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Research on the Treatment Technology of Sulfur-Containing Tail Gas Using Chelated Iron

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Abstract

This study investigates a chelated iron-based process for H_2S removal from sulfur-containing tail gas. Eight chelating agents were evaluated for iron complexation capacity at different pH values. The effects of pH, chelator mixing ratio, and Fe^{3+}/Fe^{2+} molar ratio on desulfurization performance were examined through 42 complex systems using MATLAB regression analysis. Results show that pH 8–9 enables >90% H_2S absorption. HEDP exhibited the highest iron complexation capacity (30.8 g/L at pH 10) but poor stability; TEA and HEDTA performed stably across the tested pH range. Among the three factors, pH showed the strongest synergistic effect, followed by chelator ratio, while Fe^{3+}/Fe^{2+} ratio had the weakest effect. Optimal combinations for binary chelator systems were identified. The developed novel iron-based desulfurization solution demonstrates promising potential for industrial application.

Keywords

Chelated Iron; Complexation Capacity; H_2S Removal.

1. Introduction

Hydrogen sulfide (H_2S) is a malodorous pollutant generated in petroleum refining, natural gas processing, city gas production, and various chemical synthesis processes. It poses multiple hazards, including corrosion of metal pipelines and equipment, environmental contamination, and degradation of product quality. Consequently, its removal is mandated by regulatory standards and remains a critical challenge in the purification of industrial process gases [1].

Among the available desulfurization techniques, the iron chelation method has gained widespread adoption due to its operational simplicity, high removal efficiency, and non-toxic nature [2].

In the overall reaction process, Fe ions serve two distinct functions. First, they act as electron donors and acceptors, facilitating the conversion of sulfide ions into elemental sulfur. Second, as a catalyst, they accelerate the reaction rate. Meanwhile, the organic ligand L functions solely as a chelating agent; it does not participate in the chemical reaction but maintains the iron ions in solution at a specific concentration [3].

In recent years, chelated iron desulfurization technology has advanced rapidly outside of China, driven by significant improvements in solvent formulation, process flow design, and equipment configuration. As a result, the number of chelated iron desulfurization units continues to grow, gradually replacing traditional wet redox processes. Among the commercial desulfurization technologies developed overseas, the LO-CAT process (Merichem), the French Sulfint process, and the SulFerox process have achieved notable progress [4,7]. In China, research on chelated iron desulfurization has also made some headway; however, challenges remain concerning the

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chelated iron desulfurization solution itself, including a relatively low concentration of the catalytically active chelated iron species and a low sulfur loading capacity [2,4].

2. Research Content

1. Preparation Technology of Wet Desulfurization Agents

The early iron-alkali method utilizes the strong oxidizing property of high-valent iron ions for desulfurization. However, it is prone to the formation of insoluble substances such as $Fe(OH)_3$ and FeS. Moreover, the high redox potential of the Fe^{3+}/Fe^{2+} couple makes the desulfurization solution difficult to regenerate, while also increasing the formation of the by-product thiosulfate, leading to dual losses of iron and sulfur. The addition of a chelating agent enhances the stability of iron ions in alkaline solutions, thereby ensuring a high desulfurization efficiency while reducing the formation of by-products like thiosulfate. Different chelating agents form complexes with iron ions of varying stability, which in turn exert different effects on desulfurization performance. Commonly used chelating agents include aminopolycarboxylic acids such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), hydroxyethylethylenediaminetriacetic acid (HEDTA), hydroxyethylidene diphosphonic acid (HEDP), diethylenetriaminepentaacetic acid (DTPA), triethanolamine (TEA), citric acid, and 5-sulfosalicylic acid dihydrate. Typically, one or a combination of several of these agents is used in a blended formulation [5].

2.1. Chelated Iron Catalyst Solution and Its Preparation Method

The raw materials include: an iron source containing sulfate ions, an organic chelating agent, a pH adjuster, and a stabilizer. The iron source comprises at least one of ferrous sulfate, ferrous ammonium sulfate, ferric sulfate, and ferric ammonium sulfate, and does not include iron salts containing chloride ions or nitrate ions (e.g., ferric chloride, ferric nitrate, ferrous nitrate). Consequently, no harmful impurity anions are introduced into the chelated iron catalyst solution. The organic chelating agent is an aminopolycarboxylic acid-type chelator, comprising at least one of ethylenediaminetetraacetic acid (EDTA), disodium ethylenediaminetetraacetate, nitrilotriacetic acid (NTA), and trisodium nitrilotriacetate. The pH adjuster comprises at least one of sodium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, and ammonia water. The stabilizer is either sorbitol or sodium benzoate, primarily used to stabilize ferrous ions.

