



Development of industrial process DTPA (diethylenetriaminepentaacetic acid) recovery for reusing in barite removal treatment

Marcel G. Martins^{1*}, Lizandra M. Nogueiraa², Luna P. Sales², Adriana Teixeira³, Anderson A. Rocha⁴

¹Programa de Pós-Graduação em Engenharia Química (PEQ/COPPE/UFRJ), Universidade Federal do Rio de Janeiro, Brazil, *mmartins@peq.coppe.ufrj.br

² Programa de Pós-Graduação em Engenharia Química (PPGEQ/EE/UFF), Universidade Federal Fluminense, Brazil

³ Programa de Pós-Graduação em Engenharia de Processos Químicos e Bioquímicos (EPQB/EQ/UFRJ), Universidade Federal do Rio de Janeiro, Brazil

⁴ Instituto de Química (IQ/NAB/UFF), Universidade Federal Fluminense, Brazil

Abstract

In the present work, a methodology for recovering diethylene triamine pentaacetic acid (DTPA) was developed by pH adjustment to reuse it as a chelating agent for removing barium sulphate scale. Since the dissolution of the barite DTPA is favored at alkaline pH, tests were performed to destabilization of the BaDTPA³⁻ chelate by the action of an acidifying agent. For this, some acids (H₂SO₄, HCl, HNO₃, H₃PO₄, CH₃COOH) were tested, and the nitric acid was identified as the most suitable for the treatment. The acidification of the solution induces the equilibrium shift of the reaction to guarantee the reprecipitation of the barite derived from the dissolution of the initial scale. In order to reuse the DTPA chelator, the precipitate is separated from the solution by filtration and the filtrate is alkalized to ensure the chelating agent in its most active form (DTPA⁵⁻). The solution containing recovered DTPA was reused in successive tests of the dissolution of BaSO₄ and subsequent regeneration process. The possibility of success of such procedures was observed. Under optimized conditions of pH, temperature and contact time, a test of reproducibility was performed and, considering the number of steps involved, it can infer a satisfactory result to the study. Additionally, a conceptual engineering design was elaborated and summarized in an engineering flowchart aiming to scale up the process.

Keywords

scale; barite; DPTA chelator

Introduction

The occurrence of inorganic scale during oil production is one of the biggest setbacks for the oil industry, with annual costs estimated at around US\$ 1 billion. The most common precipitates are CaCO₃ and BaSO₄, and can occur from the reservoir to the the Stationary Production Unit (platform). The remediation methods are different for these salts: while the carbonate can be dissolved in an acid medium, from its conversion to carbon dioxide, the sulfate salts require a basic treatment, whose principle is the complexation of the precipitating cation by a chelating agent. Several substances have already been tested for baryte removal, such as EDTA (ethylene diamine tetraacetic acid), DTPA (diethylene pentaamine pentacetic acid), HEDTA (beta-hydroxy ethylene diamine triacetic acid), NTA (nitilo triacetic acid), TTHA (triethylene tetramine hexacetic acid). Deprotonated carboxylic groups and electron pairs of nitrogen are responsible for the complexation of barium, whose binding strength exceeds that of sulfate, which allows the dissolution of barite.

However, as it is a 1:1 equimolar reaction, the volume of scale removing solution becomes significant, considerably increasing treatment costs, in addition to the generated environmental liabilities.

The objective of this work was to study alternatives for DTPA recovery after using a baryte dissolution treatment, by pH adjustments in the system. The methodology consisted of evaluating different types of acids, as well as the optimal operating pH, temperature and process time. The process DTPA recovery was scaled up, being proposed an engineering flowchart to industrial reproduction of the process developed.

Methodology

General Information

Barite scaling was simulated with the barium sulfate reagent (BaSO_4), since in the field such scale is predominantly composed of this compound. The solvent solution was prepared with the DTPA acid originally in the solid state. It was previously solubilized in basic solution of potassium hydroxide (KOH), preferably at pH 12, to favor the pentadesprotonated species.

Treatment conditions for baryta removal

The definition of the treatment conditions for barite removal was based on the kinetic dissolution study of BaSO_4 by DTPA presented by PUTNIS, KOWACZ e PUTNIS (2008) [1]. Conditions defined as ideal were reproduced to simulate the barite tail solubilized by DTPA-removing solution. Initially, an alkaline solution of KOH 2.0 mol.L^{-1} , with addition of KOH 6.0 mol.L^{-1} , was prepared as necessary for pH adjustment. Barium sulfate was then added to the solution in a molar ratio of 1: 2 (Ba^{2+} : DTPA^{5-}) under heating and stirring until a clear solution was obtained. The final solution was adopted as the reject pattern to be recovered.

