



Recovery of nitric acid from waste etching solution using solvent extraction

Chang-Hoon Shin^{a,*}, Ju-Yup Kim^{a,c}, Jun-Young Kim^a, Hyun-Sang Kim^b, Hyang-Sook Lee^a, Debasish Mohapatra^a, Jae-Woo Ahn^d, Jong-Gwan Ahn^e, Wookeun Bae^c

^a R&D Center, Daeil Development Co., Ltd., Ansan 425-836, Republic of Korea

^b R&D Team, NIT Co., Ltd., Kunsan 573-882, Republic of Korea

^c Department of Civil Engineering, Hanyang University, Seoul 133-791, Republic of Korea

^d Department of Material Science & Engineering, Daejin University, Pocheon 487-711, Republic of Korea

^e Korea Institute of Geoscience and Mineral Resources, Daejeon 305-350, Republic of Korea

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ABSTRACT

A process was developed to recover nitric acid from the waste stream of wafer industry using solvent extraction technique. Tributyl phosphate (TBP) was selected among several extractants because of its better selectivity towards HNO_3 , overall superiority in operation, favorable physical properties and economics. The waste solution containing 260 g/L CH_3COOH , 460 g/L HNO_3 , 113 g/L HF and 19.6 g/L Si was used as feed solution for process optimization. In the pre-treatment stage >99% silicon and hydrofluoric acid was precipitated out as Na_2SiF_6 . Equilibrium conditions for HNO_3 recovery were optimized from the batch test results as: four stages of extraction at an organic:aqueous (O:A) ratio of 3, four stages of scrubbing at O:A ratio of 5 and five stages of stripping at an O:A ratio of 1.5. The extraction of HNO_3 was suppressed by the presence of acetic acid (HAc) in the feed solution. To examine the feasibility of the extraction system a continuous operation was carried out for 200 h using a multistage mixer-settler. The concentration of pure HNO_3 recovered was 235 g/L with a purity of 99.8%.

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1. Introduction

Solutions containing strong mineral acids mixed with various metals/salts result as waste (or intermediate) stream in a number of industrial processes. The disposal of these waste streams is an ecological problem of the processing industry. For example, during the manufacture of silicon wafer, chemical etching methods use mixed acids (hydrofluoric, nitric and acetic acid) to remove deterioration generated in wafer cutting and grinding process of single crystal silicon. Until now the waste acids resulting from the use of etching solution has been subjected neutralization without any proper treatment resulting environmental and financial problems. The effective recovery of the acids from the waste stream in a pure and relatively concentrated form, suitable for recycling to the main process, could amply cover the separation costs. Furthermore, the removal of bulk of the free acids would greatly simplify any further treatment of the waste water.

The conventional distillation process has problems of desired acid purity and high-energy cost. Solvent extraction is an alternative to distillation process, which can be used to achieve a

selective separation, yet with much lower energy consumption. Our research group at R&D Center, DAEIL Development Co. Ltd., has been working for the past several years on the acid recovery from different waste sources [1–4]. In a recent work we have demonstrated a continuous solvent extraction process to recover acetic acid from waste etching solution [4]. The present communication shows the suitability of nitric acid recovery from waste etching solution using TBP as an extractant. The use of TBP for the purification of crude uranium, thorium and plutonium from nitric acid medium is well-documented [5]. However, the commercial use of TBP for the extraction of pure nitric acid is not well-addressed by the research community. TBP extracts acids in the order $\text{HF} \approx \text{HClO}_4 > \text{HNO}_3 > \text{H}_3\text{PO}_4 > \text{HCl} > \text{H}_2\text{SO}_4$ in a pure system as reported by Hesford and Mckey [6]. The extraction of nitric acid was enhanced by the presence of H_3PO_4 and nitrate salts in the aqueous phase [7]. On the other hand, the extraction of nitric acid was reduced by increasing HF concentration in the feed solution [8]. The literature data available for HNO_3 extraction mechanism by TBP are scarce. Among the solvates proposed, three species of the stoichiometry $\text{TBP}:\text{HNO}_3 = 2:1, 1:1$ and $1:2$ are frequently used to describe the distribution equilibrium of nitric acid in a wide range of acidity of the aqueous phase. At highly concentrated acid solutions, some researchers proposed the existence of the solvates with stoichiometry $1:3$ and $1:4$ [9] or made the hypothesis

* Corresponding author. Tel.: +82 31 498 5713; fax: +82 31 498 5723.
E-mail address: shinch777@chol.com (C.-H. Shin).