2.2. Effect of Initial Absorbent pH on the Hydrogen Sulfide Removal Efficiency

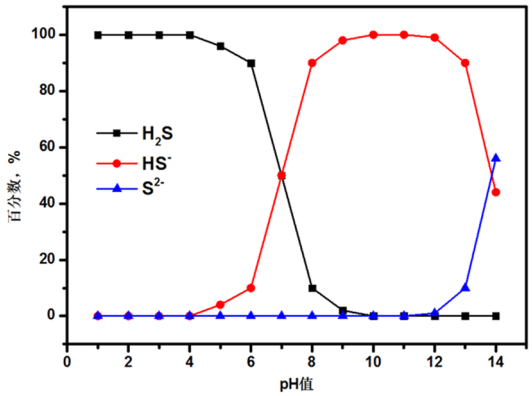

Fig 1. Percentages of [H_2S], [HS^-], and [S^{2-}] in solution at different pH values

The pH of the solution is widely regarded as a key variable in the chelated iron process for the oxidative absorption of hydrogen sulfide. Some studies have also shown that as the pH increases, the percentage of H_2S in the aqueous solution decreases sharply, while the content

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of HS^- increases significantly, indicating that a higher pH of the desulfurization solution is beneficial for desulfurization. The percentages of [H_2S], [HS^-], and [S^{2-}] in the solution at different pH values are shown in the figure.

Figure 1 shows that the H_2S concentration in the solution decreases with increasing pH, while the concentration of HS^- ions increases. During the gas–liquid mass transfer process, a higher solution pH favors the absorption of H_2S from the gas phase and its conversion to HS^-. The curve exhibits two inflection points with opposite trends. As the solution pH approaches 6, the H_2S concentration decreases sharply, while HS^- increases sharply. For pH values above 8, the H_2S concentration reaches a minimum and the HS^- concentration reaches a maximum. Excessively high pH values have little further effect on the H_2S concentration; however, at pH 12, the HS^- concentration decreases sharply while S^{2-} increases rapidly, which is detrimental to desulfurization and also leads to precipitation. Maintaining such high pH levels requires large amounts of alkali to be continuously added, making the process economically unfeasible. Therefore, in industrial practice, an alkaline aqueous solution with a pH of 8–9 is used as the absorption and transfer medium, enabling more than 90% of the H_2S to be absorbed and oxidized to elemental sulfur, thereby achieving the removal goal.

2.3. Effect of Chelating Agent Ligands on Desulfurization Performance

This study investigates the selection of chelating agents, their structural characteristics, the interactions between mixed chelating agents, and the iron complexation capacity of various chelating agents at different pH values. A total of 42 complex systems composed of mixed desulfurization agents were subjected to factor optimization. The relationship between the dosage of each chelating agent and its iron complexation capacity was examined experimentally. Furthermore, the desulfurization performance of the selected novel iron-based desulfurization solution was evaluated, with the aim of developing a new iron-based desulfurization solution with high iron complexation capacity in China.

Eight chelating agents with different structures were used in the experiments: ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), hydroxyethylethylenediaminetriacetic acid (HEDTA), hydroxyethylidene diphosphonic acid (HEDP), diethylenetriaminepentaacetic acid (DTPA), triethanolamine (TEA), citric acid, and 5-sulfosalicylic acid dihydrate.

Simulated gas was prepared by mixing H_2S with N_2, with a mass concentration of 1% H_2S in the gas mixture. A 30 mL aliquot of the desulfurization solution was bubbled into the absorption tower. Before entering the absorption tower, the H_2S concentration in the tail gas after desulfurization was periodically monitored using an H_2S analyzer. During the experiment, to ensure complete absorption of hydrogen sulfide, the gas bubbling rate in the absorber was maintained at 6 min/L.

On the basis of single-factor experiments, EDTA was used as the primary chelating agent and was separately compounded with the other seven chelating agents, resulting in seven different chelating agent systems with distinct structures. Six experiments were designed to test each chelating system, giving a total of 42 complex systems studied. For these 42 complex systems, the iron complexation capacity and redox potential were investigated under different pH values, different Fe^{3+}/Fe^{2+} molar ratios, and different mixing ratios of the two chelating agents. The optimal chelating combination was thereby identified. Multiple linear regression analysis of the experimental results was performed using regression functions in the MATLAB language to optimize the desulfurization solution selected from the 42 complex systems.

