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The Recovery of Sulfuric Acid in the Presence of Zr(IV) and Hf(IV) by Solvent Extraction with TEHA and Its Mixtures

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Abstract: The recovery of sulfuric acid in the presence of Zr(IV) and Hf(IV) was studied via solvent extraction using TEHA (tri-2-ethylhexyl amine) and its mixtures. A solidification phenomenon occurred in the loaded organic phase when a single TEHA was employed in the extraction of 1 to 5 M H₂SO₄. Octanol, decanol and TBP (tri butyl phosphate) were mixed with TEHA, separately, to prevent the solidification of sulfuric-acid-loaded organic. Due to the relatively high aqueous solubility of octanol and decanol, the mixture of TEHA + TBP was selected as the optimal system for the extraction of H₂SO₄. Simulated counter-current extraction and stripping experiments were performed on the basis of the McCabe–Thiele diagrams, indicating that sulfuric acid could be reduced by TEHA + TBP from 4.2 to around 0.5 M without Zr(IV) and Hf(IV) extraction and recovered by its complete stripping with water. The proposed sulfuric acid recovery step would contribute to the completion of the closed-circuit of the Zr(IV) and Hf(IV) separation process in our previous work and help to re-separate the remaining Zr(IV) and Hf(IV) in the sulfuric acid stripping solution.

Keywords: sulfuric acid; recovery; TEHA; mixtures; closed-circuit process



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1. Introduction

It is well known that sulfuric acid (H₂SO₄) is extensively used in hydrometallurgical processes for various treatments, such as electrowinning, leaching, ion exchange and solvent extraction. The removal and recovery of sulfuric acid from the acidic effluent are considered to be valuable from both the economic and environmentally friendly points of view. To solve the sulfuric acid discharge issue, solutions including direct disposal, precipitation, electrohydrolysis, diffusion dialysis and solvent extraction have been proposed [1–6]. Nevertheless, only a few of these methods are recommended due to the sulfuric acid recovery concern.

Recent efforts to recover and regenerate sulfuric acid on a commercial scale have focused on solvent extraction due to its easy operation and extractant regenerability. Organophosphorus solvents containing P=O, such as Cyanex 923 (hexyl/octyl phosphine oxides) [7,8] and TOPO (tri-*n*-octylphosphine oxide) [9] were proposed as possible extractants for the extraction of sulfuric acid. Alguacil and Lopez [7] tested the sulfuric acid extraction equilibrium of Cyanex 923 with different diluents. It was found that diluents showed a negligible influence on sulfuric acid extraction. And, the formation of a third phase was observed above a H₂SO₄ concentration of 3 M when Cyanex 923 was diluted in aliphatic diluents. Liao et al. studied the phase behavior of a Cyanex 923-heptane/H₂SO₄ system [8]. The third phase was observed at different concentrations of sulfuric acid with a change in the Cyanex 923 concentration due to the transportation of both H₂SO₄ and H₂O by their coordination with Cyanex 923. The removal of sulfuric acid from electrowin

solutions by reactive extraction using an Alamine 336 (tri-octyl/decyl amines), isodecanol and shell sol 2325 solvent mixture was studied to evaluate the effectiveness of this system as carriers of the acid [10]. The extraction of sulfuric acid using binary extractants was reported by Brian [11]. The binary extractants studied consisted of mixtures of the acidic extractants and amine-type extractant. The best binary extractant in terms of sulfuric acid extraction efficiency turned out to be the Alamine + D2EHPA system. TBP in kerosene was also employed in the extraction of sulfuric acid by Xun et al., and the reported predominant extracted complex was $(\text{TBP})_2 \cdot \text{H}_2\text{SO}_4 \cdot (\text{H}_2\text{O})_3$ or $\text{TBP} \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ [12].

TEHA has been extensively used for the extraction of inorganic acids. The recovery of sulfuric acid from electrolyte bleed streams was developed by using TEHA as the extractant, shellsol 2046 as the diluent and octanol as the modifier [13,14]. The equilibrium data and simulation results were also compared with Cyanex 923 in these studies. Furthermore, a comparison between TEHA and Cyanex 923 by Haghshenas et al. [15] demonstrated that TEHA can extract more H_2SO_4 with fewer extraction stages than Cyanex 923 and that the stripping of sulfuric acid from TEHA is more readily. Kesieme et al. [16] demonstrated that the TEHA system was the optimization for the extraction of sulfuric acid among TEHA, Alamine 336 and Cyanex 923. An optimal organic composition consisting of 50% TEHA, 40% octanol and 10% shellsol A150 was determined. A slope analysis showed that the extracted species consisted of one acid molecule, one TEHA (A) molecule and two octanol (O) molecules with a formula of $(\text{H}_2\text{SO}_4)_1\text{AO}_2$. Literature surveys indicated that TEHA seems to be an optimal extractant for the extraction of sulfuric acid owing to its outstanding acid extraction capacity [5,16] and ease of stripping [15,17]. Meanwhile, modifiers such as octanol and decanol should be presented in the organic phase with TEHA to prevent the formation of a third phase [13,15–18].

