Research Progress on Anaerobic Scale Inhibitors for Municipal Solid Waste Leachate

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Abstract: During the treatment of leachate from the municipal solid waste incineration plant, the anaerobic treatment process is required due to the high COD content of the leachate in the incineration plant. Due to the high content of calcium and magnesium ions in the leachate, the primary crystal nucleus can be formed and attached to the surface of equipment, pipelines and activated sludge. This paper first analyzes the research on the treatment process of domestic landfill leachate. Secondly, the scale inhibition mechanism of the current scale inhibitors commonly used in circulating cooling water is introduced in detail, including lattice distortion, complexation solubilization, aggregation and dispersion, regeneration-self-release membrane hypothesis, and electric double layer mechanism. Finally, this paper analyzes the research progress of new scale inhibitors, including copolymer-based scale inhibitors with good comprehensive performance and environmentally friendly scale inhibitors. Through the analysis of the research progress of the anaerobic scale inhibitor of domestic waste leachate, it can provide technical support for the development of leachate anaerobic scale inhibitor.

1. Introduction

The ions that induce the fresh leachate are fixed in the crystal lattice of the crystal nucleus, and gradually grow into hard calcium carbonate, calcium sulfate, calcium phosphate and other inorganic salt scales [1]. This not only reduces the volumetric ratio of the equipment, but also leads to an increase in the weight of the packing, a risk of collapse, and blockage of the pipeline, affecting the flow of water. It increases the pipe pressure, causing safety risks, resulting in corrosion under the scale, causing safety hazards. It requires frequent parking cleaning and consumes a lot of manpower and resources.

Suppressing dirt growth, improving heat transfer efficiency, and reducing energy and raw material consumption are common aspirations of many industrial processes [2]. At present, the scale inhibition methods used in the industry can be divided into two major categories, physical methods and chemical methods [3]. The former includes the use of electrostatic fields, magnetic fields and ultrasonic waves, seed crystal technology, anti-adhesive materials, and application of polymer coatings. Chemical softening, acidification, carbonization, and the use of scale inhibitors are all chemical methods. Although the physical scale inhibition method has been applied under certain conditions, its scale inhibition effect cannot be compared with the chemical method. The softening treatment method in the chemical method achieves the purpose of preventing scale by eliminating the scale-forming ions in the aqueous solution, and the treatment cost is high, and is suitable for the occasion where the quality of the raw water is high. In industrial circulating cooling water systems, the acidification and carbonization methods may cause corrosion of equipment and complicate facilities, and are rarely used. At present, scale inhibitors are commonly used in circulating cooling water systems at home and abroad to prevent fouling on the heat exchange surface [4]. The advantages of this anti-scaling measure are convenience, economy and high efficiency.

Scale inhibitors are inorganic salts that are widely used in industrial circulating cooling water systems, seawater desalination, boilers, geothermal resource development, and oil and gas fields. In this paper, the existing scale inhibitors are combed and summarized, in order to provide technical support for the development of subsequent leachate anaerobic scale inhibitors. With the continuous

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development of scale inhibitors, many new methods for effectively evaluating scale inhibition performance have emerged. In this paper, the scale inhibition mechanism of scale inhibitors and several traditional methods for assessing scale inhibitors and their development are reviewed.

2. Study on Treatment Process of Municipal Solid Waste Leachate

2.1 Activated Sludge Method

The activated sludge process has a good treatment effect and is suitable for treating sewage treatment with high purification degree and stability. In actual production, the level of sewage treatment can be flexibly adjusted according to specific conditions. Because of these advantages, the traditional activated sludge process can be widely used in the field of sewage treatment, but when the load of organic pollutants in the activated sludge aeration tank is high, the rate of oxygen consumption is fast, so in order to avoid the lack of aeration tank oxygen, and form an anaerobic state, the organic load of the influent should be controlled within a suitable range. Therefore, the activated sludge method is not ideal for the treatment of high-concentration sewage. The traditional activated sludge method achieves a certain decontamination ability. The required aeration tank has a large volume, occupies more land, and has higher capital construction costs. In addition, sludge expansion is prone to occur, which brings inconvenience to daily management and maintenance. For this reason, there have been many improved activated sludge processes, such as oxidation ditch process, SBR process, etc. These processes can improve the sewage treatment effect to a certain extent, but there are still many defects and deficiencies, so it is necessary to continuously research new ones.

