The research progress of water treatment technology on recirculated cooling water

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Abstract. The treatment technology of circulating cooling water used in industry is summarized, and the existing problems are discussed. Then, a new environmentally friendly treatment technology of circulating cooling water-physical-chemical combined water treatment technology is introduced. Combined water treatment technology is more in line with the basic requirements of China’s sustainable development strategy. It is an important direction of circulating water treatment to study and optimize the current circulating water treatment technology.

1. Introduction
In China, industrial water consumption accounts for about 40% of the total water consumption, and industrial circulating cooling water accounts for 80% of the industrial water consumption. Therefore, the treatment and recycling of industrial circulating cooling water can greatly reduce water consumption and save limited water resources. The circulating cooling water treatment methods are mainly divided into two types, chemical treatment and physical treatment.

2. Chemical water treatment technology
Chemical treatment usually involves adding a certain amount of scale inhibitor and corrosion inhibitor to the supplementary water to prevent scaling and corrosion of the water system. Among industrial water treatment chemicals, scale inhibitors and corrosion inhibitors are the most commonly used chemicals, which are important for preventing equipment scaling, reducing energy consumption, extending equipment life, and ensuring the safe operation of equipment.

2.1. Natural polymer water treatment agent
Natural agents such as tannin, sulfonated lignin, and humic acid have received great attention and extensive research in the water treatment industry. As a water treatment agent, tannin can prevent the depolarization effect of dissolved oxygen on the cathode, or form an impermeable protective film on the metal surface. Sulfonated lignin is a by-product of the paper industry. Its molecule contains...
sulfonic acid group, hydroxyl group and methoxy group, which has a good dispersing effect on iron oxide. It is often used as a formula in the formula of water treatment agent. Humic acid is mainly some natural aromatic hydroxyl carboxylic acid, which has the properties of ion exchange and adsorption. These natural polymer water treatment agents have the advantages of convenient sources, low prices, and non-toxicity. In addition, they can play effective roles in corrosion and scale inhibition in water treatment and extend the operation life of the equipment. However, the disadvantages of natural polymer water treatment agents are that they are natural substances, which have unstable performance, easy decomposition, large dosage and high impurity content. Moreover, their scale and dispersion properties are not as good as synthetic scale inhibitors, and they are now rarely used.

2.2. Phosphonocarboxylate
Phosphonocarboxylate is called POCA for short. Organic phosphonic acid was a new product developed in the late 1960s abroad. It was widely used in circulating cooling water treatment in the 1970s. Their molecular structure contains C-P bonds. This chemical bond has good stability, which makes the molecules difficult to hydrolyze and resistant to high temperatures. The phosphonocarboxylate polymer is polymerized under normal pressure, and there is no emission of harmful substances during the reaction. The production process and the use of the product can meet the environmental protection requirements. This kind of polymer is mainly effective on calcium carbonate scale, and has a certain synergistic effect on inhibiting calcium phosphate scale, calcium sulfate scale and dispersing iron oxide. It has been reported that this kind of polymers not only has excellent scale inhibition and dispersion, but also have a good corrosion inhibition effect on carbon steel. They are good for environmental protection, and they already have the concept of a green water treatment agent.

2.3. Environmentally friendly polymer water treatment agents
One of the main driving forces for the development of cooling water treatment technology is environmental protection. At present, the most commonly used scale inhibitor products in the industry generally contain phosphorus that makes the water body eutrophic and some are not biodegradable. Today, with the increasingly strict environmental regulations, phosphorus is also included in the list of restricted emissions. For example, Germany has required phosphorus emissions to be less than or equal to 1 mg•L⁻¹[1]. Phosphine-based formulations face the fate of being restricted and eliminated. Under this situation, the development and application of low-phosphorus and non-phosphorus green water treatment agents have increasingly become the focus of attention at home and abroad[2]. Green water treatment agent means that its manufacturing process is clean, which is non-toxic to human health and the environment during its use. And it must be biodegradable into environmentally friendly water treatment agents. Polyaspartic acid (PASP) and polyepoxy-succinic acid (PESA) are two internationally recognized green water treatment agents[3]. This type of water treatment agent has good scale and corrosion inhibition properties, and does not cause eutrophication of the water body, which is easily accepted by the environment.

