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A Review of Environmentally Friendly Corrosion and Scale Inhibitors

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Abstract: This literature review comprehensively examines the latest research developments in the field of corrosion inhibitors and scale inhibitors, analyzing in depth the current research outcomes, trends, and challenges. As a core area of interdisciplinary research, corrosion and scale inhibition technologies have profound implications for technological advancement and economic development. The review covers key technological innovations and future development prospects in the petrochemical industry. The article begins by tracing the historical development trajectory of corrosion and scale inhibitors, providing an overview of the current situation both domestically and internationally, and highlighting significant breakthroughs over the past few decades. The concluding section outlines future research directions for corrosion and scale inhibitors, indicating that this technology will continue to play a significant role in driving innovation and sustainable development on a global scale.

Keywords: Compound; corrosion and scale inhibition; imidazoline-based inhibitors; oil field water environment.

1. Research Background

Currently, with the rapid development of the global economy and the continuous improvement of people's living standards, there is a sustained and rapid growth in global energy demand. Although other energy sources are being developed globally, it is expected that petroleum and natural gas will continue to dominate the energy supply for a long time to come. Meanwhile, as the average international crude oil prices continue to rise, the prices of imported crude oil worldwide are also increasing. However, with petroleum extraction becoming increasingly challenging, the phenomenon of rising oil prices is unavoidable. Therefore, there is an increasingly urgent need to enhance the level of independent development technology for oil and gas fields and improve the recovery rate of unit oil and gas fields.

In the development of global oil and gas fields, there are several processes involved, including drilling, acidizing, production, gathering and transportation, oil-water treatment, and oil and gas storage and transportation. Among these processes, acidizing, as a major means of increasing oilfield production, can improve the oil recovery rate to a certain extent. However, acid can also cause severe corrosion to metal equipment, leading to corrosion damage, hydrogen embrittlement cracking, and even brittle fracture of oil and gas well pipelines and downhole equipment. This can affect the exploitation of oil and gas resources to varying degrees, and even pose safety hazards. Additionally, after the drilling mud is separated from the oil and water, the water phase is reused as injection water for further oil recovery, while the separated oil phase is stored in oil tanks and transported through pipelines to oil transfer stations for further processing. Each of these processes typically occurs in complex, highly corrosive wet environments, often accompanied by corrosive substances such as oxygen, hydrogen sulfide, carbon dioxide, and chloride ions. These corrosive substances can cause a series of problems, such as pipeline perforation and energy waste, leading to significant economic losses and even serious safety accidents.

Injection water flooding technology is widely used in major oil fields globally to improve the oil recovery rate. In this process, for every ton of crude oil refined, an average of 2 to 3 tons of water is consumed, leading to a higher water content in the produced crude oil. This not only increases the complexity of crude oil processing but also makes the crude oil more prone to scaling during transportation, gradually increasing the cost of crude oil extraction. As most oil fields worldwide enter the middle and late stages of development, water flooding conditions become more unfavorable. The presence of high concentrations of sulfate ions and oxidizing bacteria in the injected water makes scaling problems more severe, becoming a key bottleneck restricting the development of global oil fields and the advancement of oil and gas transmission technology.

2. Purpose and Significance of the Project

In various oil fields globally, particularly those in the stage of water injection development, the water present contains substances such as carbon dioxide and hydrogen sulfide, making it prone to corrosion. Therefore, corrosion inhibitors are commonly used to prevent corrosion. However, existing corrosion inhibitors on the market often suffer from issues such as easy detachment and insufficient corrosion inhibition and scale inhibition properties.

The purpose of this project is to optimize the corrosion inhibition performance and scale inhibition properties of imidazoline-based corrosion inhibitors. This will be achieved by modifying them through the Mannich reaction to enhance their adsorption properties. Additionally, scale inhibition functional groups will be introduced to augment scale inhibition. Furthermore, existing synthesis approaches will be optimized to further research corrosion and scale inhibitors.