Table 1
Chemical composition of waste mixed acids [4]

Constituents	Value (g/L)
CH ₃ COOH	260
HNO ₃	460
HF	113
Si	19.6

of simple dissolution of nitric acid in the organic phase [10]. Mokili and Poitrenaud [11] reported the possibility of the formation of more complex species such as TBP·H₂O, (TBP)₂·HNO₃·H₂O and HNO₃·H₂O in presence of salting-out agents. From the above discussions, it can conclude that extraction of nitric acid using TBP is feasible; however, each process has to be designed around specific conditions. In the available literature, no proposition was found of an economical process to recover pure nitric acid at a relatively high concentration from a binary mixture of nitric and acetic acid.

The objective of the present investigation was to develop a solvent extraction process for treating an etching waste to extract and isolate pure nitric acid. To achieve the above object, in the present communication, we report that the results generated by studying the extraction of nitric acid by TBP at various operating conditions such as the extractant concentration, phase ratio, counter-current extraction, scrubbing and stripping stages. Prior to solvent extraction silicon and fluoride was separated from the feed solution by precipitation method. The batch test findings were optimized to run a mixer–settler for continuous 200 h and the results were presented.

2. Materials and methods

2.1. Reagents and apparatus

The waste acids used for this investigation was procured from L-Chemistry Company, South Korea. The chemical composition of the waste acid is shown in Table 1. In the pre-treatment stage, silicon and fluoride was removed by precipitation method. The detailed procedure for precipitation was reported earlier [4]. The extractant, TBP (C₁₂H₂₇O₄P) was procured from Daejung Chemicals and used as such without any further purification. TBP has an average molecular weight of 266, density: 0.976 g/cm³, flash point 146 °C, viscosity 4.0 cps with 99.0 wt% assay concentration. In some cases, extra pure kerosene supplied by Junsei Chemical Co., Japan (b.p. 180–270 °C) was used as diluent. All other chemicals used in this work were of analytical grade procured from Daejung Chemicals, Korea. Experiments were carried out using Teflon[®] containers to avoid fluoride interference.

The cation and anion analysis was done by Varian 720-ES model inductively coupled plasma optical emission spectrometer (ICP-OES) and ion chromatography (761, Compact IC, Metrohm), respectively. The concentration of TBP in the organic phase was determined by GC–MS (Hewlett Packard, 6890N series). An Orion expandable ion analyzer EA 920 equipment was used for the pH measurement of the aqueous phase.

2.2. Solvent extraction procedure

Equilibrium experiments were conducted by contacting the corresponding aqueous and organic phases in separatory funnels using mechanical shaker for 5 min. Preliminary experiments showed that 2–3 min is sufficient to reach equilibrium between organic and aqueous phases. After phase disengagement, the aqueous phase was separated and its equilibrium pH was measured. The cation/anion concentrations in the aqueous phase were estimated

directly by ICP-OES/IC after suitable dilutions. Scrubbing of acetic acid from loaded organic (LO) was carried out using 3 M nitric acid. Stripping of nitric acid from the LO was conducted using deionized water as the stripping agent. All experiments were carried out at room temperature (22 ± 1 °C). Reproducibility of results were checked by repeating several experiments and found to be within ±6%.

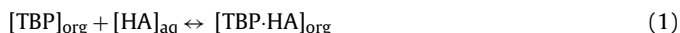
2.3. Pilot plant tests using mixer–settler

The mixer–settler used in this work was composed of box-type mixer–settlers made of Teflon[®] with similar internal arrangement and dimension. The active volume of one mixer–settler was 1050 mL, while the ratio of the mixer and settler volumes was 1:6 (150 and 900 mL, respectively). In the extraction step, aqueous feed containing waste acids and the extractant (TBP) were mixed at a flow rate of 10 and 30 mL/min, respectively, maintaining an A:O ratio 1:3. In the scrubbing stage, co-extracted acetic acid was scrubbed by adding 3 M nitric acid at an O:A ratio 5:1. Finally, in the stripping step, deionized water was used as the stripping agent and inputted at an O:A ratio 1.5:1. Flow rate was maintained using master flex pump. Stirring was carried out using turbine impeller also made of Teflon[®] having six flat blades, connected to speed controller. The continuous operation was carried out for 200 h and the aqueous and organic solutions of extraction, scrubbing and stripping units were sampled at regular intervals for analysis.

