



Recovery and separation of sulfuric acid and iron from dilute acidic sulfate effluent and waste sulfuric acid by solvent extraction and stripping



Wei Qifeng*, Ren Xiulian, Guo jingjing, Chen Yongxing

School of Marine Science and Technology, Harbin Institute of Technology at Weihai, Weihai Wenhua West Road 2, Weihai, Shandong 264209, China

HIGHLIGHTS

- A recovery and separation method of sulfuric acid and iron from acidic sulfate effluents was developed.
- TOA and TBP has a synergistic effect on the extraction of Fe(III) and sulfuric acid in sulfate medium.
- The extraction complex of sulfuric acid and iron(III) can be described as $(TOAH)_2Fe(OH)(SO_4)_2$.

ARTICLE INFO

Article history:

Received 25 July 2015

Received in revised form 22 October 2015

Accepted 23 October 2015

Keywords:

Solvent extraction

Triethylamine

Tributyl phosphate

Sulfuric acid

Iron

ABSTRACT

The recovery and simultaneous separation of sulfuric acid and iron from dilute acidic sulfate effluent (DASE) and waste sulfuric acid (WSA) have been an earnest wish for researchers and the entire sulfate process-based titanium pigment industry. To reduce the pollution of the waste acid and make a comprehensive use of the iron and sulfuric acid in it, a new environmentally friendly recovery and separation process for the DASE and the WSA is proposed. This process is based on the reactive extraction of sulfuric acid and Fe(III) from the DASE. Simultaneously, stripping of Fe(III) is carried out in the loaded organic phase with the WSA. Compared to the conventional ways, this innovative method allows the effective extraction of sulfuric acid and iron from the DASE, and the stripping of Fe(III) from the loaded organic phase with the WSA. Triethylamine (TOA) and tributyl phosphate (TBP) in kerosene (10–50%) were used as organic phases for solvent extraction. Under the optimal conditions, about 98% of Fe(III) and sulfuric acid were removed from the DASE, and about 99.9% of Fe(III) in the organic phase was stripped with the WSA.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Based on the statistics from Chemical Industry Productivity Promotion Center of China, 2.44 million tons of titanium dioxide was produced in 2014 [1]. Approximately 95% of the production was manufactured by sulfate process [2], in which the raw material (mainly ilmenite, $FeTiO_3$) is decomposed with sulfuric acid. The resulting titaniferous leach liquor is subject to cooling for iron removal before titania precursor is hydrolyzed. The precursor is then calcined to produce TiO_2 pigment. In the cooling stage, eight tons of waste sulfuric acid (WSA, with sulfuric acid concentration of ~20% by weight, and with ferrous sulfate concentration of ~50 g/L) is discharged for one ton of titanium dioxide. The remaining ferrous

ion and sulfuric acid are still in the hydrolytic slurry of titania precursor [3], therefore, a great quantity of washing water is required to reduce the content of iron ion in the precursor, and about 100 tons of dilute acidic sulfate effluent (DASE, with sulfuric acid and ferrous sulfate concentration of ~2% by weight and ~5 g/L, respectively) is generated for one ton of TiO_2 . Generally, approximately 50–60% of impurities such as iron, aluminum and unreacted sulfuric acid distributes in the WSA, and the rest in the DASE [3]. The discharge of the massive WSA and the DASE causes serious environmental problems.

Traditionally, sulfuric acid in the DASE is mainly neutralized by limestone, while Fe(II) is oxidized by pumping air and subsequently hydrolyzes as $Fe_xO_y \cdot nH_2O$. Although this method is simple and effective, water, sulfuric acid, and sulfate salts are lost in the process. Moreover, large amount of gypsum needs to be disposed as a result [4]. Therefore, methods that are more economically and environmentally friendly are developed to reuse the WSA for

* Corresponding author. Fax: +86 631 5687205.

E-mail address: weiqifeng163@163.com (W. Qifeng).

recovering sulfuric acid, water and valuable metals, including ion exchange [5], evaporation [6,7], diffusion dialysis [8], and solvent extraction [9–11]. Also, efficient techniques for the recycling and reusing of sulfuric acid and/or metal sulfates from the DASE are needed [12]. Many researchers try to develop new processes for producing titanium dioxide to avoid the pollution of the sulfate process [13,14]. However, the sulfate process will still be employed as the main method in China for a long time. Therefore, the key question is how to deal with the WSA and the DASE as resources efficiently.

The most established separation technology for removing iron and sulfuric acid from the waste acidic solution is solvent extraction [15] for its advantages of high volume production, low cost and easy operation. The commonly used extractants of sulfuric acid are alcohols [16], methyl-diphenyl phosphate and TBP [17], Cyanex 923 [18], tri-*n*-octylphosphine oxide [19], tris-2-ethylhexylamine (TEHA) [20,21], and binary extractants [22]. Compared to Bronsted-base agent, water is more suitable for stripping sulfuric acid in the organic phase due to its economic and environmental benefits. However, during the stripping process, iron(II) is normally left in the raffinate because it cannot be successfully extracted by basic extractants such as amine. The general approach is to oxidize Fe(II) into Fe(III) and then Fe(III) is extracted with Lewis acid, base or salt. Several extractants such as octylphenyl acid phosphate [23], Cyanex 272 [24], Cyanex 923 [25], methyl isobutyl ketone [26], *n*-tributyl phosphate [27], di(2-ethylhexyl) phosphoric acid [28], mono (2-ethylhexyl) phosphoric acid [29], alquat 336 [30], *N,N'*-dimethyl-*N,N'*-diphenyl malonamide [31] are used for extracting iron(III). Synergistic extraction of ferric ion in sulfate solutions was also studied by amine and HEHEHP [32].