Zirconium was invariably accompanied by hafnium in its major sources such as zircon (ZrSiO_4) [19]. Due to the great difference in the transmission of thermal neutrons, zirconium and hafnium play opposite roles in the nuclear industry. Zirconium is generally used as raw material for nuclear neutron insulator construction, while hafnium is a powerful nuclear neutron absorber [20]. The demand for zirconium and hafnium with high purity for application in the nuclear industry was thus highlighted. However, the separation of zirconium and hafnium is quite difficult because of the great similarities in their chemical and physical properties [20,21]. The separation of Zr(IV) and Hf(IV) from various media has thus been widely studied with different extractants [20–24]. Previous work revealed that zirconium was extracted into the organic phase prior to hafnium by most extraction systems [22]. Wang and Lee [23] reported that Zr(IV) was separated over Hf(IV) with amine extractants in the 0.1–3 M H_2SO_4 concentration range due to its stronger complexing tendency with sulfate ions. The proposed extraction mechanism was anion exchange. However, the selective extraction of Hf(IV) over Zr(IV) was only seen in strong sulfuric acid solutions using acidic organophosphorus extractants, such as D2EHPA [22]. The extraction mechanism was demonstrated to be cation exchange. And thus, the extraction efficiency was greatly influenced by the sulfuric acid concentration in the aqueous phase. In order to separate Hf(IV) over Zr(IV) using D2EHPA, a separation process in which metals extracted at 0.5 M H_2SO_4 and then selectively stripped by 4 M H_2SO_4 and oxalic acid solutions was proposed. It has been verified by simulated counter-current extraction and stripping experiments that around 20% of Zr(IV) and a portion of Hf(IV) are detected in the first stripping step together with sulfuric acid with a concentration of 4 M [20]. With the purpose of re-separating these amounts of metals, a reduction in H_2SO_4 from 4 to 0.5 M in the presence of Zr(IV) and Hf(IV) is thus a required step.

In this work, the extraction and recovery of sulfuric acid in the presence of Zr(IV) and Hf(IV) were investigated using TEHA and its mixtures with octanol, decanol or TBP to prevent the solidification of the loaded organic phase. The mixture of TEHA and TBP in kerosene was found to be the best extractant system for sulfuric acid extraction in terms of the extraction efficiency. Complete stripping of sulfuric acid from the loaded organic was

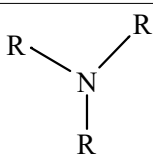
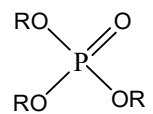
achieved with water. Moreover, extraction and stripping isotherms were constructed and verified by batch simulation experiments for the counter-current extraction and stripping.

2. Materials and Methods

2.1. Reagents

The commercial solvent TEHA (Tri-2-ethylhexyl amine, purity 99%) was supplied by BASF Chem Co., Ltd. (Beijing, China), while TBP (Tri butyl phosphate, purity 98%) was purchased from Yakuri pure chemical Co., Ltd. (Kyoto, Japan). The molecular structures of TEHA and TBP are presented in Table 1. Octanol (Acros Organics, purity 99%) and decanol (Acros Organics, purity 98%) were utilized as the modifiers and kerosene (Daejung Chemicals and Metals Co., Ltd., Siheung, Republic of Korea, purity 95%) as a diluent. All of the employed reagents in this work were of analytical grade and without any further purification.

Table 1. Molecular structures of TEHA and TBP.

Extractant	Structure	R
TEHA Tris 2-ethylhexyl amine		$\text{C}_4\text{H}_9\text{—}\underset{\text{C}_2\text{H}_5}{\text{CH}}\text{—CH}_2\text{—}$
TBP Tri-butyl phosphate		$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—}$

The mixed feed solutions containing sulfuric acid and metals were prepared by dissolving the necessary amounts of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (Alfa Aesar, Johnson Matthey Company (Ward Hill, MA, USA), purity 98+%), $\text{Hf}(\text{SO}_4)_2$ (Alfa Aesar, Johnson Matthey Company, purity 99.9%) and analytical grade sulfuric acid in double deionized water. The concentrations of both zirconium(IV) and hafnium(IV) were kept at 0.2 g/L throughout the experimental work, while the sulfuric acid concentration was varied from 1 to 5 M.

2.2. Experimental Procedure

The general batch experiments for extraction and stripping were conducted by adding equal volumes of the aqueous and organic phases in a 100 mL sealed glass container and by mechanically shaking the two phases for 30 min using a wrist action shaker (Burrell model 75, Burrell Scientific, Zelienople, PA, USA). After shaking, separation funnels were used for disengagement of the two phases. To determine the number of extraction and stripping stages in a continuous operation, a McCabe–Thiele plot was constructed based on the acid extraction/stripping isotherms. During the extraction and stripping equilibrium isotherm experiments, the aqueous and organic phases were mixed with different phase ratios at a constant total volume of the solution. Subsequently, counter-current simulation experiments were performed in a batch-wise scale. All of the experiments were performed at ambient temperature (25 ± 1 °C).