2.3.1. Polyepoxysuccinic acid
In 1973, U.S. patent[4] developed a new cleaning agent: 1-oxyacylopane-2,3-dicarboxylic acid, which is the so-called polymer Epoxy Succinic Acid (PESA). Prector&Gamble Company and Betz lab in the United States used it as a scale inhibitor in the late 1980s and early 1990s respectively.

Formula 1 is the synthesis process of polyepoxysuccinic acid, which is mainly divided into three steps. The first step is the hydrolysis of maleic anhydride to produce sodium maleate, the second step epoxidation of sodium maleate to sodium epoxy succinate, and the third step polymerization of sodium succinate to produce polyepoxy sodium succinate.
Formula 1. The synthetic route of PESA.

In China, the development of PESA began in the late 1990s. Xiong Rongchun and others from Beijing University of Chemical Technology[5] used maleic anhydride as a raw material and first hydrolyzed it with water and alkali to produce maleate. CatA(peroxide catalyst) and CatB(vanadium catalyst) were used as catalysts for epoxidation to produce epoxy succinic acid, then CatC(rare earth catalyst) as the catalyst to the polymerization of PESA. The dosage of CatA was 2.5%-3.6%, when the CatB 1.0%-5.0%, and CatC 4.0%-7.5%. The pH value was 5-7, and the reaction temperature was 65-100℃.

Polyepoxysuccinic acid is currently mainly used as a scale and corrosion inhibitor because of its non-phosphorus and non-nitrogen structure, and also has the dual function of scale and corrosion inhibition. It is a green water treatment agent with good biodegradability. Polyepoxy succinic acid not only has excellent scale inhibition and dispersion performance, but also has certain corrosion inhibition performance. It can be combined with other agents to form a low phosphorus or no Phosphorus formula[6].

2.3.2. Polyaspartic acid

Polyaspartic acid(PASP) is an amino acid with a carboxylic acid side chain. The structure is as follows in formula 2.

![Formula 2. The structure of PASP.](image)

Polyaspartic acid makes it have good biodegradability, calcium ion exchange ability and the characteristics of destroying the crystal structure of calcium salt. In particular, its environmental compatibility and biodegradability make it a very promising and environmentally-friendly multifunctional polymer material in many fields. It is a polymer of amino acids. In addition to the properties of water-soluble carboxylic acid, it also has valuable biodegradation properties. Since the first artificial synthesis of polyaspartic acid in 1850, it has gradually attracted the attention of major companies in the world. As an environmentally friendly product, polyaspartic acid is mainly used in plant nutrient accelerators, industrial dispersants, cleaning aids, scale and corrosion inhibitors, super water absorbents, etc.

PASP is usually prepared by first synthesizing the intermediate polysuccinimide (abbreviated as PSI), and then polymerizing. The production of PSI from raw materials is a key step, which affects the product structure, relative molecular mass and performance. According to different raw materials, there are the following two synthetic routes. The first is to oligomerize or copolymerize maleic acid, maleic anhydride, fumaric acid and its derivatives with ammonia and this technology is very mature abroad, and the product application has already achieved a considerable market scale. The second synthesis route uses solid ASP as the raw material for direct heat shrinkage polymerization which is simple to operate, and there are no three waste emissions in the production process.

3. Physical water treatment technology

Physical water treatment technologies mainly include magnetic treatment, electrostatic treatment, membrane separation treatment, photochemical treatment, and ultrasonic treatment. Compared with
the chemical method, the physical method is a newcomer in the water treatment technology. This technology is less restricted by the environment and microorganisms, and it generally has the characteristics of environmental protection, energy saving, convenient operation, maintenance, and low cost. These advantages make the technology very great development potential and broad application space.