During the experiments, the iron complexation capacity of the desulfurization solution was determined by the o-phenanthroline ultraviolet spectrophotometric method. The equipment shown in Fig. 2 was used to simulate an industrial wet desulfurization unit. The concentration

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of hydrogen sulfide in the simulated acid gas was measured by iodometric titration, while the H_2S concentration in the desulfurized gas was measured using a gas detector.

Fig 2. Laboratory-scale simulated industrial wet desulfurization unit

3. Development of a Novel Iron-Based Desulfurization Solution

3.1. Investigation of Iron Complexation Capacity of Different Chelating Agents at Various pH Values

To compare the complexation performance of the eight chelating agents [5], the iron complexation capacity of each chelating agent was measured at pH values of 7, 8, 9, 10, 11, and 12. The results are shown in Figure 3.

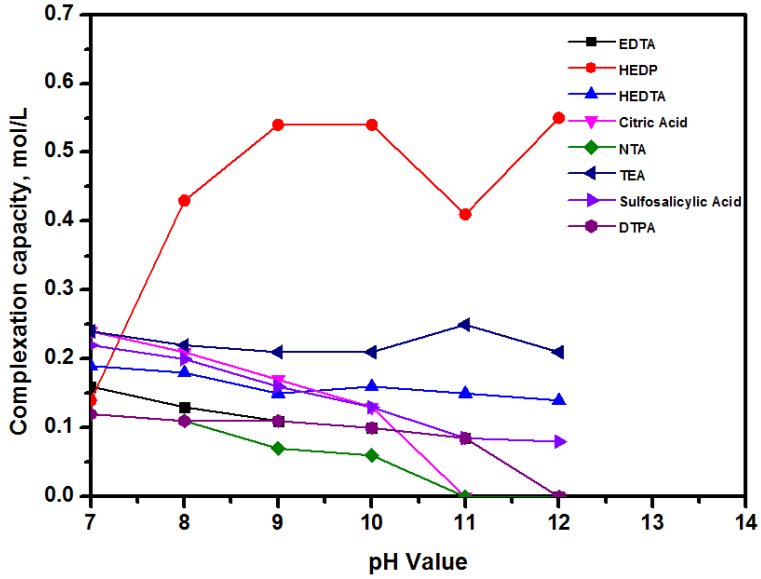

Fig 3. Iron complexation capacity of different chelating agents at various pH values

As shown in Figure 3, within the readily testable range, the phosphate HEDP exhibits the highest iron complexation capacity and the greatest alkali resistance. At pH 10.0, the iron complexation capacity of HEDP reaches up to 30.8 g/L; however, the complexed solution is

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extremely unstable and prone to severe degradation, which greatly limits the applicability of HEDP. The complexation capacities of TEA and HEDTA are not affected by changes in pH, showing good alkali resistance and relatively high complexation capacity. For the aminopolycarboxylic acid-type chelating agents EDTA, DTPA, and NTA, the iron complexation capacity decreases with increasing pH, and their alkali resistance is poor when the pH exceeds 10.0; nevertheless, within the pH range of 8.0–10.0, they exhibit good alkali resistance.

Literature studies indicate that among iron ions complexed with NTA, EDTA, or DTPA, the complexed Fe(III)–NTA shows the best absorption performance for hydrogen sulfide. NTA is an excellent ligand to date, with a long degradation time and low cost, making it the preferred catalyst in the desulfurization process. Citric acid and sulfosalicylic acid, which are hydroxycarboxylic acid homologs, contain certain amounts of hydroxyl and carboxyl radicals; they are biodegradable and non-toxic, and are currently a hot topic in research and development activities. The complexation capacity of citric acid for iron ions decreases rapidly with increasing pH, exhibiting the poorest alkali resistance, whereas sulfosalicylic acid is less affected by pH changes and shows relatively stable alkali resistance. Within the pH range of 8.0–9.0, the iron complexation capacities of the other seven chelating agents range from 4.37 to 14 g/L.

3.2. Investigation of the Effect of Different Chelating Agent Ratios

In the experiments on the synergistic effects among various influencing factors, the synergy coefficients for each composite system were processed using MATLAB software based on the results of six experiments. Chelating agents were selected pairwise from EDTA, NTA, and HEDTA to form mixed systems. The synergistic effects of the factors were studied through range analysis of two-factor repeated experiments. The results are shown in the figure.