2.3. Analytical Techniques and Data Analysis

The concentration of zirconium and hafnium in the aqueous phase were measured by ICP-OES (Optima 4300DV, PerkinElmer Ltd., Shelton, CT, USA), and H_2SO_4 concentration was analyzed volumetrically using the acid–base titration method with a standard Na_2CO_3 solution [25]. The amount of metal or sulfuric acid extracted by the organic solvent was estimated with the mass balance. D (distribution coefficient) was defined as the amount of H_2SO_4 in the extracted organic phase compared to that in the raffinate when the extraction

reached equilibrium. The extraction percentage was calculated as the difference in H_2SO_4 amount at equilibrium compared with the initial amount in the aqueous phase.

3. Results

TEHA was reported to be the most suitable extractant for H_2SO_4 recovery via the solvent extraction method due to its good extraction efficiency and ease of stripping [15–18]. In this study, the extraction of sulfuric acid was investigated by using TEHA and its mixtures when Zr(IV) and Hf(IV) metals co-exist in aqueous solutions. The concentrations of both zirconium and hafnium were fixed at 0.2 g/L, and the concentration of H_2SO_4 was varied from 1 to 5 M. According to the research work on the study of the complexing formation of Zr(IV) and Hf(IV), anionic zirconium/hafnium complexes ($\text{Zr}(\text{SO}_4)_3^{2-}$ and $\text{Hf}(\text{SO}_4)_3^{2-}$) are the prevailing species in an aqueous solution when the concentration of H_2SO_4 is higher than 0.25 M. Kerosene was used as a diluent in the organic phase.

3.1. Extraction of H_2SO_4 by TEHA in Kerosene

Firstly, the effect of the sulfuric acid concentration in a feed solution was investigated using 1 and 1.5 M TEHA in kerosene, as shown in Figure 1. The extraction percentage of H_2SO_4 by both concentrations of TEHA was remarkably affected by the initial H_2SO_4 concentration. Below a 2 M sulfuric acid concentration in the initial aqueous phase, the extraction percentage increased rapidly with the increasing of H_2SO_4 concentration. It was reported by Nguyen and Lee [18] that there was a minimum sulfuric acid concentration remaining in the raffinate due to the hydrolysis and complexing effect of sulfate ion and other ions. This could be used to interpret the low extraction percentage presented when the initial concentration of sulfuric acid was low. A maximum extraction percentage of 34.3% and 49.3% was observed when the concentration of H_2SO_4 was 2 M, with 1 and 1.5 M TEHA, respectively. After that, the extraction of H_2SO_4 decreases steadily from 2 to 5 M H_2SO_4 concentrations. The decrease at a high aqueous phase concentration of H_2SO_4 is supposed to be related to an overload of sulfuric acid in the organic phase.

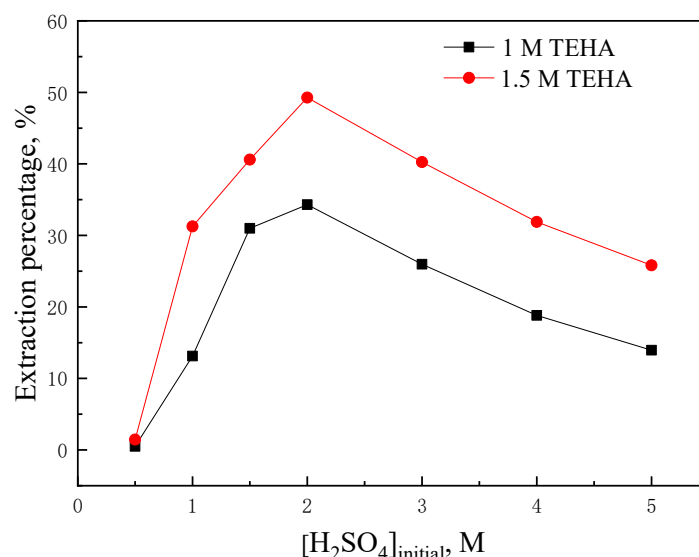


Figure 1. Effect of H_2SO_4 concentration on the extraction of sulfuric acid by 1 and 1.5 M TEHA in the presence of Zr(IV) and Hf(IV).

To illustrate the extraction behavior of H_2SO_4 in Figure 1, Figure 2 was constructed to show the variation in sulfuric acid concentration in the loaded organic phase and raffinate after extraction by 1 and 1.5 M TEHA. As reflected in Figure 2, the organic loaded H_2SO_4 increased up to 3 M initial H_2SO_4 and then leveled off. This phenomenon demonstrates that the newly added sulfuric acid can no longer be extracted by TEHA into the organic phase. Thus, the decreased in sulfuric acid extraction percentage in Figure 1 in the range

of 3 to 5 M for the initial H_2SO_4 concentration was determined. In addition, the dashed curves in Figure 2 also proved that the minimum sulfuric acid in raffinate after extraction is around 0.47 M.

