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Comparison of Several Processes for Removing Fluoride from Coal Chemical Wastewater

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Abstract: fluorine-containing industrial wastewater treatment is a hot topic of current concern of many enterprises. With the intensification of industrial production, the discharge of high-concentration fluorine-containing industrial wastewater is also increasing. Coal mine water, coal chemical industry, photovoltaic industry, fluorinated chemical industry, metal smelting industry, electroplating industry, electronics industry and other industries all have fluorine-containing wastewater and need to be treated in depth before they can be discharged or reused. These enterprises contain fluorine The wastewater fluorine concentration is generally above 10mg/L. Failure to meet the standards will not only pollute the environment, but also threaten human health. And because the nature of the industry is different and the location of the company is different, the implementation standards for the treatment of fluoride are also different. The most stringent at present is to achieve less than 1mg/L.

1. Introduction

China's energy structure is “rich coal”, which determines the national conditions of China's coal and coal chemical industry. The development of modern coal chemical industry, especially the chemical industry led by coal gasification, can promote the sustainable development of China's chemical industry. However, the coal chemical industry consumes huge amounts of water, produces large amounts of waste water, has complex water quality, high pollutant concentrations, and difficult treatment. Coal chemical wastewater treatment is currently a recognized problem in domestic sewage treatment. The search for wastewater treatment technology with good treatment effect, stronger process stability and lower operating cost has become the own and external requirements of the development of coal chemical industry. There are some problems in the treatment of fluorine-containing wastewater, such as unstable water quality, excessive use of chemicals, large amount of sludge and high water content. Especially with the rapid development of electronic information industry in recent years, and the international environmental standard ISO14000 has been generally recognized in the world, it has become an important task for the industry to fundamentally solve the problem of fluorine-containing wastewater treatment.

2. Coal Chemical Wastewater Classification

Coal chemical industry, essentially using coal as raw material, through a series of chemical processing methods, is the conversion of coal into various forms of energy fuel and chemical raw material products we need. Coal chemical industry currently has three stages of primary, secondary and in-depth processing. From the perspective of time, it is divided into traditional and new types. Traditional coal chemical industry generally includes gas, coal coke, synthetic ammonia, etc .; Fuel, oil liquefaction, multi-molecular olefin compounds and other aspects. Coal chemical wastewater is divided into three aspects from the nature of products, mainly including coking wastewater, gasification wastewater and liquefaction wastewater. This article mainly takes the application of coal gasification fluorine-containing wastewater as an example.

3. Sources of Coal Gasification Fluorine-Containing Wastewater

Fluorine is one of the higher trace elements in coal. The average mass fraction of fluorine in coal is about 140×10^{-6}. Coal gasification fluorine-containing wastewater mainly comes from gas washing, condensation, fractionation tower and storage tank drainage . Fluorine coal gasification process, a portion of the gaseous form into the atmosphere of hydrofluoric acid, a portion of the feed into the gasification wastewater, wastewater characterizes contaminants.

4. Comparison of Current Defluorination Technologies

At present, the domestic fluorine removal equipment and technology are not mature, and the domestic sewage fluorine removal process is not perfect. At present, two methods commonly used in the treatment of industrial fluorine-containing wastewater in China are the adsorption method and the precipitation method. Activated alumina, hydroxyapatite, carbon-based apatite and other adsorption materials were originally used to remove fluorine in purified water, but also because of their obvious defects (such as: water production aluminum exceeds the standard, complex regeneration operations, adsorption Small capacity, poor mechanical strength, odor in effluent, etc.), first of all because these materials can barely reach the standard for low concentration (<2mg/L) of fluorine; secondly because the technology and equipment in the field of sewage defluorination are not yet mature, There are not many reliable processes available, but from the overall situation of the current domestic industrial wastewater defluorination project, activated alumina, hydroxyapatite, carbon-based apatite and other materials are less practical and are not suitable for industrial fluorine Advanced treatment of wastewater.

