A solvent extraction approach to recover acetic acid from mixed waste acids produced during semiconductor wafer process

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ABSTRACT

Recovery of acetic acid (HAc) from the waste etching solution discharged from silicon wafer manufacturing process has been attempted by using solvent extraction process. For this purpose 2-ethylhexyl alcohol (EHA) was used as organic solvent. In the pre-treatment stage >99% silicon and hydrofluoric acid was removed from the solution by precipitation. The synthesized product, Na_2SiF_6 having 98.2% purity was considered of commercial grade having good market value. The waste solution containing 279 g/L acetic acid, 513 g/L nitric acid, 0.9 g/L hydrofluoric acid and 0.030 g/L silicon was used for solvent extraction study. From the batch test results equilibrium conditions for HAc recovery were optimized and found to be 4 stages of extraction at an organic:aqueous (O:A) ratio of 3, 4 stages of scrubbing and 4 stages of stripping at an O:A ratio of 1. Deionized water (DW) was used as stripping agent to elute HAc from organic phase. In the whole batch process 96.3% acetic acid recovery was achieved. Continuous operations were successfully conducted for 100 h using a mixer-settler to examine the feasibility of the extraction system for its possible commercial application. Finally, a complete process flowsheet with material balance for the separation and recovery of HAc has been proposed.

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1. Introduction

Acetic acid is one of the simplest and most widely used carboxylic acids having many important chemical and industrial applications. Total worldwide production of acetic acid is about 6.5 million tonnes per year; out of which about 5 million tonnes are produced by methanol carbonylation process and by bacterial fermentation and the remaining 1.5 million tonnes by recycling [1,2]. Since methanol carbonylation process is dependent on natural gas which is a non-renewable resource, it is sparsely able to support the acetic acid industry for a long time. The biological route accounts for only about 10% of world production which is mostly used in food industry. So there is an urgent need to develop some alternative sources to support the recycling industry of acetic acid.

The production process of semiconductors and liquid crystals passes through several stages such as deposition, resist coating,

light exposure, etching, resist removal, rinsing which generate huge amount of acid wastes. For example, in the manufacturing process of silicon wafer, chemical etching methods use mixed acids to remove deterioration generated in wafer cutting and grinding process of single crystal silicon. Due to a rapid growth of those industries in Korea, the amount of waste acids generated during etching and cleaning processes is increasing rapidly. The composition of waste acids though vary according to the reaction conditions of the etching process, generally comprised of 10–25% hydrofluoric acid, 30–40% nitric acid, 7–12% acetic acid and 1.5–2.5% silicon. Because of appreciable concentration, it is economically viable to recover those acids prior to treatment in wastewater plant for final disposal.

Until recently, however, the acid waste has been mostly subjected to neutralization without any proper treatment. However, the conventional neutralization treatment has problems of formation of precipitation in a large quantity, cost of alkali, sludge disposal and treatment of waste water to reduce BOD and COD, which consequently cause an increase in the treatment cost. On the other hand, in this era of recycling it is important to minimize the waste by possibly reusing several components of the waste. This is not

only important from economical point of view but also from the environmental aspects.

Many research groups in different countries are working in this field and some methods are proposed in the literature for the separation and recovery of acetic acid from different waste sources [3–11]. Most of these processes are concerned to an aqueous solution that does not contain high concentration of inorganic acids. In the absence of any mature technology, conventional physical separation method such as distillation is preferred by the industries; although, distillation is not economical because of the high-energy costs involved in vaporization process. The membrane separation and ion exchange methods are not suitable when multi anions are present in the system [12].

In view of these constraints, it is timely to explore alternative methods of recovering the valuable acid. The solvent extraction method has the potential to replace the existing distillation process used for acetic acid recovery. The solvent extraction method is advantageous in that it is performed in a closed system continuously and the equipment cost is cheap. Recently, solvent extraction processes have been proposed by several research groups including our team to separate acetic acid from mixed waste acids [12–16].

To the best of our knowledge, there is no such commercial process available to recover acetic acid from a mixed waste acid containing hydrofluoric acid, nitric acid, acetic acid and silicon. Accordingly, the present research is aimed to recover acetic acid from such a solution by solvent extraction method. In the pre-treatment stage, silicon and HF are separated by precipitation method. The raffinate containing HAc and HNO_3 is subject to solvent extraction using 2-ethylhexyl alcohol (EHA) to separate and recover HAc at high purity. The batch test results are optimized to run a mixer-settler for continuous 100 h and the result are presented. Experimental parameters such as contact time, phase ratio, solvent loss, numbers of stages for complete separation have been discussed. Finally, a complete process flowsheet with material balance is proposed.