3.1. Magnetized water treatment technology

The investment in magnetized water treatment is small, the operation is simple, non-toxic and non-polluting. Moreover, it has multi-functions such as anti-scaling, descaling and sterilization, which makes it a promising anti-scaling technology. Magnetization is a very simple process. As shown in figure 1, when water flows in the magnetic field, the magnetic lines of force are cut to complete the magnetized water treatment.

![Figure 1. Schematic of magnetic treatment of water](image)

1. water inlet 2. rare earth permanent magnet 3. water storage tank at inlet 4. magnetization gallery 5. water storage tank at exit 6. water outlet

In 1945, T. Vermerien of Belgium discovered that the use of "magnetized water" can reduce the formation of boiler scale. He successfully applied magnetized water to inhibit boiler scale and applied for a patent, which opened the prelude to the development of magnetized anti-scaling technology. He believed that when water flowed through the magnetic field, the calcium carbonate would change the crystal form, temporarily lose the ability to adhere to the wall surface, and it would be discharged by sewage. Based on this, in the mid-1950s, an anti-scaling device called CEPI was built, and a factory named EPORO was established to produce a magnetized anti-scaling device. This device is widely used in the anti-scaling and resistance of industrial boilers. China has started the research and application of magnetic technology for boiler water descaling and anti-scaling since the 1950s[7], and the first magnetic processor was produced in 1959. In recent years, when the domestic magnetic processor is applied to the scale and descaling of boilers, it has achieved good results.

3.2. Electrostatic water treatment technology

Electrostatic water treatment technology is a new physical water treatment technology developed in recent decades, and has shown unique performance in water treatment. The research and application of the technology have now achieved a series of staged results. At present, the research of electrostatic water treatment technology has basically formed a system, and its direction involves circulating cooling water treatment, sewage treatment, and sludge dehydration. The research results show that the electrostatic water treatment technology, especially the high-pressure electrostatic field water treatment technology has the characteristics of low energy consumption, no pollution, and high efficiency which has great application prospects and needs urgent research and development. As early as the end of the 1960s, Niigata Washington Company developed the first electrostatic scale controller. In just a few years, hundreds of units have been adopted by the first-class enterprises in the United States, and its practical effect evaluation is very high. Electrostatic water treatment not only has the effect of descaling but also can prevent scaling, and also has the functions of sterilization, algae elimination, corrosion inhibition and anti-corrosion. Electrostatic water treatment and anti-scaling are
currently widely used in reactors, coolers (condensers) in oil refining, chemical, thermoelectric, air conditioning and refrigeration industries. A brief introduction of electrostatic water device is shown in figure 2.

![Schematic of electrostatic water device](image)

1. water storage tank 2. valve 3. drive pump for circulation 4. glass rotameter 5. electrostatic water device 6. water collecting tank

Figure 2. Schematic of electrostatic water device

Ye Qunshi et al.[8] conducted a more comprehensive test on the application effect of the ion bar electrostatic water processor, and found that the ion bar electrostatic water processor had a good treatment effect in industrial circulating water and low-pressure boiler water, which proved that the ion had obvious scale inhibition effect. Zhou Wenyuan et al.[9] applied electrostatic water treatment to power plants, and found that electrostatic water treatment technology successfully solved the problem of condenser fouling. Dong Zhenqiang et al.[10] introduced the installation of a small electrostatic water treatment device in a solar water heater, and comparative test tests showed that the device has a significant anti-scaling effect.

Physical methods have various advantages such as easy to control, easy to use and friendly to the environment. However, for the complex water quality with high hardness in our country, the effect of physical water treatment alone is not satisfactory.