2.2 Membrane Technology

Membrane separation technology refers to a technique for achieving selective separation of a mixture of molecules of different particle sizes at a molecular level through a semipermeable membrane. According to the pore size, it can be divided into: microfiltration membrane (MF), ultrafiltration membrane (UF), Nanofiltration membrane (NF), reverse osmosis membrane (RO), etc. In recent years, microfiltration, ultrafiltration, nanofiltration, reverse osmosis and other membrane technologies have been widely used, membrane technology has developed rapidly, biofilm has wastewater quality. The change of water quantity has strong adaptability, good operation stability, and has the characteristics that sludge expansion does not occur and operation management is convenient. Table 1 lists the types of membrane technology used in the field of wastewater treatment.

Table 1 Types of Membrane Technology Used for Sewage Treatment

Kind	Aperture size	Target substance
Microfiltration	0.01-10um	Particles with a particle size >50 nm
Ultrafiltration	0.01-0.001um	5-100nm particles
Nanofiltration	0.001-0.0001um	Molecular weight 200-2000da
Reverse osm	<0.0001um	Removal of dissolved salts in aqueous solution

At present, membrane technology is widely used in the field of sewage treatment. The application of membrane technology in water treatment accounts for about 85% of the domestic separation membrane market, and is the main application field of separation membrane.

3. Research on Scale Inhibition Mechanism of Scale Inhibitor

The scale inhibition mechanism of scale inhibitors is complicated. With the kinetics of precipitation process, scale prediction model and various scale inhibition techniques, the research on scale formation mechanism and scale control have made great progress. It is generally believed that there is a dynamic balance between the scale-forming substance and the solution, and the scale inhibitor can adsorb onto the scale-forming substance and affect the dynamic balance of scale growth and dissolution. The scale inhibition mechanism of scale inhibitors mainly includes the following:

3.1 Lattice Distortion

When the calcium carbonate crystallites grow, they are arranged in a certain lattice, and the crystals are dense and hard. After adding the scale inhibitor, the scale inhibitor is adsorbed on the crystal and doped in the lattice of the crystal lattice, which interferes with the crystal of the inorganic scale, causes the crystal to be distorted, or increases the stress inside the large crystal.

3.2 Complex Solubilization

Complexation solubilization is a scale inhibitor that forms a stable soluble chelate with calcium and magnesium ions in water, and stabilizes more calcium and magnesium ions in water, thereby increasing the solubility of calcium and magnesium salts and inhibiting the deposition of scale.

3.3 Condensation and Dispersion

When anion generated by dissociation in water collides with calcium carbonate crystallites, physicochemical adsorption occurs, and the surface of the microcrystals forms an electric double layer, which makes it negatively charged. Since the chain structure of the scale inhibitor can adsorb a plurality of crystallites of the same charge, the electrostatic repulsion prevents the crystallites from colliding with each other, thereby avoiding the formation of large crystals. When the adsorbed product encounters other scale inhibitor molecules, the adsorbed crystals are transferred, and the uniform dispersion of crystal grains occurs, thereby hindering the collision between grains and grains and the metal surface, and reducing the number of crystal nuclei in the solution. Calcium carbonate is stabilized in the solution.

3.4 Regeneration - Self-Release Film Hypothesis

The polyacrylic scale inhibitor can form a film co-precipitated on the metal heat transfer surface together with the inorganic crystal particles. When the film is increased to a certain thickness, it is broken on the heat transfer surface and has a certain size of the scale layer to leave. The growth of the scale layer is suppressed due to the continuous formation and rupture of the film.

3.5 Mechanism of Action of Electric Double Layer, Etc.

It is believed that the effect on the organic phosphonate scale inhibition system is due to the enrichment of the scale inhibitor in the diffusion boundary layer near the growth nucleus, forming an electric double layer and inhibiting the condensation of scale ions or molecular clusters on the metal surface.

The x-diffraction observation method is an effective method for studying crystal growth. From the x-diffraction pattern of the scale, by comparing the diffraction intensity, the change of the diffraction angle and the crystal axis, it is possible to judge the degree of fineness of the scale before and after the scale inhibitor. The inhibition process of crystal growth is explained above. The types and performance characteristics of scale inhibitors are shown in Table 2.

Table 2 Types and Performance Characteristics of Scale Inhibitors

Category	Representative products	Main feature
Polycarboxylic acid	Polyacrylic acid	Good calcium carbonate resistance
	Hydrolyzed polymaleic anhydride	The scale is softer
Organic phosphonates	ATMP	Corrosion inhibition
	HEDP	Corrosion inhibition
Organophosphates	Polyol phosphate	High stability

4. Research Progress in the Development of New Scale Inhibitors

Since the advent of the chemical treatment of dirt, the development of new scale inhibitors has never been interrupted. In recent years, the development of new scale inhibitors has shown the following trend.