Although sulfuric acid and iron occur in the same solution, and should be removed simultaneously, the solvent extraction of sulfuric acid and iron are performed mostly in three steps [28]. This process is obviously impracticable because huge investment is needed and the production process is far too complex. As for the DASE and the WSA, no publication has been found that describes how to remove sulfuric acid and iron from these two solutions and separate them simultaneously.

Concerning the situation of the current industry, and to separate and recycle sulfuric acid and iron, a new method of extracting iron and sulfuric acid simultaneously and separating them in one step was developed, and the optimal conditions for the extraction and separation were investigated. In this method, the sulfuric acid and Fe(III) of the DASE are transferred from the aqueous phase into the organic phase by the solvent extraction, in the mean time, iron and sulfuric acid are separated by mixing the loading organic phase with the WSA. Fe(III) in the organic phase is stripped into the aqueous phase, and Fe(II) in the WSA is remained in the aqueous phase. Sulfuric acid in the WSA is extracted into the organic phase which loads sulfuric acid from the DASE. The organic phase loading sulfuric acid can easily be stripped as Ref. [8], therefore, the study of stripping sulfuric acid from organic solution was omitted. The aqueous phase containing Fe(II) and Fe(III) can be used as raw material to produce a suitable production after further purification. The raffinate of the solvent extraction of DASE can be reused as water in the process by removing the undesirable components. And sulfuric acid with a desired concentration can be obtained by condensation of the stripping solution from the loading organic phase. The process was illustrated in Fig. 1. Obviously, this method is an effective way for the recovery of sulfuric acid and iron from DASE and WSA. Compared to the existing methods, this method can make a comprehensive use of the resources and reduce the cost on the treatment of the waste acid, and comparatively simple technical process for the separation of iron and sulfuric acid. Also, since it is easy to be duplicated and industrialized, the titanium pig-

ment production industry based on sulfuric acid can be benefited economically and environmentally.

2. Materials and methods

2.1. Materials

TOA (98%), TBP(98%) and kerosene were supplied by Riyue Chemical Co., Ltd. The DASE and the WSA used in this study were supplied by Shandong Doguide Group Limited Company. The concentration of iron and sulfuric acid in the waste sulfuric acid was 0.56 mol/L and 3.1 mol/L respectively. Fe(II) ions in the DASE were oxidized into Fe(III) with concentrated H₂O₂ solution (40%) until Fe(II) ions were not detected with potassium ferricyanide. The concentration of Fe(III) and the initial pH was 0.0509 mol/L and 0.64 respectively in the DASE. The detail components of the DASE were Fe, Mg, Ca, Ti, Mn and Cr and their concentrations was the same as listed in ref. [33]. The components of the WSA were similar with that of the DASE, and their concentrations were about ten times to that in the DASE. The pH and the Fe(III) concentration were adjusted with H₂SO₄/NaOH solutions of 2.0 mol/L and ferric sulfate solution of 1 mol/L. Ferric sulfate (99%) and sulfuric acid (98%) and other chemicals used were analytical grade reagents from Shanghai Boer Company without further purification.

2.2. Extraction experiments

The reactive extraction of sulfuric acid and Fe(III) simultaneously were performed in a 250 mL beaker at desired temperature and ambient atmosphere. The experiment was commenced by stirring the mixture of organic solution and aqueous solution for 15 min unless stated otherwise. After the desired reaction time was reached, the mixture was left for 30 min for phase separation, and samples (2 mL) of aqueous solution were withdrawn for analytics. Following the procedure described above, the reagent concentrations, the temperature and the volume ratio of the ferric solution and the extraction solution were adjusted to determine their effects upon the pH and the Fe(III) concentration of the raffinate. The counter current extraction is performed as description in the ref [9].

The separation experiments of iron and sulfuric acid were performed by mixing the WSA with the loaded organic phase in a simulative way as the reactive extraction. The initial and final concentrations of Fe(II) and Fe(III) were analyzed by the potassium dichromate (K₂Cr₂O₇) volumetric method [34]. The concentration of ferric in the organic phase is obtained by mass balances. The acid content in the equilibrium water phase was determined by potentiometric titration with aqueous NaOH [35].

3. Results and discussion

3.1. Reactive extraction of Fe(III) and sulfuric acid from the DASE

3.1.1. The synergistic extraction of TOA and TBP

The influence of different extraction systems on the distribution coefficient of Fe(III) was investigated, and the results are shown in Table 1. Under the experimental conditions, TBP essentially does not extract Fe(III) in the sulfate solution, and the corresponding distribution ratio is less than 0.01. However, it can reach up to 8.09 in the TOA-TBP system, which is greater than the sum (6.143) of distribution ratio in the systems of TBP and TOA. The result shows that the mixture of TOA and TBP has a synergistic extraction effect on the extraction of Fe(III) and sulfuric acid in the sulfate solution. Meanwhile, it is believed that sulfuric acid is preferentially extracted by the TOA solution or binary solution of TOA and TBP based on the D_{SA}

Download English Version:

<https://daneshyari.com/en/article/575453>

Download Persian Version:

<https://daneshyari.com/article/575453>

[Daneshyari.com](https://daneshyari.com)