weakest:  $Ca^{2+} > Mg^{2+} > Na^+$ . Since the affinity of H<sup>+</sup> ions is greater than other ions and the extremely small dissociation degree of the carboxylic acid group, the tendency of the carboxylic acid root and H<sup>+</sup> to combine is great. Thus it is difficult for the H<sup>+</sup> carboxylic acid ion to dissociate, and more to spread out. Only by relying on HCO<sub>2</sub> diffusion into the interior of the resin to neutralize H<sup>+</sup> ions, can it make the metal ions diffuse into the resin together. It is generally thought that weak acid resin can only remove temporary water hardness [30].

After dealing with the weak acid cation exchange technology the water has the characteristics of low pH value, low alkalinity (sometimes slight acidity), and generally zero temporary hardness. This technology can effectively prevent scaling in the circulating cooling water system of a thermal power plant. However, it is still necessary to improve the water quality stabilizer, the corrosion resistance of the system, since corrosion would result from improper control of metal components in the system.

Combined treatment with an anti-sludge agent can boost the concentration ratio to a preferred level. It refers to using the make-up water consisting of raw part and treated with weak acid ion exchange part and adjusting the amount of water treated in ion exchange, to lower the average hardness of carbonates to 0.8 mmol/L. Taking amino trimethylene phosphonic acid as an example, while ensuring the alkalinity of the make-up water, it can meet the requirement of a high concentration ratio under the condition that the average alkalinity of the effluent during the weak acid treatment period is 0.5 mmol/L and a finite amount of anti-sludge agent is added.

A new zero-discharge process has been adopted by Bayswater/Liddell Electric power integrated enterprise. This technology uses exchangers with weak acid ion and process combining lime softening and reverse osmosis to reduce the concentration of alkali and salt. What's more, further enrichment and separation for sewage operates in evaporator and exposure tank in sequence. Then, about 24,000 t dissolved salts would be removed from the cooling water system annually. In a word, the technology includes traditional lime softening, dual-medium filtration, ion exchanging, reverse osmosis and other processing units. The flow of the process is shown in Fig. 2.

Weak acid resin exchange treatment is suitable for regions with severe water shortage. Hence it is generally required in power plants for large water-savings and high concentration ratio for circulating cooling water. The method is also applicable for some power plants that use groundwater with a carbonate hardness of more than 2 mmol/L, a high sulfate content and a suspended solids content of less than 5 mg/L as the supplementary circulating cooling water. This method is mature, operationally reliable, simple to operate and easy to automate. However, the disadvantages of this method are a large investment, large footprint, and the volumes of acid for reduction exchanger, as well as not environmentally friendly.

#### 3.3. New progress in circulating water treatment technologies

#### 3.3.1. Electrostatic water treatment

The core of the electrostatic water treatment method also referred to as high voltage electrostatic treatment, is an electrostatic water processor [31]. The principle is to remove the algal cell tissue and bacteria in the water in the high voltage electrostatic field by polarizing the water molecules and increasing the solubility of calcium carbonate from adding an anti-sludge agent. When being used in circulating cooling water, this technology has an excellent processing effect with an algal removal rate of 98%, scale inhibition of 95% and a bactericidal rate of 92% [32]. Xu and Zheng [33] explored a high voltage electrostatic ion water treatment technology to deal with circulating cooling water, the concentration ratio of which is above 3. Although the design value exceeds 3, with other indicators being under control, the system corrosion rate is much lower than the national standard. Quan et al. [34] studied the anti-scaling of circulating cooling water by utilizing low voltage static electricity. These systems have a good scale-inhibiting effect on the heat exchanger surface, and a 100% scale inhibition rate can be achieved with only 2.2 W power.