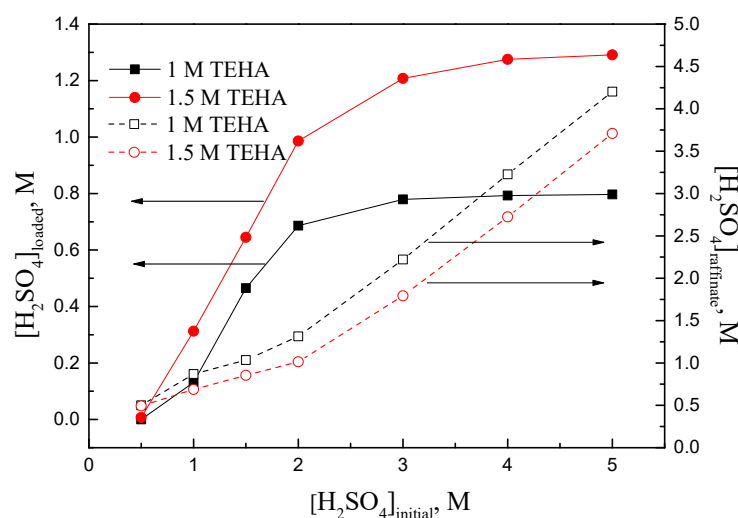


Figure 2. Variation in H_2SO_4 concentration in the loaded organic and raffinate after extraction by 1 and 1.5 M TEHA.

3.2. Extraction of H_2SO_4 by TEHA in Kerosene

To study the effect of TEHA concentration on the extraction of sulfuric acid, solvent extraction experiments were performed by varying the concentration of TEHA from 0.5 to 1.5 M at the initial sulfuric acid concentrations of 1.5, 3 and 5 M, respectively. As shown in Figure 3, the extraction tendency was similar with different concentrations of the initial sulfuric acid while the TEHA concentration increased from 0.5 to 1.5 M. From the initial sulfuric acid concentration of 3 and 5 M, it was observed that the extraction percentage of H_2SO_4 was quite low when the TEHA concentration was lower than 1 M. In order to identify the extraction reaction, the log D against log[TEHA] was plotted for the extraction of H_2SO_4 at the initial concentration of 1.5 M, and the slope analysis method was applied. In consideration of the effect of organic phase overloading, the extraction results obtained from the sulfuric acid initial concentrations of 3 and 5 M are not presented. Figure 4 indicates that the line has a value equal to that of the slope, implying that 1 mol of TEHA takes part in the reaction of one mole of sulfuric acid. In other words, the extracted species was proposed to be $\text{H}_2\text{SO}_4 \cdot \text{TEHA}$. This result matched well with the reported extraction reaction by Haghshenas et al. [15].

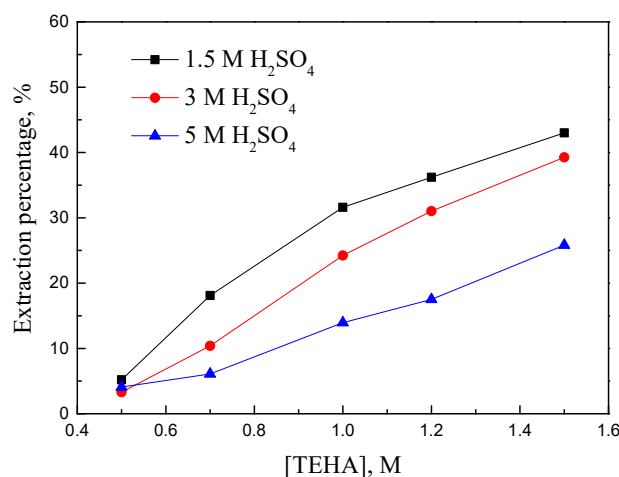


Figure 3. Effect of TEHA concentration on the extraction of 3 M H_2SO_4 in the presence of Zr(IV) and Hf(IV).

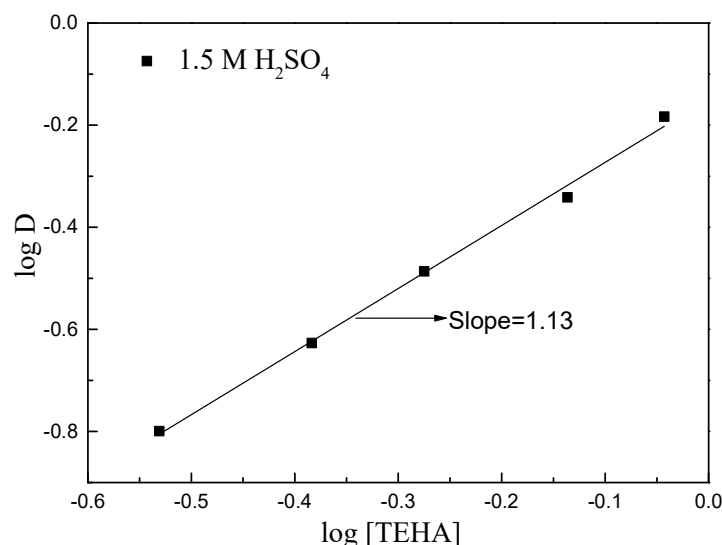


Figure 4. Plot of log D vs. log[TEHA] for the extraction of sulfuric acid at its initial concentration of 1.5 M.