3. Results and discussion

3.1. Theoretical consideration of HNO₃ extraction mechanism using TBP

The extraction of mineral acids by TBP can be interpreted by the hydrate-solvate mechanism [12], where the extraction reaction can be simply written as



where [TBP]_{org} and [TBP·HA]_{org} are the concentration of free and bound TBP in the organic phase, respectively. From the above equation, the equilibrium equation is formulated as

$$K_{\text{HA}} = \frac{[\text{TBP}\cdot\text{HA}]_{\text{org}}}{[\text{HA}]_{\text{aq}} [\text{TBP}]_{\text{org}}} \quad (2)$$

Taking the logarithm of both sides of Eq. (2) and rearranging, we can get

$$\log \left\{ \frac{[\text{TBP}\cdot\text{HA}]_{\text{org}}}{[\text{HA}]_{\text{aq}}} \right\} = \log K_{\text{HA}} + \log [\text{TBP}]_{\text{org}} \quad (3)$$

$$\log \left\{ \frac{[\text{HA}]_{\text{org}}}{[\text{HA}]_{\text{aq}}} \right\} = \log K_{\text{HA}} + \log [\text{TBP}]_{\text{org}} \quad (4)$$

where [TBP·HA]_{org} = [HA]_{org}.

For the extraction of an acid, distribution coefficient, *D*, can be expressed as a function of acid concentration in organic phase to that in the aqueous phase at equilibrium.

$$D = \frac{[\text{HA}]_{\text{org}}}{[\text{HA}]_{\text{aq}}} \quad (5)$$

Replacing *D*, Eq. (4) becomes:

$$\log D = \log K_{\text{HA}} + \log [\text{TBP}]_{\text{org}} \quad (6)$$

The log–log plot of distribution coefficient, *D*, against [TBP]_{org} at a constant value of other parameters allows an estimation of the

number of extractant molecules associated with the extracted acid complex.

Distribution coefficient, as an index of metal extractability, is used to calculate the percentage of the extracted acid, E :

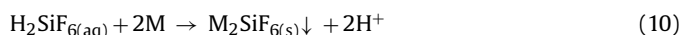
$$E = \left[\frac{DV_{\text{aq}}/V_{\text{org}}}{1 + (DV_{\text{aq}}/V_{\text{org}})} \right] \times 100 \quad (7)$$

where V_{aq} and V_{org} are the volumes of the aqueous and organic phases of the extraction process, respectively. For equal volumes of immiscible phases, E becomes:

$$E = \left[\frac{D}{1 + D} \right] \times 100 \quad (8)$$

3.2. Removal of silicon and fluoride by precipitation

As mentioned earlier, prior to solvent extraction of nitric acid, HF and Si were removed from the feed solution by precipitation method. Silicon is considered as an impurity and fluoride because of its corrosive nature has to be removed from the feed solution before carrying out the solvent extraction study. Chemical precipitation method is widely used for the removal of fluoride by using either calcium chloride (CaCl_2) or lime $\text{Ca}(\text{OH})_2$ to precipitate fluoride as CaF_2 . However, the major drawback lies in the separation of this precipitate because of its fineness. So, in most of the cases, flocculant is added for better separation from aqueous phase. To overcome this problem, we proposed a different precipitation method, which was described in our previous paper [4]. Therefore, only a crude outline of the findings is repeated here. Silicon and fluoride was precipitated as hexafluorosilicate salts in presence of alkali cations, preferably sodium. The chemical reaction that takes place is a two-stage process, which can be written as