#### 3.3.2. Ozone treatment

Ozone  $(O_3)$  is a single water treatment agent that has many features including scale inhibition, corrosion inhibition, and sterilization. By using the ozone system can run at a higher concentration ratio even a zero liquid discharge condition, which results in excellent water conservation

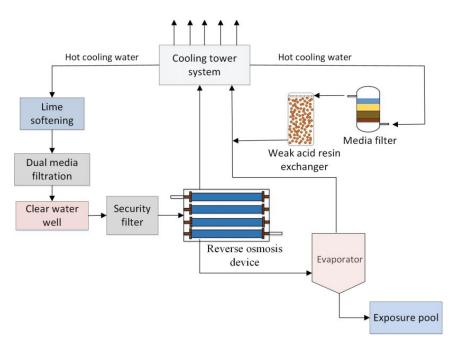
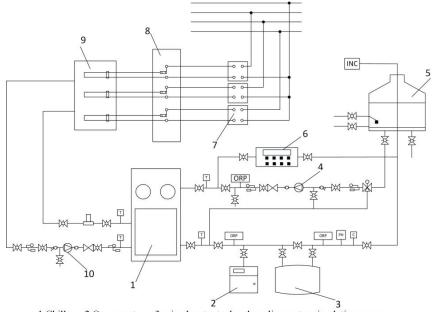


Fig. 2. Bayswater power plant cooling water treatment system.



 Chiller; 2.O<sub>3</sub> generator; 3.mixed water tank: 4.cooling water circulating pump;
 5.cooling tower; 6.Dirt heat resistance meter; 7.voltage regulator; 8.Electrical Parameter Tester; 9.electric heater; 10.chilled water circulating pump

Fig. 3. Ozone treatment system schematic.

[35–37]. It is widely used abroad and is gradually becoming popular in China.

Dong et al. [38] analyzed the benefits of energy conservation and emission reduction when using ozone treatment for circulating cooling water. They found that ozone treatment could be used for descaling, corrosion inhibition, and sterilization. Chen et al. [39] carried out an energy-saving experimental study on ozone-treated circulating cooling water. The schematic diagram of the test device is shown in Fig. 3. The result showed that ozone treatment of circulating cooling water can effectively remove dirt deposited on the surface of equipment and pipes, improve heat transfer and reduce energy consumption. At the same time, it comes to the conclusion that the energy-saving effect of the experiment is related to the original fouling situation of the system. More serious

fouling will result in a more obvious energy-saving effect. Liu et al. [40] applied ozone oxidation technology, as well as ozone treatment to treat circulating cooling water by using three different methods namely ozone treatment, combined ozone and magnetization treatment, and pre-stage membrane pretreatment together with the combined ozone and magnetization treatment method. The experiment showed that all three methods effectively remove bacteria, inhibit scale and inhibit corrosion. In addition, the latter treatment method is proved to be the best. Results from home and abroad show that ozone can replace other chemicals in the treatment of circulating cooling water for corrosion inhibition, anti-scaling, sterilization and algae removal with a high concentration ratio case, and can even achieve zero liquid discharge thus saving energy and water and protecting water resources.

#### 3.3.3. Magnetization treatment

Water is magnetized by a magnetizing water processor that uses different magnetic materials and water-flow paths. The method of magnetizing water for circulating cooling water treatment has the following benefits: environmental water pollution reduction; water conservation; energy conservation; convenient installation; and simple management. Han [41] studied the fouling of water in a magnetic field and found that an external magnetic field could reduce water scale significantly. A growth of time in the magnetization would increase its water, and the amount of fouling would be significantly reduced. Magnetic anti-scaling was more effective when the spacing between each group of magnetizers was small. The reason why it is not ideal for treating acidic or alkaline solutions is that the higher the concentration of  $Ca^{2+}$ ,  $Mg^{2+}$ ions are in the solution, the worse the scale inhibition effect.

In summary, people are exploring other treatment methods to save energy and protect the environment. The scale inhibitor method is the simplest and most reliable one; the lime softening method has certain advantages in cases of high hardness and alkalinity; the membrane method is indispensable for increasing the concentration ratio and achieving zero discharge in water-scarce areas; electromagnetic anti-scaling technologies have many attractive advantages for practical application, but further research is needed for its mechanism and scale inhibition effects. Specific comparisons of several methods are given in Table 4.