4. Physical-chemical combined water treatment technology

Due to the complexity of industrial water, any single technology is difficult to achieve ideal results, so we should focus on the development and application of water treatment technology, integrated research, such as chemical-physical combination, in the hope of finding efficient, low consumption, environmental protection of the new treatment technology. Studies have shown that when physical water treatment technology and chemical water treatment technology are combined, the scale inhibition rate of chemical agents can be improved to a certain extent, which effectively reduces the dosage of chemical agents. This solves the environmental problems caused by excessive dosage of chemical agents and the unsatisfactory effect of physical water treatment technology. Therefore, the combination of physical water treatment technology and the addition of chemical agents is a development trend of industrial water treatment technology, and it is also necessary.

Polyepoxy-succinic acid is a new phosphorous free water treatment agent developed in recent decades, which has good biodegradability and dual functions of scale inhibition and corrosion inhibition. However, in the high alkali and high solid water system, a larger amount of polyepoxy-succinic acid is needed to achieve a higher scale inhibition rate. In response to this situation, Liu Zhenfa[11] and Li Haihua[12] studied the scale inhibition, corrosion inhibition and biodegradability of polyepoxy-succinic acid. Then they combined it with magnetic field or static electricity to study the synergistic scale inhibition performance of the two, which could reduce the amount of scale inhibitor, aiming to develop a new physical and chemical water treatment technology.

The synergistic scale inhibition performance of magnetic field and polyepoxy-succinic acid under different operating conditions was investigated by Liu Zhenfu et al. The results of static experiments showed that when the mass concentration of polyepoxy-succinic acid was 2 mg/L, the concentration factor was 1.5, the static scale inhibition rate of the combined action of magnetic field and polyepoxy-succinic acid was 18.9% higher than that of the single action of polyepoxy-succinic acid.
The dynamic experimental results showed that when the mass concentration of polyeoxy-succinic acid was 4 mg/L and the concentration factor was 2.0, the dynamic scale inhibition rate of the magnetic field under the synergistic action of polyeoxy-succinic acid was 12.8% higher than that under the single action of polyeoxy-succinic acid. The scale samples were observed by SEM. The results showed that the magnetic field and the polyeoxy-succinic acid had a synergic effect, which could cause the calcium carbonate crystal to break and twist more obviously, then the grain obtained by experiment was more fine and dispersed.

Wu Xiuli et al. studied the synergistic scale inhibition performance of electrostatic water treatment technology and polyeoxy-succinic acid by using physical-chemical comprehensive treatment method. The results of static and dynamic experiments showed that PESA and high voltage electrostatic field had obvious synergistic scale inhibition. Dynamic experimental results also showed that after high-voltage electrostatic treatment, the fouling thermal resistance was significantly reduced, and the synergistic effect of PESA and high-voltage electrostatic field was 7.5% higher than that of PESA alone. The use of electrostatic water treatment and pharmaceutical treatment of circulating water has a wide range of applications.

5. Conclusion

With the rapid development of industry and the enhancement of people's awareness of environmental protection, the shortcomings of traditional processing technology are increasingly prominent. Therefore, the development of water treatment methods with low energy consumption, simple operation, economical operation, high efficiency and safety, and no secondary pollution has become the general development trend of modern industrial water treatment technology[13].

Although physical water treatment method has the advantages of easy operation, non-toxic and pollution-free, it is not suitable for the existing water quality in China. At present, the development of chemical technology mainly focuses on the research and application of biodegradable multi-functional green water treatment agent[14]. However, the operation cost of the enterprise will increase with the increase of the dosage of pharmaceuticals. The physical-chemical combined water treatment technology that combines the physical water treatment method and the chemical method not only makes up for the shortcomings of the poor effect of the physical water treatment technology, but also reduces the dosage of the chemical agent. Therefore, the physical-chemical agent combined water treatment technology is more in line with the requirements of environmental protection, which will be a development trend of the circulating cooling water treatment process.

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