where M represents alkali metals such as Na, K, Ca, Li, etc. The choice of sodium was because of its higher precipitation efficiency, lower solubility of its hexafluorosilicate salt in acidic medium and good-market value of the final product. Since the present feed solution contain less silicon than stoichiometrically required to form hexafluorosilicate, extra silicon was added to the feed solution in the form of SiO_2 to match the silicon:fluoride ratio of 1:6. Using three equivalent times higher dosing of Na (as NaNO_3) compared to Si, which is equal to 1.5 times higher require stoichiometrically, 99.9% silicon and 99.2% fluoride was precipitated out as sodium hexafluorosilicate. It was observed that temperature had a negligible effect on precipitation process and it was difficult to separate silicon and fluoride quantitatively from the feed solution. This was attributed to the increasing ionic strength of the solution in acidic medium, which increases the solubility of Na_2SiF_6 . The precipitated Na_2SiF_6 was 98.2% pure, and can be considered as commercial grade. Under the best experimental conditions (3 h contact time; temperature 22°C , molar ratio Na:Si = 1.5) sufficient quantities of raffinate were generated with a composition of 279 g/L CH_3COOH , 513 g/L HNO_3 , 0.9 g/L HF and 0.03 g/L Si. The raffinate was used as feed solution for nitric acid separation and recovery by solvent extraction.

3.3. Batch experiments for HNO_3 solvent extraction

3.3.1. Effect of extractant type

Several neutral solvents were studied for their effectiveness to extract HNO_3 preferentially. An undiluted solvent was used as the organic phase in all cases. The results are presented in Fig. 1. As shown in the figure, solvents such as 2-ethylhexyl alcohol (EHA), decanol, octanol, heptanol and hexanol were more selective for HAC

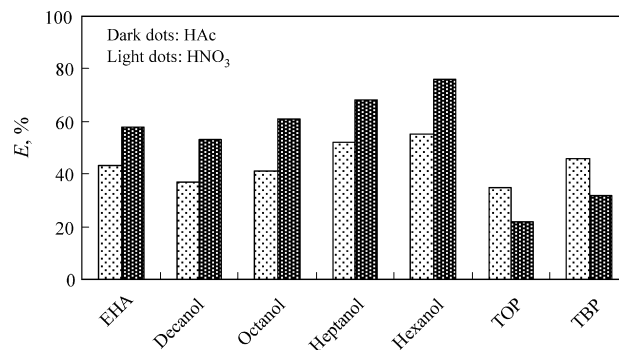


Fig. 1. Effect of extractant type on the extraction efficiency of HNO_3 and HAC (O:A = 1, single-contact 5 min, 22°C , undiluted extractant, aqueous phase: 279 g/L HAC and 513 g/L HNO_3).

over HNO_3 . Tri-octyl phosphate (TOP) and TBP showed more preferential extraction of HNO_3 compared to HAC. The extraction of HNO_3 was about 46% against a co-extraction of 32% HAC in case of TBP in a single-contact. The corresponding figures in case of TOP were 35 and 22% for HNO_3 and HAC, respectively. The high polarity of the phosphoryl ($\text{P}=\text{O}$) group in TBP and TOP enables it to act as a strong Lewis-base and as a result it can form acid-base complex when contacted with strong acids. Finally, TBP was chosen for the extraction of HNO_3 for its overall superiority in operation, favorable physical properties and economics. Therefore, all further experiments were carried out using undiluted TBP, except extractant concentration study where kerosene was used as a diluent.

3.3.2. Effect of TBP concentration

The effect of the TBP concentration on the extraction efficiency of HNO_3 and HAC at O:A ratio of 1 and 22°C was studied and the results are shown in Fig. 2. It was observed that the extraction of nitric acid increased from 19 to 46% ($D = 0.23\text{--}0.85$) in a single contact when TBP concentration increased from 20 to 100%. During the same period, the co-extraction of HAC also increased from 9.4 to 32.2% ($D = 0.10\text{--}0.47$). In the extracted species, the protons of an acid can form a hydrogen bond with an oxygen atom of TBP molecules and thus the co-extraction of HAC together with HNO_3 is quite reasonable. Generally, the extraction of an acid tends to be enhanced by the common-ion effect of protons that is produced by the dissociation of the acid, and reduced by the competing extraction of another acid. To study the effect of HAC presence in feed solution, another experiment was carried out. In that case, a synthetic solution was prepared containing only nitric acid having the same concentration