### 4. Recycling technology of circulating cooling sewage

The circulating water system of a power plant can operate at a concentration ratio of 6.5, and the cooling water can also be used in a poor water quality system. For example, make-up water for a desulfurization system or a coal transportation system to achieve "zero liquid discharge" of the circulating water system.

According to the actual water balance condition of a power plant, the thermal power plant with a hydraulic ash handling system and an ash storage yard discharges the circulating water directly to replenish water for ash washing and desulphurization, which can achieve cascade utilization. In the ash storage field, evaporation forms part of the natural water cycle. A shortcoming of this method is that a lot of natural precipitation will lead to less evaporation, resulting in an overflow of water in the ash storage field and a larger amount of wastewater that has to be discharged [42].

Under the traditional water treatment control concentration ratio of 3.0–5.0, most of the circulating water discharge sewage is used as supplementary water for a desulphurization system to achieve cascade utilization of water resources. Simultaneously, there is still a large amount of circulating sewage that needs to be reduced by the addition of a bypass treatment system to ensure the balance of the water used in the cascade. The shortcoming of this method is the additional investment for a circulating water bypass system or for sewage treatment [43]. This system requires area, buildings, infrastructure, daily operation, and maintenance, that is to say, greater economic requirements.

With the exception of the above, the water discharged from the cooling water systems is in large volumes and with highly saline. This limits the energy conservation and reduction of emissions from coal-fired power plants. The water needs to be desalinated before being able to be recycled. Thus exploring efficient, fast and economical desalination methods is the key to achieving zero discharge of wastewater. This section presents several domestic and foreign studies into the use of desalination cooling water technologies.

#### 4.1. Ultrafiltration - reverse osmosis process

Ultrafiltration is a water treatment technology by means of selective separation membranes [44]. The membrane can realize separation, concentration, and purification of various components in sewage with differences in pressure, potential, and concentration. Ultrafiltration is often employed in the pretreatment process of reverse osmosis to make the quality of the effluent water meet the requirements of the reverse osmosis membrane. Reverse osmosis is a membrane separation process in which the solvent is separated from the solution under the action of external pressure [45]. Ultrafiltration and reverse osmosis technology usage, which is to achieve reuse of cooling water in power plants, has been successful in many studies.

Combined with the existing process of recycling the cooling and drainage water of thermal power plants, Li et al. [46] studied two processes experimentally. The first process is coagulation-ultrafiltration (UF)-reverse osmosis (RO) (see Fig. 4.), and the second is a clarificationfiltration-UF-RO. The results indicate that the pretreatment of RO plus ultrafiltration has great advantages. The first process's treatment is simple, although the small membrane flux results in unreduced overall investment and low operational reliability. On the other hand, process two can fully meet the requirements for water quality of the boiler's replenish and circle-cooling water (UF effluent SDI value is less than 2, RO salt removal rate reaches 99%). With the membrane flux of UF reaching  $3 \text{ m}^3/(\text{m}^2 \text{ d})$ , this process is reasonable for a low operation-maintenance cost and high system operation reliability.

Guohua Dingzhou Power Generation Co., Ltd. in China successfully put an ultrafiltration-reverse osmosis treatment system for circle-cooling and draining water into operation. The process flow is shown in Fig. 5. The result of the operation shows that when the water production is 70 t/h, the salt rejection rate would be stable at around 98.5%. Then it can

#### Table 4

Comparison of the characteristics of different circulating cooling water treatment methods