Methodology for acid recovery of DTPA

The simulated tailings were ideally acidified to reprecipitation of barium as sulfate. The following acids were used as acidifying agents: sulfuric (H_2SO_4), hydrochloric (HCl), nitric (HNO_3), acetic (HAc) and phosphoric (H_4PO_4). After acidification of the medium, the formed precipitate was removed by vacuum filtration. The filtrate had the pH restored to 12, by addition of KOH solution (6 mol.L^{-1}), thus regenerating the DTPA solution.

The concentration of barium in solution after precipitation induced by the acidifying agent (Step A) and after solubilization of a new aliquot of barite by the recovered DTPA solution (Step B) was quantified, when necessary, by ICP-OES. This analysis was also used to determine the ideal pH, for greater removal of barium and less use of the acidifying agent. In this assay the medium was acidified with nitric acid.

Precipitated solids by sulfuric acid at different pH values were characterized by x-ray diffraction. Solids precipitated at pH 6 were also characterized by the action of the other acidifying agents.

The activity of the regenerated DTPA was confirmed by the solubilization of a new aliquot of barium sulfate, under the ideal treatment conditions for barite removal. The methodology was validated by evaluating the repeatability of the regeneration process eight times in triplicates.

Conceptual Project for scale transition

After identifying the opportunity to recover the DTPA chelating agent and selecting the methodology that best fits, it is necessary to develop a conceptual engineering project for the scale transition of the process. In the area of

engineering processes, the conceptual project has as its main document the Process Flow Diagram (PFD), which is a diagram that, through graphic symbols, represents the process sequence from the main equipment. Thus, for the DTPA regeneration process, a PFD was proposed where the main selected equipment are presented, as well as their operational arrangement, for the industrial application of the DTPA recovery process.

Results and Discussion

The concept of the proposal is to destabilize the complex, protonating the chelator. The ligand being partially protonated forms more labile complexes with the metal. In this way, the residual sulfate present in the solution to be regenerated, becomes competitive in the barium reaction, which was complexed.

For the sulfate to be competitive to the DTPA, compared to the barium, it is desirable that the sulfate is fully available as the SO_4^{2-} and the DTPA is partially protonated. Analyzing the availability of the species composing the sulfuric acid equilibrium (Fig. 1), it is noted that the sulfate species (SO_4^{2-}) is 100% available for any pH value above 4. In contrast, it is worth remembering that The DTPA protonated at pH values below 12, significantly at pH values below 7 [2]. At pH 7 the chelating species is biprotonated, which strongly impacts the complex formation constant with the barium.

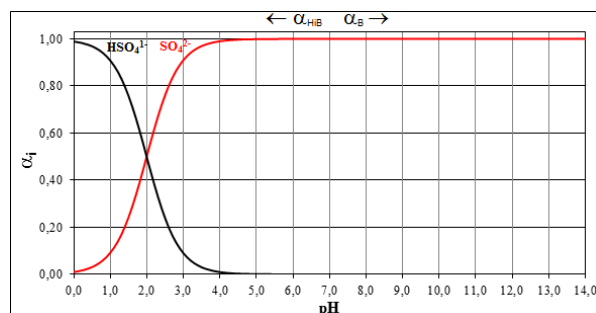


Figure 1. Distribution of the H₂B species of the acid/base system of sulfuric acid.

The recovery DTPA methodology consists in precipitating the barium as sulfate by adjusting the pH of the medium by means of an acidifying agent. In this proposal the sulfate (precipitating agent) does not need to be inserted into the system, since this is the counter ion of the original barium source and is already present in the solution to be regenerated. The Eq. (1) summarizes the foundation of this methodology. By acidifying the medium, the BaDTPA^{3-} complex is destabilized, once the equilibrium is shifted towards the direction in which the barite precipitation is favored.



The recovery methodology was initially performed using sulfuric acid as an acidifying agent. The

sulfate ion favors the removal of barium because it displaces the equilibrium towards the formation of barium sulphate by the effect of a common ion. It was observed that the solution presents a discrete turbidity at pH 8 and the most intense turbidity was observed when reaching pH 6. The samples of precipitated solids were analyzed by X-ray diffraction (Fig. 2), confirming the formation of barium sulfate and also discarding the possibility of DTPA formation as crystalline solid in the acid form.