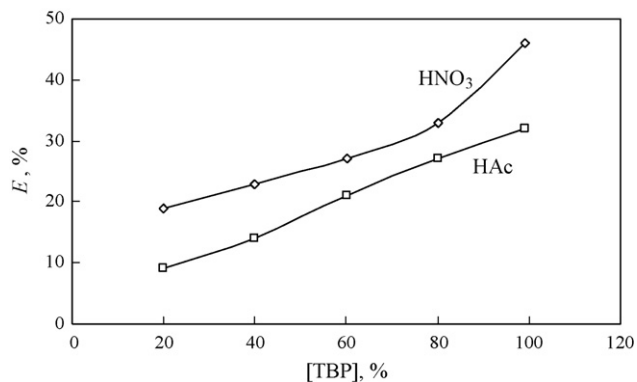


Fig. 2. Effect of extractant concentration on the extraction efficiency of HNO_3 and HAC (O:A = 1, single-contact 5 min, 22°C , aqueous phase: 279 g/L HAC and 513 g/L HNO_3).

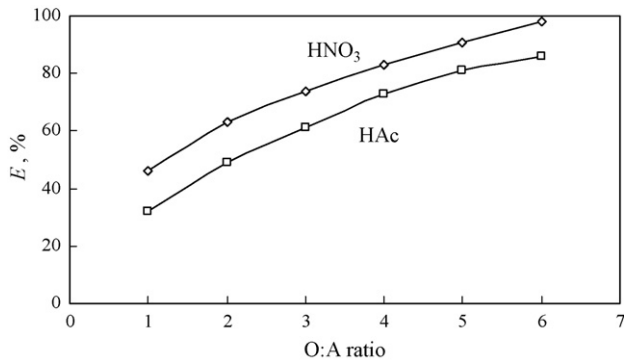


Fig. 3. Effect of phase ratio on the extraction efficiency of HNO₃ and HAc (single-contact 5 min, 22 °C, undiluted extractant, aqueous phase: 279 g/L HAc and 513 g/L HNO₃).

to that of actual solution. It was observed that, the HNO₃ extraction efficiency increased by 12–14% in case of single acid compared to a binary mixture of acids (HNO₃ and HAc) using same TBP concentration. This showed that, the extraction of HNO₃ was suppressed by the co-extraction of HAc as both may be chelating with the same functional group. The log–log plot of $[\text{HNO}_3]_{\text{org}}/[\text{H}^+][\text{NO}_3^-]$ against [TBP] gave a straight line with a slope of 1.88 and regression coefficients of 0.99, suggesting that two molecule of HNO₃ was extracted by one molecule of TBP. However, the mechanism is much more complicated than mentioned above, with the involvement of water in the complex formation as suggested by several authors [7,11]. Another parameter that has significant importance for plant designing is the phase separation time. It was observed that, phase separation time increased from 20 to 80 s, when TBP concentration increased from 20 to 100%. No third-phase formation was observed during the experimental conditions used in our study.

3.3.3. Effect of phase ratio

The effect of HNO₃ extraction and HAc co-extraction was studied varying phase ratio (O:A) from 1 to 6 and keeping other factors constant such as TBP concentration, 5 min mixing time and temperature 22 °C. The results are shown in Fig. 3. In general, the extraction efficiency of nitric acid and acetic acid increased with increase in O:A phase ratio. For example, the nitric acid extraction increased from 46 to 98% when O:A phase ratio was increased from 1 to 6. At the same time the co-extraction of acetic acid also increased from 32 to 86%. In order to determine the theoretical number of stages required to quantitatively extract nitric acid, a number of experiments were carried out at different phase ratio keeping the total volume constant and the results are shown in Fig. 4. The curve was

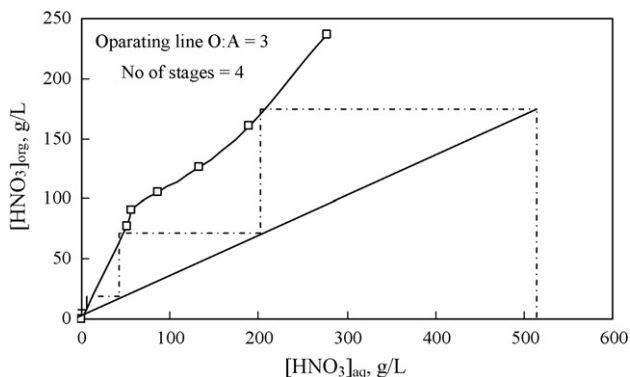


Fig. 4. Extraction isotherm for HNO₃ using undiluted TBP and McCabe-Thiele analysis.