Method	Technical principle	Advantages	Shortcomings	Improvement measures
Acid addition	Neutralize alkalinity, control pH of the water	Comprehensive technology, low investment, high concentration ratio	Difficult to control acid, $SO_4^{2-}$ corrosion, large maintenance workload	Coupling other methods
Stable treatment of anti-sludging agent	Hinders crystallization and growth of scale	A small footprint, water composition is simple	Increased $SO_4^{2-}$ and organic phosphorus, water bioaccumulation	Combined with reverse osmosis technology; use of composite scale inhibitors
Water softening and desulfurization of make-up water	Lime reacts with calcium and magnesium ions in water to form a precipitate	Cheap raw materials, no pollution, together with remove some organics, silicates, iron	Specific treatment ratio needs to be determined by experiment	Adopt the mixed make-up water pattern
Weak acid resin exchange	Ion exchange	Mature technology, reliable operation, simple operation, easy regeneration, low acid consumption, solve scaling problems	High standard, a large amount of wastewater discharge	_
Electrostatic treatment	Water molecular structure changes, physical methods	Good scale inhibition and corrosion inhibition, low operating costs, and no pollution	High accuracy requirements for the dosing agent and daily management of the system	A small amount of chemicals used in combination
Ozone	Oxidation and decomposition	Chemical-free, No secondary pollution, economic, long equipment life	The high cost of equipment and staff, difficult to control ozone dosage	Combined use of magnetization technology
Magnetization	Magnetic field changes the crystal structure of scale	Nontoxic, pollution-free, convenient application	Magnetic field affects magnetic suspension adsorption	Auxiliary chemicals, combined with other technologies

meet the index for intake water of the subsequent desalination process [47]. However, as for the characteristics of high concentration ratio and complex water quality, it is the key to reasonably selecting the pretreatment process and membrane component model for circle-cooling and draining water.

### 4.2. Membrane distillation

Membrane distillation (MD) is a novel wastewater treatment method combining membrane technology with distillation [48]. A hydrophobic microporous membrane is used as a medium, and the volatile components in the feed liquid are vaporized through the membrane pores under the condition of poor vapor pressure on both sides of the membrane to achieve separation. Compared with other commonly used separation techniques, MD has the advantage of high separation efficiency, mild operating conditions, and limited requirements of the mechanical properties of the membrane. Besides, the membrane material used for MD is a hydrophobic, microporous membrane [49]. Only steam can pass through the film pores, and at the same time, no capillary action occurs in the film pore, nor is the vapor-liquid balance of all the components in the feed liquid influenced by the film when the feed liquid is in direct contact with at least one side of the film.

Li and Lv [50] used the polyvinylidene fluoride compound film prepared in the laboratory to do the vacuum membrane distillation experiment in the cooling pumping system of a power plant. The experiment concluded membrane flux and the temperature of the entrance is proportional to vacuum degree. The self-made hydrophilic/hydrophobic membrane has a good influence on the reuse of circulating water in power plants. On the other hand, the preset sequential malfunction of sodium hydrogen carbonate helps the increasing of membrane flux and ensuring the operation of the circulating water system with a high concentration ratio stably.

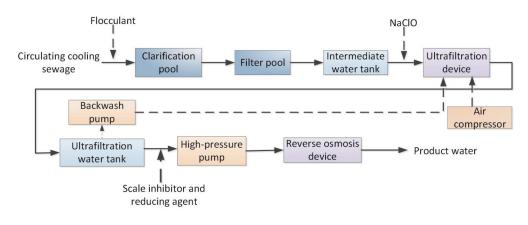


Fig. 4. Flow chart of the first process.

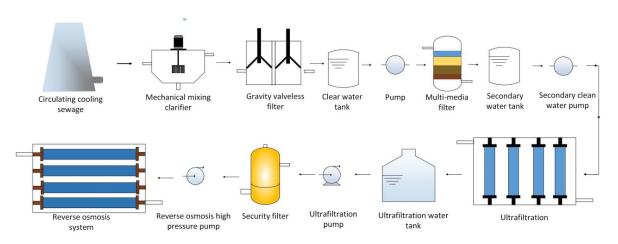


Fig. 5. Process flow of recycling treatment of circulating cooling sewage.

The experimental system diagram used by Yu et al. [51] is shown in Fig. 6. After the concentration process with the temperature of the front-side at 60°C, it gets permeation flux of about 30 J and desalination ratio of above 99.95%. As for the simulated solutions containing silicate, if the concentration ratio is between 3.2 and 5.0, it would produce an insoluble calcium carbonate scale on the membranes. Concentration multiple can be increased to 8.0, and the corresponding water recovery to about 87%, after adding scale inhibitor. In a word, it can reach the conclusion that membrane distillation is valid for desalination and reusing of cooling water in power plants.