3.3. Extraction of H_2SO_4 by TEHA Mixed with Octanol, Decanol or TBP

Although the extraction of sulfuric acid by a single TEHA in kerosene displayed a fine extraction ability, it has to be pointed out that the solidification of the organic phase occurred when TEHA was loaded by H_2SO_4 . To prevent TEHA from being solidified after being loaded by H_2SO_4 , octanol, decanol or TBP was added into the organic phase. Figure 5 exhibited the extraction behaviors of sulfuric acid when using TEHA mixed with octanol or decanol in kerosene. The concentration of sulfuric acid in the feed solution was constant at 4 M. As can be seen, the extraction percentage slightly decreased with the addition of various volumes of octanol or decanol to 1 M TEHA. The solidification of the loaded organic phase could be prevented when the volume percentage of octanol or decanol was higher than 20 vol%. However, the high volume percentage of octanol or decanol in the organic phase is not operable or commercially available due to their high aqueous solubility.

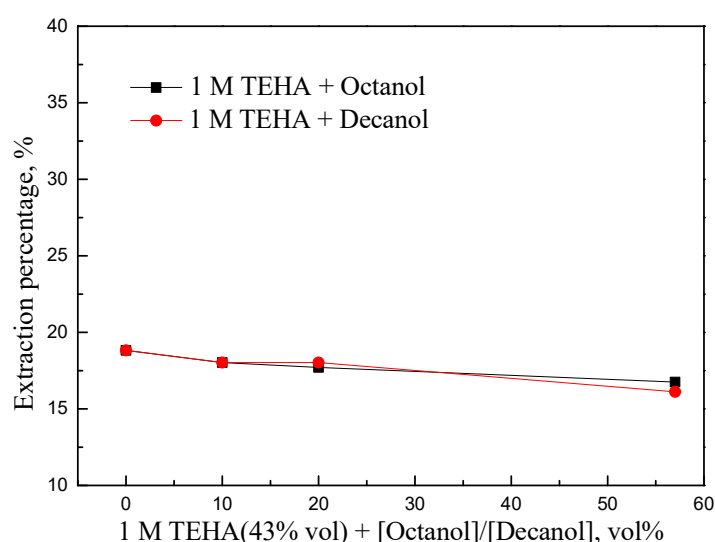


Figure 5. Effect of adding octanol and decanol to 1 M TEHA on the extraction of sulfuric acid in the presence of Zr(IV) and Hf(IV).

In the following experiments, TBP was added to TEHA to improve the solidification phenomenon of the loaded organic phase. The concentration of TEHA was kept at 1 M, while that of TBP was varied from 0.1 to 1 M. As shown in Figure 6, a slight increase in the

sulfuric acid extraction from 18.8 to 23.0% was observed with the increasing concentration of the added TBP. This increase is explained by the fact that TBP also showed extraction abilities on acids, as reported by Sarangi et al. [26]. When 1 M TBP was added to 1 M TEHA, solidification was prevented. With lower concentrations of TBP in the mixtures, the solidification of the organic phase after loading by sulfuric acid cannot be prevented.

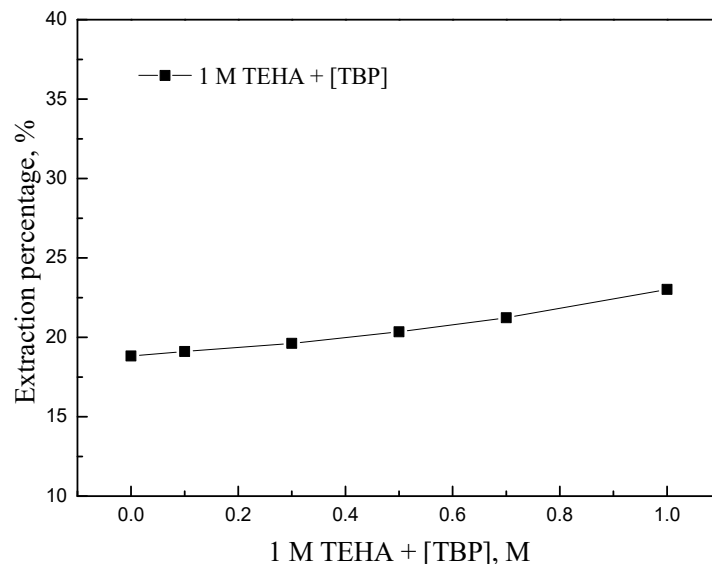


Figure 6. Effect of adding TBP to 1 M TEHA on the extraction of sulfuric acid in the presence of Zr(IV) and Hf(IV).

In general, the polymerization of the extracted species or its low dissolution rate in organic diluents was considered the main reason for the formation of a third phase or the loaded organic solidification phenomenon. TEHA is one kind of branched tertiary amine. The extraction of acid (HX) by a tertiary amine, denoted as R_3N , is generally regarded as $R_3NH^+ \bullet X^-$. Octanol and decanol containing oxhydryl ($R-OH$) are considered to be electronegativity polar molecular and thus have good affinity for R_3NH^+ . They may replace the hydrogen-surrounded R_3NH^+ and thereby promote the dissolution of loaded TEHA in kerosene. In terms of the addition of TBP to TEHA, Xun et al. [12] investigated the three-phase behavior of the TBP-kerosene/ H_2SO_4 - H_2O extraction system and the composition of the extracted complexes in the middle phase. They reported that H_2SO_4 and H_2O could be transferred into the middle phase mainly by their coordination with TBP and the outer layer of water composed by $P=O \cdots H_3O^+$. Based on this, it is assumed that the addition of TBP to TEHA may promote the generation of $[R_3NH \bullet (H_2O)_n \cdots O=P(OC_4H_9)_3]^+$ and HSO_4^- [8,12,27]. Due to the steric hindrance, both $[R_3NH \bullet (H_2O)_n \cdots O=P(OC_4H_9)_3]^+$ and HSO_4^- would be maintained in an organic as cations and anions, hence facilitating dissolution in a diluent and preventing the generation of polymerization. Therefore, the solidification of a loaded organic phase could also be prevented by adding TBP.