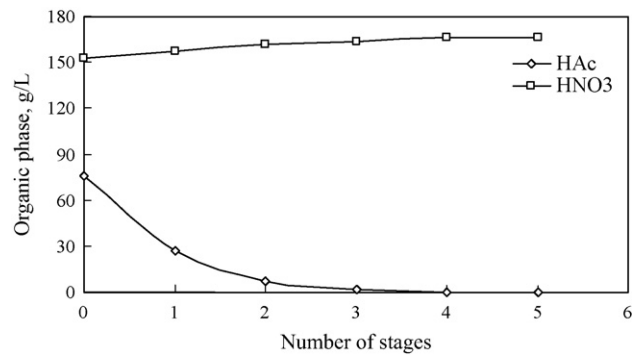


Fig. 5. Scrubbing efficiency of HAc from organic phase as a function of number of stages (scrub feed: 3 M HNO₃, single-contact 5 min, O:A = 5 and temperature: 22 °C).

applied to the McCabe-Thiele method to theoretically calculate the number of stages needed for complete extraction. From the extraction isotherm, it was observed that at an O:A ratio of 3, quantitative extraction of nitric could be achieved in four stages which was further supported by counter-current studies. The extraction efficiency was around 97% for HNO₃ and the loaded organic contained 153 g/L HNO₃ and 76 g/L HAc.

3.3.4. Scrubbing of HAc

Scrubbing is an important step in solvent extraction process to achieve the desired product purity. The obtained LO phase from the extraction stages contained co-extracted acetic acid, which is undesirable in the nitric acid extraction process. Elimination of such impurities were carried out by multiple scrubbing stages using 3 M HNO₃ as scrubbing agent at an O:A ratio of 5. As shown in Fig. 5, four scrubbing stages were required to remove more than 99% HAc from the loaded organic phase. It is possible to control the scrubbing stages either by increasing scrub solution concentration or decreasing O:A phase ratio. The loaded organic after acetic acid scrubbing contained 166 g/L HNO₃ and 0.316 g/L HAc which was subsequently used for stripping studies.

3.3.5. Stripping of HNO₃

Since the objective was to obtain a strip solution of high purity and with reasonably good concentration, stripping of HNO₃ from LO was carried out at different phase ratios to determine the stripping efficiency and possible enrichment of HNO₃ (Fig. 6). Deionized water was used as the stripping agent. The results showed that, a five stage counter-current stripping at the phase ratio of O:A = 1.5 was necessary to obtain maximum stripping efficiency.

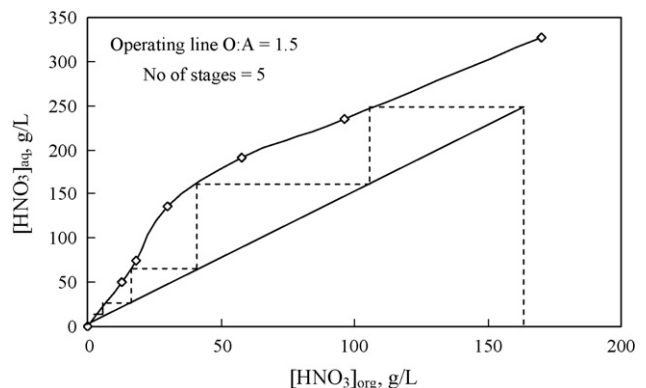


Fig. 6. Stripping isotherm of HNO₃ using deionized water and McCabe-Thiele analysis.