Membrane distillation applies simple and easy to operate equipment, functions under normal pressure at low solution temperature, and can make use of engineering waste heat and solar or other low-cost energy, along with the treated water is of high quality, it is expected to become the key technology for ultrapure water preparation in the future [52]. But on an industrial scale, membrane distillation processes still have many problems to be solved, such as the need for a hydrophobic microporous membrane, higher film cost, lower membrane flux, and membrane fouling. Future studies should include perfecting the heat transfer and mass transfer models of membrane distillation so as to reduce the need for experimentally determined parameters of the model and for a complete understanding of the mechanism of membrane distillation.

#### 4.3. Comparison of desalination methods

Distillation is not limited by the salt content in water and is suitable for applications of which residual heat is available and capacity in the power plant is large. Therefore, it is mainly used in coastal thermal and nuclear power plants. Since brine evaporation concentrators are not yet produced in China, the cost of equipment is quite high. In addition, corrosion and scaling of the equipment and pipes are serious. For these reasons, brine evaporation concentrators are not economically viable for treating a great deal of cooling water.

Ion exchange technologies are more mature and commonly used. Some enterprises have taken advantage of weak acid ion exchange technology into cooling water sewage recovery systems. The cost of this kind of equipment is low, but ion exchange regeneration consuming large volumes of acid and alkali must be done frequently. If not, it would lead to secondary pollution of which consists of high operating costs, larger production of acid and indigestible alkali waste.

Reverse osmosis is a type of membrane separation technology. Membrane technologies have the following advantages:

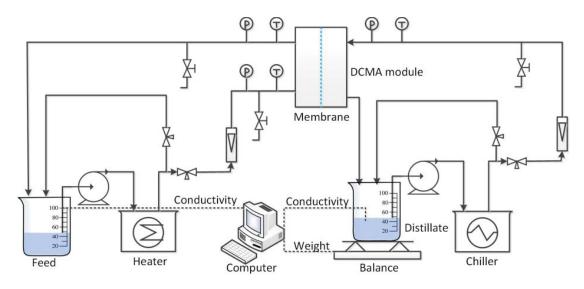


Fig. 6. Direct contact membrane distillation experimental system diagram.

simple equipment; small size; single operating procedure; larger separation factor; low energy use; high efficiency; and no secondary pollution. What's more, usually, fewer operators are required and the process is easier to manage Longterm stable operation of the membrane device benefits from large scale cleaning of the film once a year but regular small scale washing. At present, some domestic plants use reverse osmosis technology to treat the sewage. The effluent from this process enters an ion exchange resin to remove the impurities and is finally used as boiler make-up water. The membranes required for this process still need to be imported. Table 5 provides a comparison of the current power plant circulating wastewater desalination technologies.

#### 4.4. Electro-adsorption technology

Electro-sorption technology (EST), also called capacitive deionization, is a new water treatment technology that enriches and concentrates dissolved salts and other charged substances on the surface of electrodes by using the phenomenon of adsorbing ions and charged particles onto the surface of charged electrodes, thus being able to realize the purification and desalination of water [53].

The principle of electro-sorption is shown in Fig. 7. When the solution passes between two energized electrodes and the voltage applied to the electrodes is lower than the decomposition voltage of the solution, the positively-charged electrode draws negative ions from the solution, and the negative electrode attracts positive ions, forming an electric double layer. The role of the electrode is only to provide electrons or to remove electrons from the interface. Thus, the size of the interface charge depends on the applied potential. The capacitor on the double layer has the characteristics of being able to be charged or discharged. When charging, the charge on the side of the electrode is supplied by electrons or positive charges on the electrode. While the charge on the side of the solution is provided by cations or anions in the solution, the electrons are introduced into the negative electrode from the positive electrode through an

external power source. Then the positive and negative ions in the solution reach the electrode surfaces separately. The discharge is in the opposite direction.