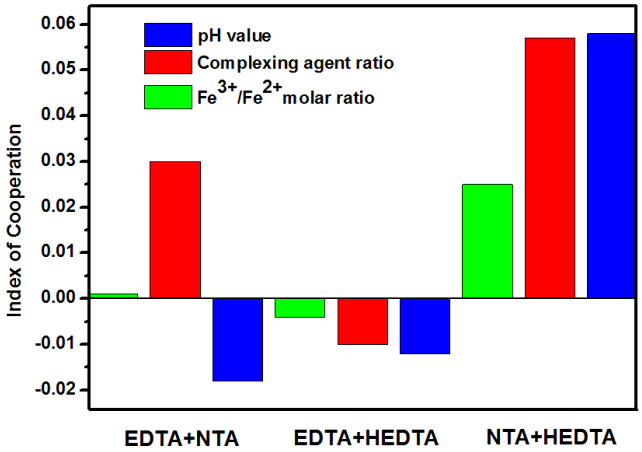

Fig 4. Synergistic effects of various factors in the composite system

As shown in Figure 4, the pH of each chelating system exhibits the greatest synergistic effect, because a high pH of the alkaline solution promotes the absorption of hydrogen sulfide. However, only the composite system consisting of NTA and HEDTA shows a positive effect of pH, while the other two systems show a negative pH effect [6].

The synergistic effect of the chelating agent ratio ranks second among the factors in each system. Nevertheless, in the EDTA–HEDTA composite system, the synergistic effect of the chelating agent ratio is negative, whereas the other two chelating agent combinations show a positive synergistic effect. Among the various factors affecting iron complexation capacity, the Fe^{3+}/Fe^{2+} molar ratio exhibits the smallest synergistic effect. The HEDTA–NTA composite system shows a relatively strong synergistic effect, the EDTA–NTA composite system shows a very weak

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synergistic effect, and the chelating agent ratio in the EDTA–HEDTA system shows only a negative synergistic effect. Although the Fe^{3+}/Fe^{2+} molar ratio does have a synergistic effect, its overall influence is relatively low.

When two chelating agents are mixed to form a composite system, the interaction among the factors and its effect on the iron complexation capacity was established based on the results of six experiments and processed using MATLAB software [8]. EDTA, NTA, and HEDTA were mixed in pairs to form binary composite systems. The interaction effects were analyzed by range analysis based on two-factor repeated tests, and the results are shown in Figures 5, 6, and 7.

Figure 5 shows that in the EDTA–NTA composite system, there is an interaction among the three factors: pH, Fe^{3+}/Fe^{2+} molar ratio, and chelating agent mixing ratio. The range analysis of the experimental results indicates that the interactions among the factors in the EDTA/NTA composite system are mainly reflected in the pH and the chelating agent ratio, and they exhibit an inverse interaction. Since the interaction is less affected by the Fe^{3+}/Fe^{2+} molar ratio, priority should be given to studying the effects of pH and chelating agent ratio on the iron complexation capacity. The results show that at pH = 9.0 and a chelating agent ratio of 4:1, the interaction effect is optimal.