Table 2
Recovery of HNO₃ from mixed waste acids using liquid–liquid extraction

Parameter	Condition
HNO ₃ recovery	
Extraction	
Extractant	Undiluted TBP
O:A	3:1
Mixing time	5 min
Extraction rate	97%
Number of stages	4
HAc scrubbing	
Scrub feed	3 M HNO ₃
O:A ratio	5:1
Mixing time	5 min
Scrubbing rate	98%
Number of stages	4
Stripping	
Stripping solution	Deionized water
O:A	1.5:1
Stripping rate	94.4%
Number of stages	5

Accordingly, a five stage counter-current test at O:A ratio of 1.5 was conducted, which resulted in a strip solution of 235 g/L HNO₃ corresponding to 94.4% stripping efficiency. The impurities such as Na, Si, HF and HAc accounted to about 0.2% of the total concentration generating a HNO₃ solution of 99.8% purity. This strip solution can be further concentrated to any desired concentration by evaporation method. Finally, the optimum conditions for extraction, scrubbing and stripping are summarized in Table 2. Based on the above findings it is assumed that TBP can be used as a solvent for nitric acid separation and recovery from a binary mixture containing nitric and acetic acid.

3.4. Pilot plant tests

Continuous operations were carried out to examine the feasibility of the extraction process in a long run. For this purpose the best experimental conditions generated from the batch tests were used to run a mixer–settler for 200 h. The organic solution coming out of the stripping circuit was thoroughly washed with water and redirected to the extraction circuit for continuous run. The extraction efficiency of HNO₃ and concentration of TBP was measured as a function of time and the results are shown in Fig. 7. Extraction efficiency of HNO₃ and TBP concentration decreased slowly as a function of time. The HNO₃ extraction efficiency decreased from 97 to 93.5% at the end of the 200 h run. At the same time the TBP concentration decreased from 100 to 96.4% due to the solubility of TBP in the aqueous phase. Although the solubility of TBP is negligible in water (1 mL TBP/165 mL water at 25°C), there is no data

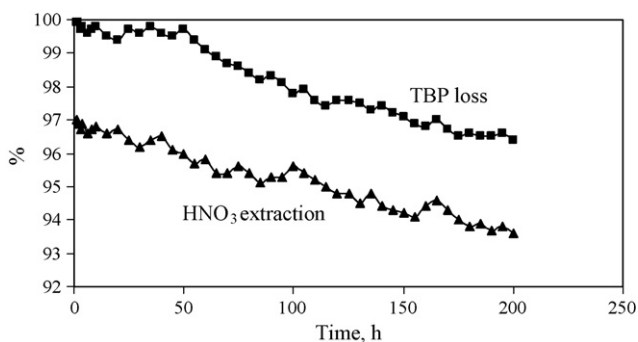


Fig. 7. Effect of time on TBP loss and HNO₃ extraction in continuous counter-current operation using mixer–settler.

available regarding the solubility of TBP in acidic medium. The problem can be resolved by periodical addition of extra solvent to balance the solvent loss. No problem of emulsification and phase separation in the settlers was encountered during continuous operation although we used a high-viscosity organic solvent. The economic feasibility of this extraction process depends on several factors such as availability and cost of the feed waste acid, infrastructure available, manpower cost, product cost, optimum parameters (number of stages, solvent to feed ratio, solvent loss), etc. It is necessary for this solvent extraction process to be examined by an economic analysis including the loss of extractant in the aqueous media. In a future paper, the continuous recovery of acetic and nitric acid from waste etching solution using a multistage mixer–settler will be discussed. Also, the optimization of process cost for the design of mini-plant will be formulated.

4. Conclusions

After optimizing the process to extract nitric acid from waste etching solution the following conclusions can be made.

1. Before solvent extraction, more than 99% silicon and fluoride was removed from the feed solution by precipitation method. The Na₂SiF₆ precipitate formed during the process was 98.2% pure and can be considered as commercial grade having good-market value.
2. Among several extractants tested, TOP and TBP showed preferential extraction of HNO₃ compared to HAc. TBP was selected for the study because of several advantages such as superiority in operation, favorable physical properties and economics.
3. Using a four stage counter-current operation at an O:A ratio of 3, 97% HNO₃ extraction efficiency was achieved.
4. Scrubbing of the co-extracted acetic acid was done by 3 M HNO₃. 99% acetic acid was scrubbed after four stages at an O:A ratio of 5.
5. Deionized water was used as the stripping agent. A five stage counter-current stripping at an O:A ratio of 1.5 was necessary to obtain 94.4% stripping efficiency.
6. The concentration of pure HNO₃ recovered was 235 g/L with a purity of 99.8%, which can be easily concentrated by vaporization depending upon the requirement.

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