When the surface of the electrode is not charged, it is primarily covered by adsorbed dipole water molecules. Other surface ions and molecules may also be adsorbed by contact. When the electrode is energized, the charge of the electrode is absorbed by the oppositely-charged ions or charged particles on one side of the electrolyte of the double layer or is compensated by the accumulation of the opposite charge on the outer Helmholtz layer and on the diffusion layer. The ions or charged particles will accumulate on the electrode surface. In this way, ions or charged particles will be enriched and concentrated on the surface of the electrode, which greatly decreases the concentration of salts, colloidal particles, and other substances in the water, thereby achieving to desalinate, soften and purify water.

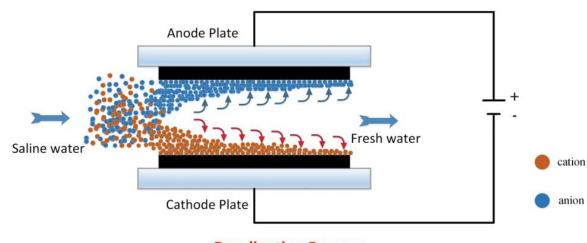
Activated carbon and carbon aerogels are widely available in electro adsorption technology. With good electrical conductivity and a large specific surface area, carbon materials, like activated charcoal and carbon aerogels, are frequently used as electrodes. When placed in an electrostatic field, the material will form a strong electric double layer at the interface with the electrolyte solution. The negative anion is removed from the water and adsorbed on the side of the positive electrode. Similarly, the positive ions are adsorbed onto the side of the negative cathode.

The development of EST technology is becoming more mature and more popular in water treatment mainly for desalination purposes. Yet the biggest advantage of EST is that even if the water quality of influent water is poor, the operation does not consume chemicals, which means there is no need to add excessive pretreatment equipment and the operation and maintenance are very convenient.

A study by Li [54] focusing on the desalination of wastewater from a circulating cooling system, shows that electro-adsorption technology can solve the desalination problems of the cooling water. And the treated water meets the water quality requirements of the cooling water which are:

Methods	Principles	Advantages	Shortages
Ion exchange method	Resin ion exchange with the same charged ions in water	High ion removal rate	Complex equipment, high investment, needs regeneration, organic pollution
Distillation	Heating evaporation with different boiling points	Without the limit of the concentration ratio of the raw water, more types of heat sources available	High energy consumption, easy scaling, high cost
Electrodialysis	Selective transfer of ion exchange resin to produce directional migration of anions and cations	No regeneration, less treatment, less pollution, good adaptability, simple process, reliable technology	Working voltage is high, prone to Faraday reaction, the membrane is easily contaminated, causing scaling
Reverse osmosis method	Overcoming the pressure difference on both sides of the membrane	The removal efficiency of organic compounds and various kinds of ions is high	High energy consumption, acid-base consumption, pre- processing requirements, low water production rate
Nanofiltration method	Like reverse osmosis, a membrane process is driven by pressure, but the mass transfer mechanism is different	Removal of harmful substances from water, preparation of quality drinking water, retention of favorable metal ions	Cannot remove monovalent ions, ammonia, scaling, high investment cost
Electro-deionization method	Combined with ion exchange and electrodialysis principle to remove ions	High water purity, no acid regeneration	High water quality requirements, high processing costs
Adsorption method	Selective adsorption uses the difference between the components and the adsorbent	With high selectivity, suitable for the removal of trace impurities from gases and liquids	Small amount of treatment, the choice of adsorbent presents a certain degree of difficulty

Table 5 Comparison of circulating cooling system sewage desalination technology



# **Desalination Process**

Fig. 7. Schematic diagram of electro-adsorption.

average removal rate of conductivity is 76.3%; water production rate of 76.1%; an average chloride ion removal rate of 85.6%. The removal of chloride ion is better, and the average removal rate of total hardness is 78%. The data shows that electro-adsorption technology is an efficient wastewater treatment technology.

The mechanism of ion mass transfer and adsorption in the process of electro adsorption is well understood. More attention is being paid to finding ways to increase adsorption capacity, achieve a faster adsorption rate, develop more economical electrode materials, improve the reliability and stability of electro-adsorption equipment, and advance research into electrical energy recovery. With the continued maturation of electro adsorption technology, it is possible for largescale industrial applications.