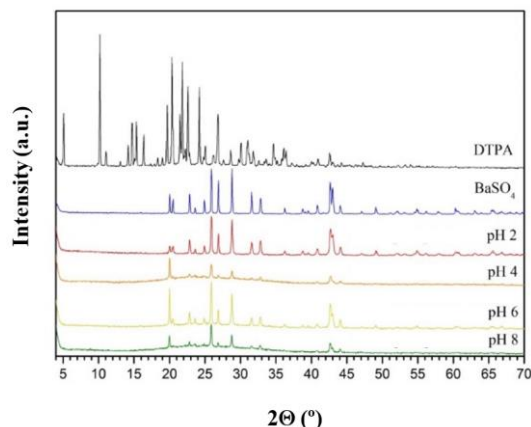


Figure 2. X-ray diffraction of standard samples of acid DTPA and barium sulfate compared to solids obtained in precipitation assay at different pH's with addition of sulfuric acid.

In addition to sulfuric acid, hydrochloric, nitric, acetic and phosphoric acids were evaluated as acidifying agents. The obtained solids in each case were analyzed by X-ray diffraction and the respective diffractograms are presented in Fig. 3, confirming same results. The filtrate obtained, after removal of the precipitate (stage A), was analyzed by ICP-OES (Fig. 4), aiming to evaluate the barium removal efficiency. After returning the pH to 12 and solubilizing a new aliquot of BaSO₄ (stage B), the barium in solution was again quantified by ICP-OES (Fig. 4). This last quantification consists of the validation of the methodology, aiming to confirm the ability of the chelator to act after recovery.

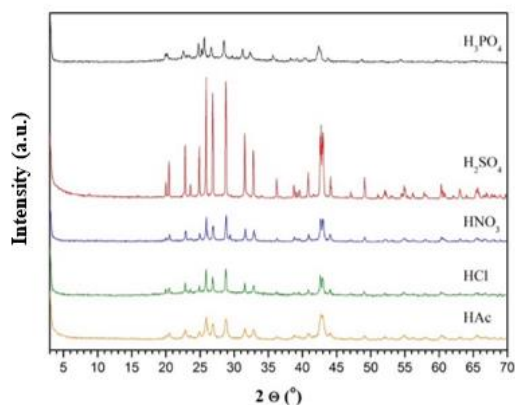


Figure 3. X-ray diffraction of samples of solids precipitated by the action of different acids.

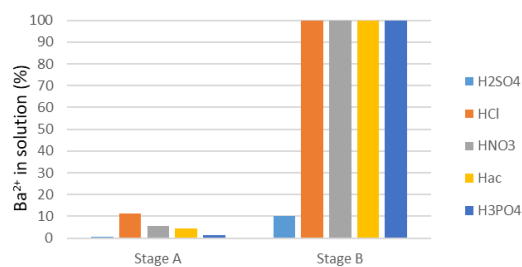
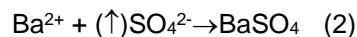


Figure 4. Determination of barium in solution by ICP-OES from the DTPA recovery assay using different acids.

The low concentration of barium in solution (Fig. 4 - A), after applying the acid recovery methodology, demonstrates the high removal efficiency of the barium. The detection of Ba²⁺ in solution, with 12% as the upper limit, confirms barium decomplexing for precipitation as sulfate. Thus, DTPA is released in solution and the chelator activity is restored, after restoration of the alkaline pH of the medium as it is deprotonated again.

The diffractograms, shown in Fig. 3, confirm the formation of barium sulfate in all cases. It is noted that the precipitated solid by sulfuric acid has a better crystalline arrangement and better orientation of the crystals, which is indicated by the more significant intensity of the peaks in this sample. The formation of a more organized solid in this case is due, as already mentioned, to the effect of the common ion introduced by the excess of SO₄²⁻ ions in solution. In contrast, only in the sulfuric acid regenerated system did DTPA show no activity when a new barite aliquot was inserted in the medium (Fig. 4 - B). In this case, only about 10% of the added solid is solubilized (complexed with the recovered DTPA). Therefore, the use of sulfuric acid as an acidifying agent is not indicated, since, despite favoring the precipitation of barium sulfate, it subsequently hampers a new solubilization of the same species. This is due to the high concentration of sulfate in solution, which has an opposite influence on the equilibrium formation of the precipitate (Eq. (2)) and equilibrium of the formation of the complex (Eq. (3)).

Stage A:



Stage B:



Since the sulfate ions must be removed due to the effect of the common ion, the acidification step has a dual purpose: the removal of both ions. The alkaline earth metal cation must be removed to release the chelator and the sulfate anion must be removed to favor the solubility of a new aliquot of barite. With the exception of the limitation imposed by the use of H₂SO₄, the methodology was shown to be feasible both by application of mineral acids (HCl, HNO₃ and H₃PO₄) and organic acids (HAc).

After validation of the methodology, the ideal pH was defined for maximum removal of barium by precipitation as sulfate. The methodology of DTPA recovery was repeated using HNO₃ as acidifying agent (Fig. 5). Nitric acid was chosen for this assay, being considered the most suitable for the most effective formation of the solid barium sulfate [3].