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 compositions of the waste acids are presented in Table 1. The concentration of cations and anions were analyzed by inductively coupled plasma optical emission spectrometer (ICP-OES, 720-OES, Varian) and ion chromatography (761, Metrohm), respectively. Except temperature variation experiments, all other experiments were carried out at room temperature ($22 \pm 1\,^\circ$C). A thermostat with a mechanical shaker was used to study the temperature effect. Identification of Na_2SiF_6 mineral phases were carried out by a Rigaku, RH-200 model X-ray diffractogram (XRD) using CuKα radiation source at 35 kV and 25 mA. For solvent extraction, 2-ethylhexyl alcohol ($C_8H_{17}OH$) procured from Daejung chemicals was used as extractant without any further purification. The extractant, 2-ethylhexyl alcohol has an average molecular weight of 130.2, density ($24\,^\circ$C): 0.834 g/cm^2, flash point 85 $^\circ$C with 98.0 wt% assay concentration. The concentra-

tion of 2-ethylhexyl alcohol in the organic phase was determined by GC–MS (Hewlett Packard, 6890N series) to estimate the loss of the organic solvents into the aqueous phase. All other chemicals used were analytical grade procured from Daejung chemicals, Korea. Experiments were carried out using Teflon® containers to avoid fluoride interference.

2.2. Silicon and fluoride precipitation

Silicon and fluoride precipitation experiments were carried out by taking 200 mL of feed in a 500 mL Teflon® beaker fitted with a mechanical stirrer at 300 rpm. In the first stage, to match the stoichiometrically required Si:F concentration of 1:6, extra Si was added to the solution in the form of SiO_2. In the second stage, excess $NaNO_3$ was added to the solution to precipitate Si and F as Na_2SiF_6. The solution was stared for 3 h at $22 \pm 1\,^\circ$C. Preliminary experiments indicated that equilibrium achieved within 3 h. After desired time, the precipitates were separated from the supernatant liquid by vacuum filtration using 0.2 μm pore size membrane filter paper. The filtrate was analyzed for cations (Si and Na) and anions (NO_3^-, F^-, CH_3COO^-) after proper dilution.

2.3. Solvent extraction procedure

Equal volumes of aqueous and organic phases (20 mL each) were equilibrated by manually shaking in a 100 mL separatory funnel for 5 min. After phase disengagement, the aqueous phase was separated and its equilibrium pH was measured. The concentration measurements related to organic phase's samples showed significant irreproducibility. So, the cation/anion concentrations in the aqueous phase were estimated directly by ICP-OES/IC after suitable dilutions. The concentrations of cation/anion in the organic phase were calculated from the concentration difference between the aqueous phase before and after extraction. Scrubbing of nitric acid from loaded organic (LO) was carried out using 2 M acetic acid. Stripping of acetic acid from the LO was conducted using deionized water (DW) as the stripping agent. Reproducibility of results were checked by repeating several experiments and found to be within ±5%. The distribution coefficient, D, was calculated as the concentration of cation/anion present in the organic phase to that part in the aqueous phase at equilibrium. From the D values, the percentage extraction and separation factor (β) were calculated using the following equations:

$$\text{Percentage extraction} = D \times \frac{100}{D + (V_{aq}/V_{org})} \qquad (1)$$

where V_{aq} and V_{org} are the volumes of aqueous and organic phases, respectively.

$$\text{Separation factor}(\beta) = \frac{D_{HAc}}{D_{HNO_3}} \qquad (2)$$

2.4. Continuous operation using lab-scale 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 designed and fabricated by our research engineers. A close view of the total set up is shown in Fig. 1. 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 (EHA) 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 nitric acid was scrubbed by adding 2 M acetic acid at an O:A ratio 1:1. Finally, in the stripping step, deionized water was used

Table 1
Chemical composition of waste acids before and after precipitation (g/L)