### 4.5. Electrochemical treatment technology

Hefengjiahui Water Treatment Company in the Shanxi province of China proposed an electrochemical method for treating cooling water in power plants and gained good results in the removal of fouling substances and biological slime. Electrochemical circulating water treatment technology uses an electrolysis reaction to remove organic and inorganic pollutants from water through electrochemical oxidation, electrochemical reduction, cathode adsorption, and other reaction methods to achieve scale inhibition, scale removal, corrosion prevention, and sterilization. When the electrochemical system starts up, the pH value of the water will up to 13 under the cathode reaction with the combination of an electrochemical reaction and a proprietary cathode coating (catalyst). This causes the bicarbonate in the circulating water to precipitate as a solid, which then adheres to the inner wall of the electrochemical device together with biofouling compounds, growing rapidly. Finally, when the scale body grows to 3 cm of the thickness, the control system activates a wiper device to expel the fouling material and biofuel mud from the circulating water system. This method provides good corrosion resistance. Under the combined action of electrochemical and patented anode coating (catalyst), the pH value of the anode reaction chamber is 3, meanwhile what is generated in the anode region are hydroxyl radicals, oxygen radicals, ozone, and hydrogen peroxide. The resulting oxidizing substances can kill algae and bacteria including Legionella species and microorganisms. In the anodic reaction chamber, up to 70% of the chloride ions are converted into free chlorine or hypochlorous acid, which form the active ingredient of the current widely used pharmaceutical agents (prototype).

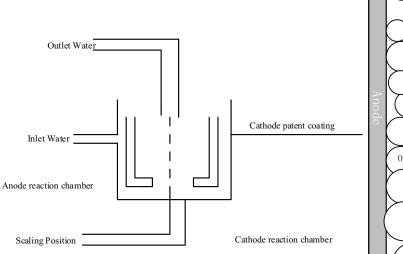
After the cooling water enters the reaction chamber, water purification is achieved through the coating and electrochemical action in the anode and cathode regions. The working principle of the electrochemical water treatment system (see Fig. 8) can be summarized as follows:

- The pH in the cathode region reaches 13, after which fouling substances and biofouling precipitate out in the solid form.
- As the pH in the anode region reaches 3, hydroxyl radicals, oxygen radicals, ozone, and hydrogen peroxide and other substances are generated, and these substances further enhance the bactericidal and algaecidal effects of the water system.
- In the anode area, chloride ions are electrochemically oxidized to generate free chlorine or hypochlorous acid.
- The descaling process includes an electronic control system to automatically scrape off fouling substances, sewage, and cleaning. At the same time, a conductivity test circuit is built in this system to automatically adapt to the conductivity fluctuation of the water quality.

At present, the most popular methods in the field of water treatment are the chemical and ion exchange methods, but these still have some problems such as secondary pollution and high cost. Meanwhile, electrochemical water treatment technology has been widely recognized for its advantages of no pollution, ease of use, low cost, and important application and research value. The comparison between the electrochemical and chemical methods is shown in Table 6.

Electrochemical circulating water treatment has the merits of no pollution, low energy consumption, less discharge of pollutants, better scale inhibition, corrosion

oacteria



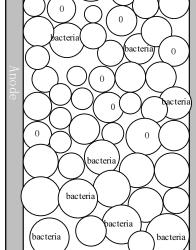


Fig. 8. Electrochemical water treatment system working principle diagram.

