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Engineering

Regeneration of Sodium-Cationic Filter with Sulfate Regeneration Solutions and their Reuse

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The paper presents the possibility of reusing a cation exchange filter for the regeneration of spent sulfate regeneration solutions after thermochemical or thermal softening. The experimental data indicate that after lime-soda softening and heating of spent regeneration solutions to 100°C, the concentration of residual total hardness decreases to 14.0-16.0 mg-eq/l. During thermal softening at 180°C, the total concentration of calcium and magnesium ions ranges from 9.0 to 11.0 mg-eq/l. In all cases, the concentration of calcium ions corresponds to the solubility of calcium sulfate at a given temperature. In addition, the presence of sodium hexametaphosphate in the regeneration solution does not prevent precipitation with increasing temperature, and the presence of magnesium ions does not increase the solubility of calcium sulfate. *© 2024 Bull. Georg. Natl. Acad. Sci.*

cationic filter, wastewater, thermochemical softening, reuse

The development of industry leads to an increase of the salinity of rivers in most industrial areas worldwide [1-3]. Due to consequence of using sodium – cationic exchange filters, regenerated with table salt. Chloride wastewater is formed, which eventually enters water bodies and increases their mineralization. The reuse of chloride wastewater after lime-soda softening is not economically justified, as it requires grate consumption of reagent.

When regenerating cation exchange filters with 3-4% sodium sulfate solutions, wastewater is formed with a high content of calcium and magnesium ions [4-6]. In spent regeneration solutions, the concentration of calcium sulfate is several times higher than its solubility. In this case, to prevent the precipitation of calcium sulfate in the thickness of the cation exchanger filter, a small amount of a stabilizer, sodium hexametaphosphate, is added to the regeneration solution, which increases the induction period of crystal formation. As a result of the discharge of such highly mineralized wastewater, soil and surface water are polluted, as well as the initial reagent is lost.

The Main Part

The use of sulfate wastewater for the regeneration of sodium-cationite filters of the installation will become possible only after the removal of calcium and magnesium from them. This can be achieved using the lime-soda softening method with increasing temperature or the thermal softening method. Currently, technologies and equipment for softening wastewater containing hardness salts have been developed [7-9]. However, the reco-mmendations for the use of a particular softening technology are possible only after testing with specific sulfate wastewater. It should be taken into account that spent sulfate regeneration solutions contain sodium hexametaphosphate, which is added to the regeneration solution to stabilize supersaturated solutions with respect to calcium sulfate. The presence of magnesium ions in solution can also affect the residual concentration of calcium ions [10].

The data on the solubility of calcium sulfate in solutions containing mixtures of chlorides and sodium sulfates, and sodium sulfate presented in [10,11] are limited to temperatures up to 100°C, and calculations of the solubility of calcium sulfate above 100°C in similar solutions also require practical verification for a specific wastewater composition.

The main objective of the study was to check the possibility of softening waste water cation exchange plant: a) lime-soda method with an increase in temperature up to 100°C;b) thermal softening of these waters at temperatures above 100°C.

When the temperature rises above 60°C, the stabilizing effects of sodium hexametaphosphate disappear, since sodium hexametaphosphate turns into orthophosphoric acid salts.

To obtain sulfate spent regeneration solutions, the cation exchange plant was regenerated with a solution of sodium sulfate with the addition of sodium hexametaphosphate in an amount of 45–50 mg/l. The cation exchange plant was loaded with sulfonated coal. The specific consumption of the reagent was 2.0 g-eq/g-eq. Tap water with a total hardness of 1.5–2.0 g-eq/m^3 was used to prepare the regeneration solution, make it work, and wash the filter.

The spent regeneration solution obtained after the cation exchanger was collected in a porcelain glass with a volume of one liter, then the total hardness and concentration of calcium ions were determined according to the standard method [12]. After that, lime was added to a porcelain glass in the form of CaO, the value was determined pH and heated to 100°C. After settling in the spent regeneration solution, the residual total hardness and concentration of calcium ions were determined.

To determine the fundamental possibility of thermal softening, the spent sulfate solution after liming was subjected to heat treatment in an auto-clave (factory-made, but not identified manufac-turer), which made it possible to raise the tempe-rature above 100°C and treat water at a pressure of up to 1.0 MPa.