In comparison with octanol or decanol, TBP has been commercially used in solvent extraction processes. Furthermore, a mixture of TEHA with TBP revealed a relatively higher extraction efficiency of sulfuric acid than that mixed with octanol or decanol. A mixture of 1 M TEHA and 1 M TBP was expected to be an effective and suitable system for sulfuric acid extraction and recovery. Furthermore, an analysis of the raffinate after the extraction of H_2SO_4 indicated that no Zr(IV) or Hf(IV) were extracted by TEHA and its mixtures.

3.4. Stripping of H_2SO_4 from Loaded TEHA + TBP

To regenerate sulfuric acid, it is of great importance to select a suitable reagent for its stripping from the loaded organic phase. Water has been demonstrated to be an effective strippant for sulfuric acid stripping from a single loaded TEHA [18,28]. To study the

stripping efficiency of sulfuric acid from mixtures of TEHA and TBP by water, stripping experiments were performed by using water with different aqueous to organic phase volume ratios (A/O ratios). The stripping results are presented in Table 2. The loaded organic phases used were obtained when 1 M TEHA and 1 M TEHA + 1 M TBP made contact with 4 M sulfuric acid, separately. The effective stripping of sulfuric acid from loaded TEHA + TBP by water is demonstrated in Table 2. Compared to the stripping results of TEHA + TBP with a single TEHA, the stripping efficiency was improved by using TEHA + TBP when the A/O ratio exceeded the unit. Additionally, 99.3% of sulfuric acid was stripped by water from loaded TEHA when the A/O ratio reached 3/1.

Table 2. Stripping of sulfuric acid from loaded TEHA and loaded TEHA + TBP with water under different A/O ratios.

A/O Ratio	Stripping Percentage, %	
	Loaded TEHA	Loaded TEHA + TBP
1/3	30.1	27.3
1/2	42.0	35.4
1/1	60.1	58.7
2/1	75.2	91.9
3/1	82.7	99.3

3.5. Extraction Isotherm of Sulfuric Acid by TEHA + TBP in Kerosene

A mixture of 1 M TEHA + 1 M TBP was employed to construct the extraction isotherm of H_2SO_4 from the solution containing 4 M H_2SO_4 . The organic to aqueous phase volume ratio (O/A ratio) was varied from 1/3 to 9/1, while the other experimental parameters were kept constant. The resultant extraction isotherm is shown in Figure 7. McCabe–Thiele plot diagram indicates that four extraction stages are needed to extract most of the H_2SO_4 from the aqueous phase by 1 M TEHA + 1 M TBP at an O/A ratio of 4. However, the extraction of sulfuric acid differs from the solvent extraction of metals in the fact that there is a minimum sulfuric acid concentration remaining in raffinate of about 0.47 M, as mentioned in Section 3.1. In other words, the complete extraction of H_2SO_4 is infeasible. According to Figure 7, to reduce the sulfuric acid concentration from 4.2 M to its minimum concentration, three extraction stages are sufficient at an O/A ratio of 4.

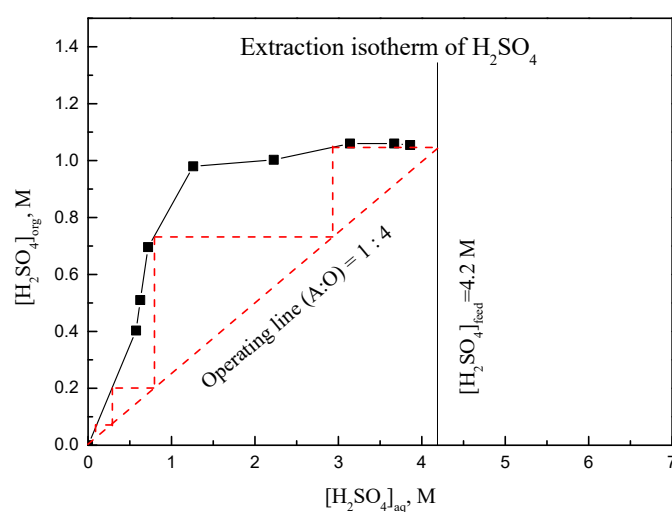


Figure 7. McCabe–Thiele plot for H_2SO_4 extraction with TEHA + TBP. Experimental condition: $[\text{H}_2\text{SO}_4] = 4.2 \text{ M}$, $V_{\text{org}}/V_{\text{aq}} = 1/3\text{--}9$, [Extractant] = 1 M TEHA + 1 M TBP, Diluent = Kerosene.