The project aims to develop an efficient corrosion and scale inhibitor tailored for oil field water environments. Compared to existing corrosion and scale inhibitors on the market, this novel inhibitor will have a broader range of applications and a more promising market outlook.

3. Research Status

3.1. Development Status of Corrosion and Scale Inhibitors in China

China's research in the field of water treatment agents started relatively late, with a gap of approximately 30 to 40 years compared to the international level. It was not until the mid-1980s that China began to develop organic acid salt corrosion and scale inhibitors. Research by Lu Zhu et al. found that tungstate water treatment agents exhibited excellent corrosion inhibition and scale inhibition effects, meeting the main technical indicators required by other water treatment agents such as phosphorus-based or platinum-based inhibitors. Tungsten-based formulations are primarily anodic corrosion inhibitors but also have inhibitory effects on cathodic corrosion by incorporating zinc salts. Additionally, the combination of sodium gluconate and sodium polyacrylate dispersants has become an excellent water treatment agent with both corrosion inhibition and scale inhibition functions. The research team led by Jian Yan successfully developed a novel corrosion and scale inhibitor named HDS-3, which is a compound based on acrylic copolymers. Experimental data confirmed that HDS-3 significantly inhibited the scaling process of calcium phosphate and exhibited a certain degree of control over calcium carbonate scaling. Moreover, even under conditions of high chloride ion content and slightly acidic environments, HDS-3 demonstrated good corrosion inhibition effects, showing its advantages as a comprehensive performance corrosion and scale inhibitor. In the 1990s, research on carboxylate/sulfonate copolymers gradually became a hot topic. Qing Wang et al. successfully prepared the polyol phosphate ester water stabilizer PC-604. When used in combination with modified polyacrylic acid and HEDP, PC-604 showed significant synergistic effects in scale inhibition, enhancing the scale inhibition effect. Currently, the main corrosion and scale inhibitors used in the market are polyacrylic acid copolymers. Jiahan Luo et al. developed JS-403 composed of PBTCA, sulfonate copolymers, organic phosphorus, and zinc salts. This product has reasonable production processes, excellent performance, wide applicability, and convenient operation. It is suitable for use in circulating water systems with high temperature, high hardness, high pH, and high concentration multiples, with main technical indicators comparable to similar foreign products, with total phosphorus content of 28%, specific gravity of 1.2±0.05, and pH of 2.5±0.5 (1% aqueous solution). Lirong Wang et al. innovated the structure of phosphorus-based polyacrylic acid in the 1990s and applied for a patent. With the development of green scale inhibitors and corrosion inhibitors such as polyaspartic acid (PASP) and polyepoxy succinic acid (PESA) internationally, domestic research teams led by Rongchun Xiong have also begun to explore this field and have achieved encouraging results. These research achievements not only promote the development of domestic water treatment agent technology but also contribute to environmental protection and resource conservation. In a study led by Professor Defang Zeng's team at Wuhan University of Technology, β-mercaptopropionic acid was synthesized from acrylonitrile and NaHS aqueous solution, which was then polymerized with maleic anhydride to successfully prepare S-carboxyethylthio succinic acid (CETSA). Systematic experimental evaluation of the corrosion inhibition and scale inhibition performance of CETSA revealed its excellent water adaptability and corrosion inhibition and scale inhibition effects. When CETSA was used in combination with other chemicals such as zinc sulfate, urazole, sodium gluconate, and HPMA in certain proportions, the corrosion inhibition rate reached 93.2% at a low dosage of 30 mg/L, which was 1.82 times that of pure CETSA, demonstrating significant advantages. This finding is of great significance for improving the performance of water treatment agents, reducing environmental pollution, and lowering costs. Furthermore, compared to traditional phosphorus-based corrosion and scale inhibitors (such as PAPE, PBTCA, and ATMPS), CETSA has obvious advantages in corrosion inhibition effects, indicating that CETSA and its compounded products have broad application prospects in industrial water treatment. Through further research and optimization, CETSA and its compounded systems are expected to become a new generation of environmentally friendly corrosion and scale inhibitors.