The treated solution was poured into a hermetically sealed cylindrical vessel 1 with a volume of 3 liters, made of stainless steel and placed in a thermally insulated casing 2 with an electric heating element 3. A sleeve for a chromel-alumel thermocouple was mounted in the lid of the vessel, the signal from which was fed to the secondary device КСД-2. The pressure was controlled using a manometer 5. Sampling was carried out with a cock 6 connected to a stainless steel tube 5 mm in diameter. Cooling of the taken samples was carried out by refrigerator 7 through which tap water was passed. Voltage was supplied to the heating elements through a LUXEON ЛАТР-5 kVA autotransformer.

Sampling was carried out in the following way. After raising the pressure to 1.0 MPa, which corresponds to 180°C, the first sample was taken. Then the autoclave was switched off, the temperature was expected to decrease, and the sample was taken again. The valve was opened to such a value that no evaporation occurred and a 25 ml sample was released to flush the tube, then samples were taken for analysis.

The data obtained show that with increasing temperature, the concentration of calcium sulfate in the solution decreases and at different temperatures is in good agreement with the calculated and experimental data of other authors [11]. From these, we can conclude that at high temperatures, the presence of sodium hexametaphosphate in solutions does not prevent precipitation, and the presence of magnesium ions in the treated solution does not increase the solubility of calcium sulfate.

Softening of wastewater from exchanger installations of the lime-soda method with an increase in temperature up to 100°C gives a good result, and the residual concentration of total hardness does not exceed 14-16 mg-eq/l. The initial addition of a dose of lime, which was calculated from the maximum values of the concentration of magnesium ions in the original spent regeneration solution, does not cause excessive consumption of technical soda. After liming and heating to 100°C, the concentration of calcium ions remains almost constant and corresponds to the solubility of calcium sulfate.

During the thermal softening of wastewater from a cationic plant at a temperature of 130-150°C, the content of calcium ions steadily decreased to 13-15 mg-eq/l and magnesium ions to 8-9 mg-eq/l. At a temperature of 180°C, the concentration of calcium and magnesium ions was 9-11 meq/l.

The residual total hardness at a given temperature does not depend on the treatment time of the solution.

In both cases, both during thermochemical and thermal treatment of wastewater, the residual content of ions of general hardness allows them to be used as a regeneration solution for cation exchange filters after replenishing the stoichiometric losses of sodium sulfate and adding sodium hexametaphosphate. Thus, the regeneration solution can be used repeatedly and thereby, avoid the discharge of mineralized wastewater into water bodies.

Conclusion

The conducted research allowed us to establish the possibility of lime-soda softening of spent regeneration solutions when the temperature rises to 100°C and thermal softening when the temperature rises above 100°C. It has been established that, regardless of softening method employed, the residual overall hardness steadily decreases and corresponds to the solubility of calcium sulfate at a given temperature. The presence of sodium hexametaphosphate in the regeneration solution does not prevent precipitation, and the presence of magnesium ions does not increase the solubility of calcium sulfate. To prevent the discharge of mineralized waters into the environment and rational use of natural resources, two technologies for the regeneration of sodium-cation exchange filters with sulfate regeneration solutions are proposed for their reuse after thermal chemical or thermal treatment.

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ინჟინერია

ნატრიუმ-კატიონიტური ფილტრის რეგენერაცია სულფატური ხსნარებით და მათი მეორეული გამოყენება

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ნაშრომში განხილულია კატიონიტური ფილტრების რეგენერაციისათვის ნამუშევარი რეგენერაციული ხსნარების გამოყენების შესაძლებლობა თერმოქიმიური ან თერმული დამუშავების შემდეგ. ექსპერიმენტული მონაცემები გვიჩვენებს, რომ კირ-სოდით დარბილებისა და 100°C-მდე გაცხელების შემდეგ ნარჩენი საერთო სიხისტის კონცენტრაცია კლებულობს 14.0-16.0 მგ-ეკვ/ლ-მდე. 180°C-ზე თერმული დარბილებისას კალციუმისა და მაგნიუმის იონების ჯამურმა კონცენტრაციამ შეადგინა 9.0-11.0 მგ-ეკვ/ლ. ყველა შემთხვევაში კალციუმის იონების კონცენტრაცია შეესაბამება მოცემულ ტემპერატურაზე კალციუმის სულფატის ხსნადობას. გარდა ამისა, სარეგენერაციო ხსნარში ნატრიუმის ჰექსამეტაფოსფატის არსებობა ტემპერატურის მომატებისას ხელს არ უშლის დალექვას, ხოლო მაგნიუმის იონების არსებობა არ იწვევს კალციუმის სულფატის ხსნადობის ზრდას.

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