4.1 Chemical Precipitation Method

Chemical precipitation is a common method in the treatment of fluoride wastewater, especially in the treatment of high concentration fluoride wastewater. For high concentration fluoride industrial wastewater, calcium salt precipitation method is generally used, that is, adding lime to the wastewater to make fluoride ion and calcium ion form CaF2 precipitation and remove. The process has the advantages of simple method, convenient treatment and low cost. The formation of calcium fluoride precipitation in conventional lime defluorination technology is not simply controlled by the solubility product. The experimental results show that the formation of calcium fluoride precipitation is actually the process of the formation of calcium fluoride crystal. In the early stage of the reaction, especially when the concentration of raw water is relatively low, the key to the success or failure of fluoride wastewater treatment is to form a sufficient number of crystal seeds.

In recent years, some researchers have proposed that magnesium salt, aluminum salt, phosphate

and other processes should be combined on the basis of adding calcium salt. The treatment effect is better than simply adding calcium salt. Compared with the calcium salt precipitation method, the aluminum salt flocculation precipitation method has the advantages of less reagent dosage, large treatment capacity and reaching the national discharge standard after one-time treatment. Aluminum sulfate, polyaluminium and other aluminum salts have better coagulation removal effect on fluorine ions.

Disadvantages:

(1)The low-fluorine wastewater treatment effect is poor, because the crystal nucleus formed by low-fluorine wastewater induced precipitation is more difficult to generate.

(2) It is easy to produce colloids during the precipitation of calcium fluoride, and colloidal calcium fluoride is difficult to settle and separate. The fluoride ion concentration in the wastewater after treatment is difficult to reach the national discharge standard.

(3) The calcium fluoride precipitate has a high water content and cannot be recycled as a product. On the one hand, it wastes resources, on the other hand, subsequent treatment will increase a certain cost

4.2 Coagulation Sedimentation Method

Adding coagulant to the fluorine-containing wastewater, through the three mechanisms of action of adsorption, ion exchange and complex sedimentation, accelerates the settling of calcium fluoride to produce large particles of flocs, and uses a static method to separate solid and liquid to achieve fluoride ion The purpose of removal.

Disadvantages:

(1) The removal of fluoride ions is greatly affected by operating factors such as stirring time and settling time, and the stability of removing fluoride ions in wastewater is insufficient.

(2) Long sludge clarification time, large sludge volume, high water content, and high cost of chemicals.

4.3 Adsorption Method

Adsorption is the concentration of components at the two-phase interface. The reason why the adsorbent has good adsorption characteristics is that it has dense pore structure and huge specific surface area, or has groups that can form chemical bonds with the adsorbate molecules. Therefore, the adsorption behavior can be divided into physical adsorption and chemical adsorption. Generally, the adsorption mechanism of adsorbents is related to Langmuir mechanism. Using the force between the surface of the adsorbent and the adsorbate. Commonly used fluorine adsorbents are divided into rare earth adsorbents and resin adsorbents. Fluorine ions are adsorbed by the adsorbents to meet the requirements of fluoride removal. When the fluorine content of wastewater exceeds the standard, the adsorbent is regenerated and used for the treatment of drinking water and other purified water.

Disadvantages:

(1) Rare earth adsorbent is expensive, the one-time investment cost is large, and the running cost is high.

(2) There are many kinds of resin adsorbents , the actual operation effect of chelating selective ion exchange resin for removing fluoride ion in aqueous solution is feasible, but the price is relatively high, the one-time investment is large, and the resin backwashing concentrated water with high fluorine content needs deal with.

4.4 Electrodialysis, Micro-Electrolysis, Reverse Osmosis Technology

Disadvantages: high operating cost, unstable operation, large equipment investment and short service life.

5. Conclusion

Based on the advantages and disadvantages of the above defluorination methods, the precipitating adsorption method should be the main process, and the subsequent deep treatment process should improve efficiency and save costs, respond to the characteristics of fluorine-containing wastewater, and develop a reasonable process.

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