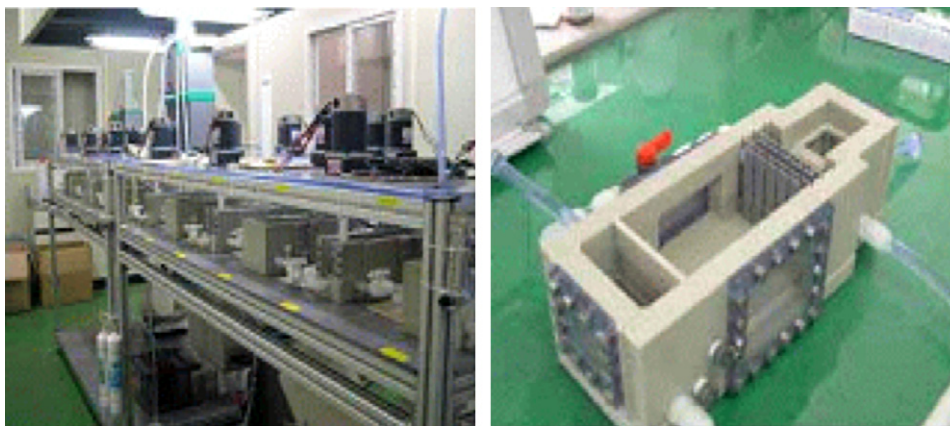|	CH_3COOH	HNO_3	HF	Si
Before precipitation	260	460	113	19.6
Precipitation at $22 \pm 1\,^\circ$C	279	513	0.9	0.030
Precipitation at $0 \pm 1\,^\circ$C	276	519	1.0	0.035
Precipitation at $55 \pm 1\,^\circ$C	278	520	0.9	0.028

Fig. 1. A close view of mixer-settler for continuous process operation.

as the stripping agent and inputted at an O:A ratio 1:1. 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 impeller was designed to minimize the formation of shear of very small droplets. These slow settling droplets are the major cause of haze in the settler, giving rise to high solvent losses in the raffinate. The operating conditions were chosen such that the resistance time of each phase in the mixer was 5 min. The continuous operation was carried out for 100 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. Removal of silicon and fluoride by precipitation

As discussed earlier, prior to solvent extraction of acetic acid, HF and Si was 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 [16]. In the present solution, silicon is mostly present as SiO_2 because of its oxidation in the presence of HNO_3. It is known that silicon and hydrofluoric acid can react with divalent and monovalent alkali metals to form corresponding insoluble alkali salts. The chemical reaction that takes place is a two-stage process which can be written as:

$$SiO_2 + 6HF \rightarrow H_2SiF_{6(aq)} + 2H_2O \qquad (3)$$

$$H_2SiF_{6(aq)} + 2M \rightarrow M_2SiF_6\downarrow + 2H^+ \qquad (4)$$
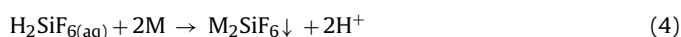
where M represents alkali metals such as Na, K, Ca, Li, etc. In the first stage silicon dioxide reacts with fluoride to form soluble hexafluorosilicic acid. In the second stage, in the presence of any alkali metal, hexafluorosilicic acid reacts with it forming the insoluble hexafluorosiliconte–metal complex. So in case of sodium, stoichiometrically 2 mol of Na react with 1 mol of Si and 6 mol of F to form 1 mol of Na_2SiF_6.

In our present feed solution, silicon concentration is less than stoichiometrically required to form hexafluorosiliconte (Si:F = 1:6). So, extra silicon was imported to the feed solution in the form of SiO_2 to match the silicon:fluoride ratio of 1:6. Our initial experiments using different alkali salts to precipitate silicon and fluoride showed significant variation in their precipitation rate, because of their indifferent solubility in acidic medium [17]. For the present study, we have chosen $NaNO_3$ as the sodium source to precipitate hexafluorosiliconte as Na_2SiF_6, which showed maximum precipitation efficiency among the salts studied. Another reason to choose