4.1 Comprehensive Performance of Copolymer Scale Inhibitor

Research and development of copolymer-based scale inhibitors with good comprehensive performance and wide application range is a research hotspot. In recent years, researchers have developed a series of multi-component copolymers with various functional groups that can simultaneously inhibit calcium, magnesium, iron, zinc and other scales according to the relationship between copolymer structure and scale inhibitor performance [5].

Related scholars synthesized a quaternary water-soluble copolymer -ZG-93 with acrylic acid, acrylate, AGP-1 and maleic anhydride as the reaction monomer and water as solvent [6]. The results show that ZG-93 is a kind of scale inhibitor with good comprehensive performance and wide application range. It can work simultaneously on the main scale particles $CaCO_3$, $Ca_3(PO_4)_2$ and $CaSO_4$ in water, and the effect is excellent. It has a good dispersion effect on iron red particles.

The TJ-102 dispersed scale inhibitor developed by the researchers is a copolymer of acrylic acid, ethylene-acrylamide and ethyl-methylpropanesulfonic acid. It has excellent calcium phosphate scale, disperse Fe_2O_3 and stabilize Zn^{2+} in water. T J-102 and T J-301 can be obtained with excellent calcium carbonate scale and calcium phosphate scale. An agent that disperses Fe_2O_3 and stabilizes Zn^{2+} in water and inhibits corrosion resistance.

Related scholars introduced sulfonic acid groups into the organic phosphonic acid molecule to synthesize dimerophosphonic acid aminomethanesulfonic acid (DPAM S), which fully utilized the phosphonic acid group to strongly chelate the carbonic acid group, and the sulfonic acid group to Fe, Zn and Ca_3 $(PO_4)_2$ have strong chelation ability and good hydrophilicity [7]. The results show that DPAMS has better effects in resisting calcium carbonate scale and calcium phosphate scale.

Related scholars studied the scale inhibition and dispersion properties of monophosphoryl carboxylic acid copolymers and compared them with organic phosphonic acids and carboxylic acid polymers [8]. The results show that the phosphinocarboxylic acid copolymer is superior to the organic phosphonic acid and carboxylic acid polymer in inhibiting the comprehensive properties of calcium carbonate, calcium sulfate and calcium phosphate scale, stabilizing Zn^{2+} and dispersing iron oxide. In addition, a phosphorus-containing acrylic acid-sodium propylene sulfonate copolymer was synthesized, and the scale inhibition performance of the copolymer on calcium carbonate, calcium sulfate and calcium phosphate was investigated, and the ability to stabilize Zn^{2+} and disperse iron oxide was discussed.

4.2 Environmentally Friendly Scale Inhibitor

With the increasing awareness of human environmental protection, the environmental protection requirements for scale inhibitors are also increasing. At present, phosphorus-based scale inhibitors in countries such as Western Europe, the United States and Japan have begun to be included in the list of restricted emissions [9]. The concept of green scale inhibitors has been proposed and is the direction of development of water treatment agents in the 21st century. The research and development of green scale inhibitor with good degradation performance has become a new research hotspot.

The scale inhibitor has the advantages of less dosage and excellent scale inhibition performance, and the scale inhibition effect in high alkalinity and high solid water is obviously better than ATM P and HEDP. Polyaspartic acid (PPP) is another green scale inhibitor developed in recent years. The starting material for the preparation of PASP is L-aspartic acid or maleimide. Studies have shown that polyaspartic acid has a simple synthesis process, good biodegradability and excellent scale inhibition performance, and can be used in water systems with high calcium ion, high alkali and high pH.

5. Conclusion

In summary, the research on anaerobic scale inhibitors for domestic landfill leachate has undergone a process of continuous improvement. It can be foreseen that with the progress of society and the development of science and technology, the requirements for anaerobic scale inhibitors for domestic waste leachate will inevitably become higher and higher. Therefore, it is necessary to strengthen the development and research of environmentally friendly scale inhibitors to meet the increasing demands of human environmental awareness. The research on scale inhibition mechanism and test methods can not be ignored, which is an important prerequisite for the development of high-efficiency resists. The development, promotion and application of scale inhibitors should be standardized to avoid duplication of research and idleness of results. Due to the widespread phenomenon of repeated research and the resistance to the promotion of results, this is extremely wasteful, and management should be strengthened and order should be regulated. In addition, since fouling is a complex problem of multidisciplinary cross-infiltration, multidisciplinary collaborative research is necessary in the research and exploration with the ultimate goal of scale inhibition.

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