To verify this, a three-stage counter-current batch simulation experiment was conducted at an O/A ratio of 4 using 1 M TEHA + 1 M TBP. As shown in Figure 8, a feed

solution in the aqueous phase contained 4.2 M sulfuric acid together with 0.2 g/L Zr(IV) and 0.2 g/L Hf(IV). After a three-stage counter-current extraction, the sulfuric acid concentration was reduced from 4.2 to 0.48 M, while all of Zr(IV) and Hf(IV) were maintained in raffinate. A loaded TEHA + TBP containing 0.83 M sulfuric acid was prepared for the subsequent counter-current stripping study.

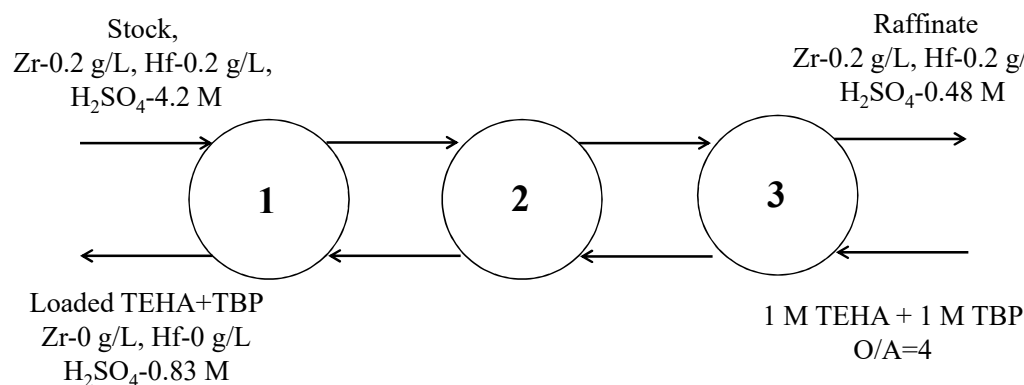


Figure 8. The extraction of 4.2 M sulfuric acid in the presence of Zr(IV) and Hf(IV) by 1 M TEHA + 1 M TBP in kerosene.

3.6. Stripping Isotherm of Sulfuric Acid by TEHA + TBP in Kerosene

A McCabe–Thiele plot of the sulfuric acid stripping isotherm was constructed to estimate the number of required stages and the flow rate of the two phases to achieve the maximum stripping of sulfuric acid from loaded TEHA + TBP by water. Stripping experiments were carried out at different A/O ratios from 1/5 to 3/1. Figure 9 suggests that complete stripping of sulfuric acid by water is possible in two counter-current stripping stages at an A/O ratio of 2/1. Based on the results obtained from the McCabe–Thiele plot, a two-stage batch simulation experiment on the counter-current stripping of H_2SO_4 was carried out. The loaded organic was obtained from the extraction batch simulation experiments in Section 3.5, and the concentration of H_2SO_4 in the loaded organic was 0.83 M. Figure 10 indicates that H_2SO_4 could be quantitatively stripped by water after 2 counter-current stripping steps at an A/O ratio of 2. Finally, a sulfuric acid solution with the concentration of 0.5 M was obtained in the stripping solutions.

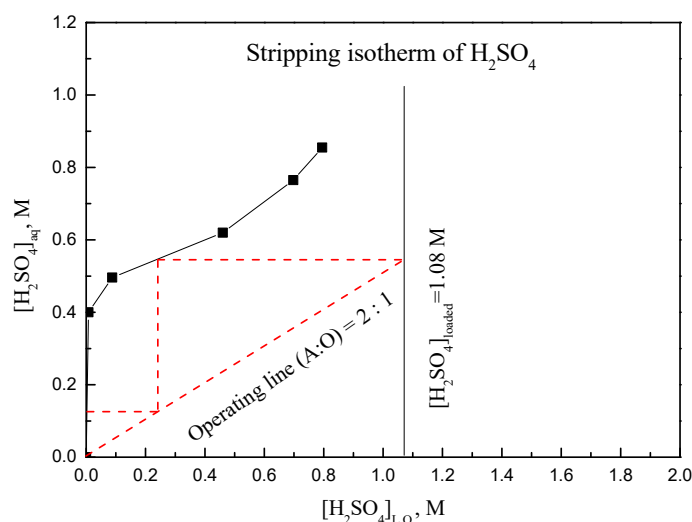


Figure 9. McCabe–Thiele plot for H_2SO_4 stripping from loaded TEHA + TBP with water. Stripping condition: [Extractant] = 1 M TEHA + 1 M TBP, Diluent = Kerosene, $[\text{H}_2\text{SO}_4]_{\text{loaded}} = 1.08 \text{ M}$, [Strippant] = water, $V_{\text{org}}/V_{\text{aq}} = 1/3\text{--}5$.