$NaNO_3$ is the good market value of Na_2SiF_6 compared to other hexafluorosiliconte salts and to avoid contamination of feed solution by other anions. The effect of sodium concentration (as $NaNO_3$) on fluoride and silicon precipitation efficiency was studied, and the results are depicted in Fig. 2. Sodium concentration was varied from 1 to 4 times of equivalent value of silicon. As shown in Fig. 2, silicon and fluoride precipitation efficiency increased with increasing sodium dosing amount up to 3 equivalent times of silicon. Any further increase in sodium concentration did not improve the silicon and fluoride precipitation efficiency. At a three equivalent times higher dosing of Na which is equal to 1.5 times higher require stoichiometrically, 99.9% silicon and 99.2% fluoride was precipitated out. The raffinate after precipitation stage contain about 0.9 g/L fluoride and 0.030 g/L silicon which is considered acceptable for acetic acid solvent extraction. The effect of temperature was studied to see its influence, if any, on the fluoride and silicon precipitation efficiency. The results are shown in Table 1. It was observe that temperature had a negligible effect on precipitation process and it is difficult to separate silicon and fluoride quantitatively from the feed solution. The solubility of Na_2SiF_6 was attributed to the increasing ionic strength of the solution in acidic medium. Frayret et al. [17] reported that the solubility of Na_2SiF_6 in 5 M nitric acid is about 0.055 mol/L. Phase identification of the Na_2SiF_6 mineral was carried out by XRD analysis at room temperature and in air atmosphere (Fig. 3). With the aid of a computer linked scanner and corresponding programs, the phase analysis were precisely determined. Semi-quantitative estimation of Na_2SiF_6 phase was made on the calibration curves. The purity of Na_2SiF_6 was further confirmed by wet-chemical analysis. Based on XRD analysis and wet-chemical analysis the purity of synthesized Na_2SiF_6 was
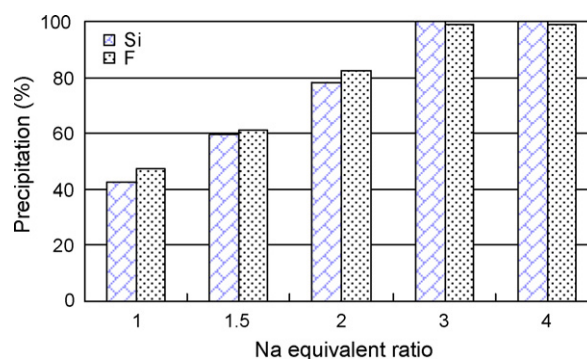

Fig. 2. Effect of $NaNO_3$ addition on silicon and fluoride precipitation efficiency (temperature = 22 °C, 3 h mixing time).
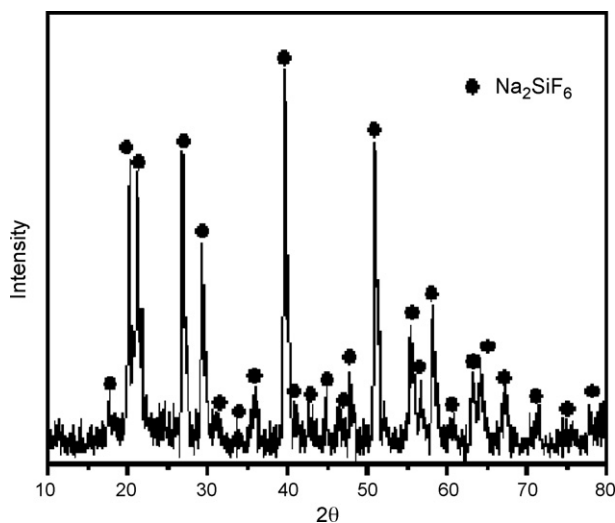
Fig. 3. XRD analysis of synthesized Na_2SiF_6.

Fig. 5. Effect of O:A ratio on HAc and HNO_3 extractability with 98% EHA (contact time = 5 min, temperature = 22 °C).

calculated to be 98.2% which is suitable to be considered as commercial grade having good market value. After silicon and fluoride removal by precipitation, sufficient quantity of raffinate was 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 further treated as feed solution for acetic acid solvent extraction.

3.2. Batch scale solvent extraction for recovering acetic acid

Based on our previous work [16], undiluted 2-ethylhexyl alcohol was selected for the acetic acid solvent extraction because of its better extraction and stripping efficiency compared to Tri-butyl phosphate. Here it is important to mention that there is no organic solvent available which is only selective for acetic acid in presence of nitric acid. So, several stages of scrubbing are essential to scrub the undesired nitric acid from the loaded organic to get high pure acetic acid. The kinetics of acetic acid extraction was evaluated by studying the time vis-a-vis acetic acid extraction. The HAc and HNO_3 extraction percentage as a function of contact time is shown in Fig. 4. It was observed that the kinetics of acetic acid extraction into EHA was very fast and equilibrium was achieved within 2 min. More than 99% of the total extractable amount was transferred to the organic phase within first 2 min. For example, when 98% EHA was used to an aqueous solution containing 279 g/L acetic acid and 513 g/L nitric acid, about 57.8% acetic acid extraction was achieved within 2 min mixing time. There was no appreciable
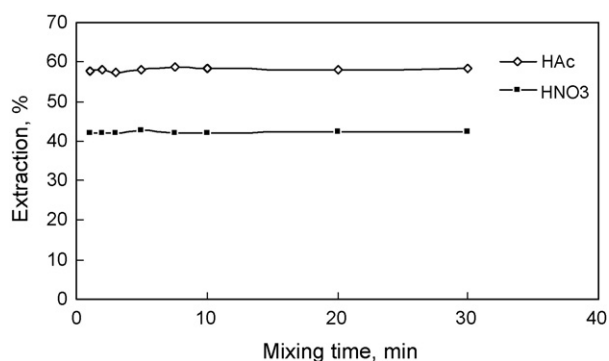