Table 6
Comparison of electrochemical and chemical methods

Working principle	Electrochemical treatment	Chemical treatment
	Electrochemical water treatment technology	Scale inhibitors, corrosion inhibitors, biological
	(HF-wing-smXEst electrochemical water treatment	dispersants, killing agents/disinfectants, acid strip-
	system), using electrochemical properties of water	ping agents, chlorination and deoxidizer, various
	and minerals in water to regulate the balance of	agents are used to stabilize the mineral balance in
	minerals in the water	the water
Scale control	Scale is removed by pre-precipitation in the	Scale inhibitors increase the solubility of fouling
	cathode, reducing the total hardness of the system,	minerals to prevent them from precipitating and
	releasing metal ions by the electrochemical system,	disrupting the growth of carbonated crystals; dis-
	preventing silica precipitation and high-tempera-	persants and surfactants mutually repel suspended
	ture precipitation of calcium carbonate, suspended	solid particles; acids, phosphates and water-soluble
	matter flocculation, sedimentation, washing, and	polymers are inorganic scale inhibitors
	scaling, and then being discharged	
Corrosion control	Control the pH value of cooling water to minimize	Improve the pH of cooling water; Corrosion inhib-
	the corrosion by water; the concentrated magne-	itor reduces the relieving area of the metal surface
	sium hardness is deposited on the inner wall of the	and blocks the electrochemical corrosion circuit,
	pipe in the form of magnesium hydroxide in the	Phosphate, zinc salt, molybdate, and polymerized
	cooling water and plays a role in corrosion inhibi-	silicate are corrosion inhibitors of low carbon steel
	tion and inhibition of the biofilm	
Microbial control	Chloride ions are oxidized to form free chlorine or	Microbial inhibition compounds include bromine
	hypochlorous acid; hydroxyl radicals, ozone and	compounds, ozone, and so on; surface-active agent,
	hydrogen peroxide are generated to strengthen	hydroxyl radicals, hydrogen peroxide, ozone and
	the sterilization in the reaction chamber; micro-	hypochlorite, and chlorine are oxidants that can kill
	organisms die in the reaction chamber via strong	microorganisms
	currents, and moving through strong bases and	
	strong acids	

prevention, and bactericidal and algaecidal properties. The successful deployment of an electrochemical water processor benefits from the advantages and processing effects of this technology. It saves 45% water consumption over the normal, considerably reduces chemical costs and also meets the requirements of environmental protection indicators. With the continuous tightening of requirements including clean production, energy-saving, and emission reduction, electrochemical water treatment technology looks to become the preferred choice for circulating water systems of power plants.

#### 5. Conclusions

The crux of the efficient operation of power plant water systems is the water-saving technologies for cooling water. In order to save water and reduce the cost of water treatment in industrial cooling water systems, some important measures including reducing the amount of sewage and increasing the concentration ratio are being taken now. In the later studies, as for saving water in power plants, we should focus on declining the amount of sewage, treating it for reuse, developing an efficient high-concentration ratio cooling water treatment technology.

Increasing the concentration ratio of cooling water is critical to meet water conservation, energy conservation, and environmental protection requirements. Different industries should adopt different methods according to their own actual conditions. Although there are some drawbacks, adding acid and scale inhibitors is still the most simple and reliable method of water treatment. Lime softening treatment has some advantages in high hardness and alkalinity. Membrane softening is an effective method of enhancing the concentration ratio and achieving zero emissions in waterscarce areas. Electromagnetic scale inhibition technology has some attractive advantages and some practical applications but requires further research on its mechanism and scale inhibition effects. Ozone, an efficient and clean water treatment agent, has become a new water-saving technology. Electrostatic water treatment has excellent germicidal and algaecidal properties. The treatment effect of combining several treatment technologies, which can effectively improve the concentration ratio and save water for power plants, is far better than a single. Increasing the concentration ratio to save water and treat sewage water for reuse is a new idea for cooling systems. Ultrafiltration, reverse osmosis, and other pressure-driven membrane separation technologies are the main technologies used in the treatment of circulating system sewage water. All have been deployed on a large-scale both at home and abroad. Emerging technologies such as membrane distillation, electro-sorption, and electrochemistry are still in the laboratory research and development stage. The focus of water treatment research and development tends to green water treatment agents and clean water treatment processes with zero pollution. The choice of treatment process should be determined by the characteristics of sewage water, the existing condition of equipment, and the requirements for reuse water quality. In further studies, the research of electrochemical technology will be the dominant trend. In addition, how to achieve the most optimized combinations of different technologies is an important research direction in water conservation and emission reduction for cooling water systems in power plants.

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