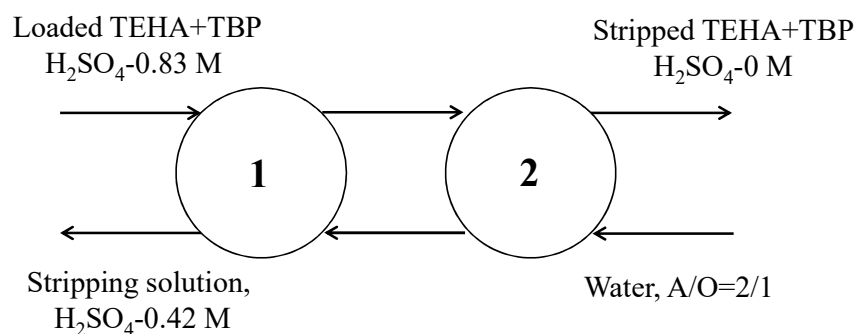


Figure 10. Counter-current simulation of the stripping of sulfuric acid from loaded TEHA + TBP by water.

3.7. Proposed Closed-Circuit Process

Based on the aforementioned data, the process developed for the separation of Zr(IV) and Hf(IV) by inserting a H_2SO_4 recovery step is presented in Figure 11. As denoted by the green box in Figure 11, the regeneration of sulfuric acid was achieved after stripping the H_2SO_4 -loaded organic with water. Moreover, the concentration of H_2SO_4 reduced from 4 M to 0.5 M after extraction by 1 M TEHA + 1 M TBP, without loss of Zr(IV) and Hf(IV). This indicates that the raffinate obtained after H_2SO_4 extraction can be directed back toward the Zr(IV) and Hf(IV) starting solution for metal re-separation. A good closed-circuit could be created by inserting a sulfuric acid recovery step into the whole flowsheet, making the process economic and eco-friendly. Furthermore, the recovery and regeneration of sulfuric acid in the effluent is also necessary to address environmental issues.

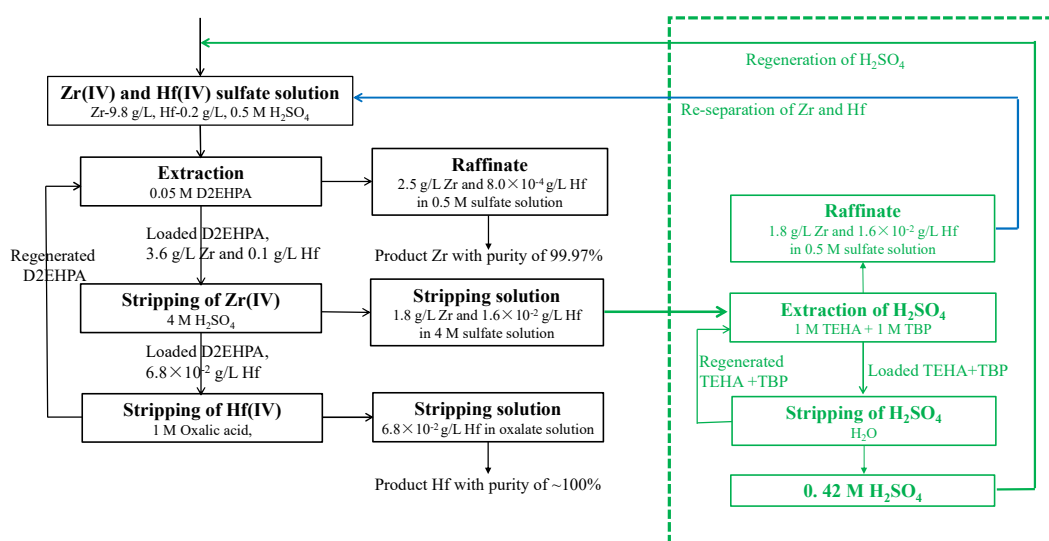


Figure 11. Flowsheet of the proposed closed-circuit process for the separation of Zr(IV) and Hf(IV) by inserting a H_2SO_4 recovery step.

4. Conclusions

TEHA and its mixtures with octanol, decanol and TBP were employed to recover sulfuric acid in the presence of Zr(IV) and Hf(IV). The extraction of H_2SO_4 by TEHA in kerosene was found to be influenced by the minimum sulfuric acid concentration in raffinate when the feed concentration of H_2SO_4 was low and to be limited by the loading capacity of TEHA in a high initial sulfuric acid range. The extracted species was determined to be $\text{H}_2\text{SO}_4 \cdot \text{TEHA}$ based on the slope analysis method. The solidification phenomenon could be prevented when more than 20% vol of octanol or decanol, or 1 M TBP were added. The possible roles played by the three additives on the prevention of solidification was

interpreted by analyzing the characteristics of their functional group. The mixture of TEHA and TBP in kerosene was found to be the best system for the extraction of H_2SO_4 . The effective stripping of sulfuric acid from the loaded TEHA + TBP was achieved by using water. In the whole experimental procedure, Zr(IV) and Hf(IV) could not be extracted into TEHA or its mixtures. McCabe–Thiele diagrams for the extraction and stripping isotherms were also constructed. Batch-type simulation experiments for the multi-stage counter-current extraction and stripping demonstrated that 4.2 M sulfuric acid could be reduced to a minimum concentration of 0.5 M in raffinate by 1 M TEHA + 1 M TBP without the co-extraction of Zr(IV) and Hf(IV) and could be easily stripped by water.

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