3.2. Development Status of Corrosion and Scale Inhibitors Overseas

The research and application of water treatment agents have a long history internationally. Initially, chromate salts were banned due to their high toxicity, which posed a threat to aquatic organisms and human health and caused environmental pollution. Since the 1960s, researchers have begun exploring various water-soluble polymers to seek safer alternatives. Copolymer inhibitors have become the focus of research due to their excellent scale inhibition and dispersion effects. Among many new copolymer inhibitors, those containing sulfonate monomers have received widespread attention due to their outstanding performance. Additionally, phosphorus-containing polymers have regained favor among researchers due to their dual functions of corrosion inhibition and scale inhibition, as well as their ability to dissolve silicate scale. Especially in the late 1980s, scientists developed hydroxyphosphoryl acetic acid (HPA), an efficient organic phosphonic compound designed specifically to prevent corrosion of black metals. Subsequently, in the 1990s, in response to the eutrophication problem in water bodies, researchers introduced low-phosphorus-content phosphonyl carboxylic acid (POCA), a novel compound with multiple functional groups aimed at improving water treatment efficiency. With the advent of the 21st century, the research focus in the United States shifted to the development of organic film-forming corrosion inhibitors that are non-toxic or low-toxic, biodegradable, and environmentally compatible. Natural and biological high-molecular-weight materials have been widely applied in response to this trend. In particular, polyaspartic acid (PASP) not only provides excellent corrosion inhibition but also is highly regarded for its environmental friendliness. The multifunctionality of PASP makes it an ideal choice for dispersants, scale inhibitors, corrosion inhibitors, and washing aids. Compared to traditional corrosion and scale inhibitors, PASP exhibits better performance and biodegradability, making it a truly green chemical. Meanwhile, research on organic amine compounds has also made significant progress. Studies have shown that amine compounds such as tributylamine, AMBT, ATR, and ARH exhibit significant corrosion inhibition effects on metals in acidic environments.

4. Commentary

4.1. Green Development of Corrosion inhibitor and scale inhibitor

Currently, the concept of green chemistry has become deeply ingrained, and the green, efficient, and multifunctional development of corrosion and scale inhibitor products has become the main direction of industry development. This article comprehensively examines the latest research dynamics in the field of corrosion and scale inhibitors, analyzing in depth the current research outcomes, trends, and challenges. The article first reviews the historical development trajectory of corrosion and scale inhibitors, outlines the current situation domestically and internationally in this field, and highlights significant breakthroughs over the past few decades. Subsequently, the article elaborates on the development status of corrosion and scale inhibitors in China and abroad, demonstrating the transition from traditional chromate salts to modern green corrosion and scale inhibitors.

In the section on research status, the article points out that China started relatively late in the field of water treatment agents, but has made significant progress in recent years. Domestic research teams have successfully developed various new corrosion and scale inhibitors, such as HDS-3, PC-604, JS-403, etc., which have shown excellent performance in enhancing corrosion inhibition and scale inhibition. Meanwhile, international research is also actively advancing, particularly in the development of non-toxic or low-toxic, biodegradable green water treatment agents, such as polyaspartic acid (PASP) and polyepoxy succinic acid (PESA).

The article notes that traditional phosphorus-containing compounds are gradually being restricted due to their potential environmental hazards, and low-phosphorus or phosphorus-free, biodegradable green scale inhibitors have become the focus of research. In addition, copolymer inhibitors have received widespread attention due to their excellent scale inhibition and dispersion effects, especially those containing sulfonate monomers.

In the concluding section, the article looks ahead to the future research directions of corrosion and scale inhibitors, indicating that this technology will continue to play an important role in driving innovation and sustainable development globally. With the increasing awareness of environmental protection and technological advancements, it is expected that more environmentally friendly corrosion and scale inhibitors will be developed in the future to meet the needs of industrial water treatment while also contributing to environmental protection.

5. Project

The article represents a phase achievement of the 2023 Sichuan Province College Students' Innovation and Entrepreneurship Project titled "Synthesis and Performance Evaluation of Imidazoline Double Mannich Base (S202310615169)."

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