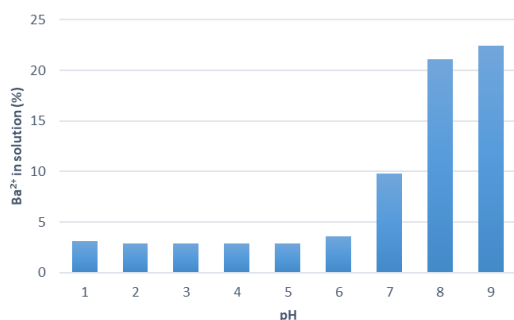


Figure 5. Residual barium evaluation (ICP-OES) of the tests aiming to determine the optimal pH of BaSO₄ precipitation by acidification with HNO₃.

The result shown in Fig. 5 identifies the optimum pH of BaSO₄ precipitation in the range of 5 to 6. At pH less than or equal to 5 the concentration of Ba²⁺ quantified in solution was lower than 3.5% in relation to the initial barium. This very small concentration suggests that was precipitated practically all barium as barium sulphate. From pH 6 the concentration of Ba²⁺ in solution starts to be significant, indicating a non-effective BaSO₄ precipitation. It is noteworthy that any pH below 5 is satisfactory to precipitation. However, it is ideal to work at the upper pH limit (less acid), since the DTPA recovery procedure culminates with the pH return of the solution to 12.

The proposed methodology guarantees the regeneration of DTPA by precipitation of Ba²⁺, initially present in the BaDTPA³⁻ complex, as barium sulfate. However, it is necessary to pay attention to the optimized conditions presented below, since they affect significantly in the regeneration procedure: HNO₃ as acidifying agent, 5-6 as pH range for BaSO₄ precipitation and 12 as ideal pH at the end of procedure.

Once the feasibility of the proposed method was evaluated, and the process variables optimized, the DTPA acid recovery methodology was validated for its repeatability. The result of barium quantification after acid recovery (Step A) and after solubilization by the recovered solution of new barite aliquot (Step B), in consecutive series, is shown in Fig. 6, confirming the repeatability of the DTPA recovery methodology. The significant solubilization of barium sulfate in step B confirms the activity of the DTPA, even after the recovery process has been employed several times.

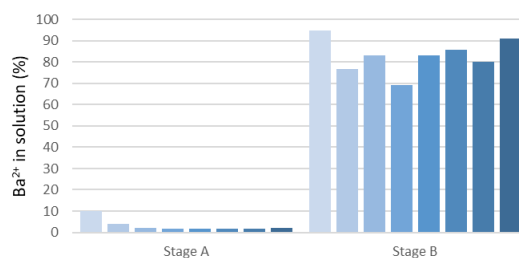


Figure 6. Analysis in ICP-OES of the test to evaluate the repeatability of DTPA recovery (8 consecutive series of recovery process).

Once the DTPA recovery methodology has been validated a Process Flow Diagram (Fig. 7) was design like a first step in a conceptual engineering project for the scale transition of the process.

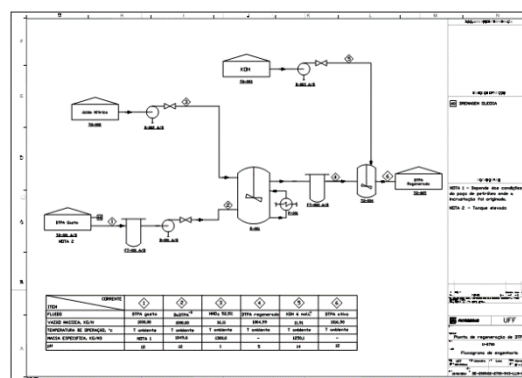


Figure 7. Engineering flowchart of the DTPA regeneration process.

Conclusions

Based on the quantitative results presented, it can be inferred that the methodology for recovery of DTPA by acid path is satisfactory. In short, by reducing the pH to a value below the range of 5 to 6, with a non-sulfuric acid, the barium sulfate precipitate is formed. The chelating agent (DTPA) is destabilized by reaction with the hydrogen ions and makes the barium ions more available for reaction with residual sulfate ions. Residual sulfate, remaining from the baryta solubilised by DTPA, present in the solution to be regenerated is therefore advantageously used to remove the barium, as a sparingly soluble salt, in the original form as presented in the scale. Once the alkaline pH (preferably 12) of the recovered solution has been restored, DTPA resumes its activity as an inorganic scale remover rich in barium sulfate.

Responsibility Notice

The authors are the only responsible for the paper content.

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