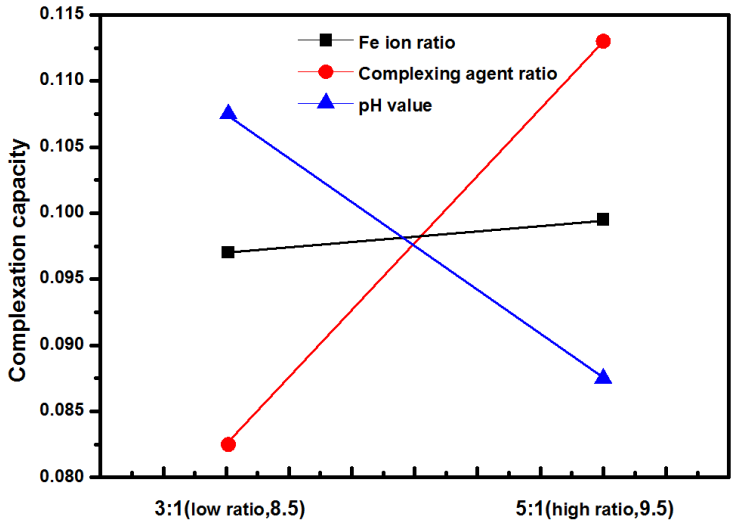

Fig 5. Interactions among various factors in the EDTA–NTA composite system

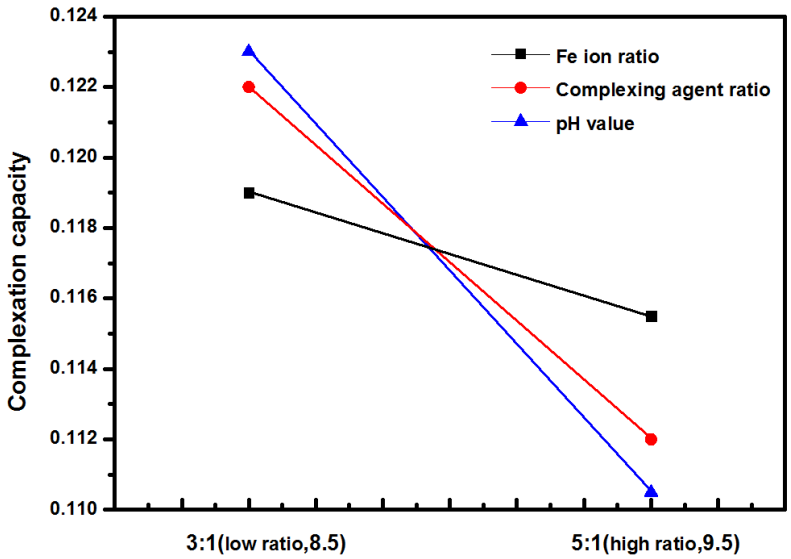

Fig 6. Interactions among various factors in the EDTA–HEDTA composite system

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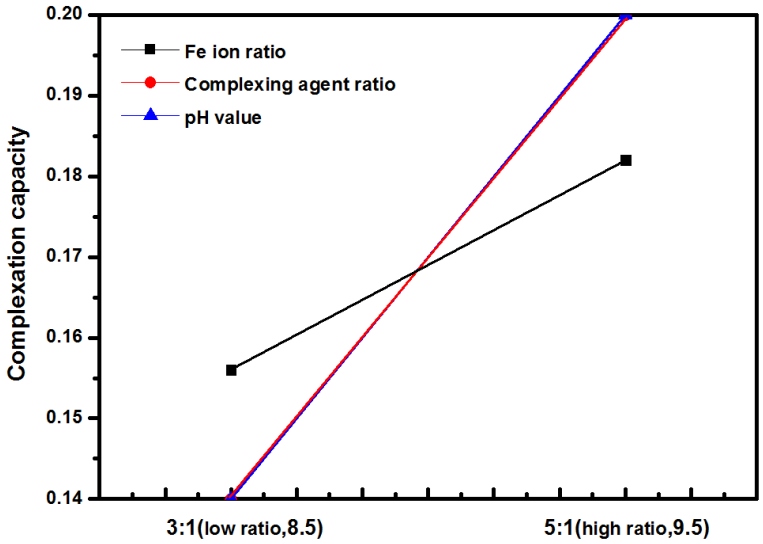

Fig 7. Interactions among various factors in the NTA–HEDTA composite system

There is an interaction among the three factors: pH, Fe^{3+}/Fe^{2+} molar ratio, and chelating agent mixing ratio. According to the range analysis of the experimental results, the interactions among the factors in the EDTA–HEDTA composite system are of a positive regression type. The optimal combination for the EDTA–HEDTA composite system is obtained at pH = 8.5, a chelating agent ratio of 1:3, and an Fe^{3+}/Fe^{2+} molar ratio of 3:1. Since the interaction of the Fe^{3+}/Fe^{2+} molar ratio is greater than those of the chelating agent ratio and pH, it is recommended to prioritize the chelating agent ratio and pH over the Fe^{3+}/Fe^{2+} molar ratio.

As shown in Figure 7, for the composite system composed of NTA and HEDTA, there is an interaction among the three factors: pH, Fe^{3+}/Fe^{2+} molar ratio, and chelating agent ratio. The range analysis of the experimental results indicates that the interactions among the factors in the NTA–HEDTA composite system are mainly reflected in the interaction between the Fe^{3+}/Fe^{2+} molar ratio and the other two factors, showing a positive regression type of interaction. The interaction between the chelating agent ratio and pH is negligible. The optimal combination for the NTA–HEDTA composite system is obtained at pH = 9.5, a chelating agent ratio of 5:1, and an Fe^{3+}/Fe^{2+} molar ratio of 5:1.

4. Conclusion

The iron complexation capacity and alkali tolerance of eight chelating agents at different pH values were compared. HEDP exhibits the highest iron complexation capacity at pH = 10, while the iron complexation capacities of the other seven chelating agents range from 4.37 to 14 g/L.

Among the three factors affecting the iron complexation capacity of the chelating systems, pH shows the strongest synergistic effect, followed by the chelating agent dosage, and the Fe^{3+}/Fe^{2+} molar ratio shows the weakest synergistic effect. All factors involved in the chelating systems can be combined to achieve an optimal level.

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