Fig. 4. Effect of contact time on acetic acid extractability with 98% EHA (O:A = 1, temperature = 22 °C).
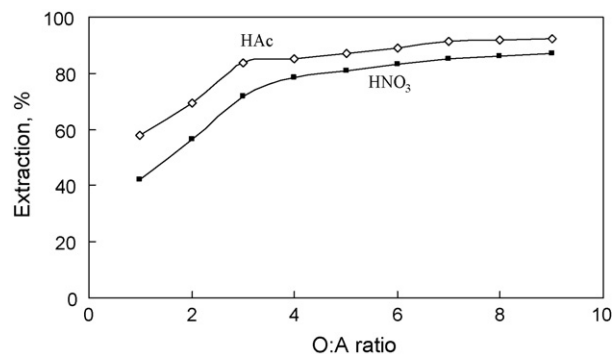
increase in acetic acid extraction when mixing time was increased up to 30 min. It was also observed that, the role of mixing time on acetic acid extractability was independent of initial acetic acid concentration and initial extractant concentration. Similar type of conclusion was drawn for nitric acid co-extraction, although the magnitude was quite different. The effect of silicon and fluoride were negligible in the extraction process because of their low concentration in the feed solution. So, their presence was overlooked in subsequent studies. Five minute mixing time was used in subsequent experiments to assure independence of this variable.

The effect of HAc extraction and HNO_3 co-extraction was studied varying phase ratio (O:A) from 1 to 9 and keeping other factors constant such as 98% EHA, 5 min mixing time, and temperature 22 ± 1 °C. The results are presented in Fig. 5. In general, the extraction efficiency of acetic acid and nitric acid increased with increase in O:A phase ratio. For example, the acetic acid extraction increased from 57.8 to 92.5% when O:A phase ratio was increased from 1 to 9. At the same time the co-extraction of nitric acid increased from 41.9 to 87%. So it was concluded that, both acetic acid and nitric acid has strong affinity for EHA extractant molecules and it is difficult to get selectivity. The exact mechanism of extraction is not quite clear. However, it is expected that, acetate and nitrate anions is extracted by forming ion-pair complexes with EHA dimer. Although we used undiluted EHA, there was no problem in phase disengagement and clear phase separation was achieved within 1 min. Table 2 shows the respective distribution coefficient (D) ratios for acetic acid and nitric acid, as well as the separation factors (β) as a function of phase ratio. As shown in the table, phase ratio has a significant effect on the separation factor, $\beta(D_{HAc}/D_{HNO_3})$. Separation factor increased with increase in O:A phase ratio up to 3 followed by a decreasing trend with further increase in O:A phase ratio. The maximum separation factor (1.98) was achieved at O:A phase ratio of 3. So, all further extraction studies were carried out at a fixed O:A ratio of 3 to achieve best separation factor and minimum dilution of the extracted acids.

In order to determine the number of stages in the continuous counter-current multistage operation, an extraction isotherm was made by contacting the aqueous phase with the organic phase at different phase ratios, following equilibrium, measuring the acid concentration of the extracted phase (organic phase) and the acid concentration of the raffinate phase (aqueous phase) and plotting the data (Fig. 6). The curve was applied to the McCabe–Thiele method to theoretically obtain the number of stages needed for complete extraction. From the extraction isotherm, it was observed that at an O:A phase ratio of 3, quantitative extraction of acetic acid can be achieved in four stages. To confirm the McCabe–Thiele predictions, a four stage counter-current study with 98% EHA was carried out at phase ratio (O:A) of 3. In that case, about 99% extrac-

Table 2
Effect of phase ratio on distribution ratio (D) and separation factor (β) of HAc and HNO$_3$ (feed: 279 g/L HAc and 513 g/L HNO$_3$)

Phase ratio (O:A)	[HAc]$_{org}$ (g/L)	[HAc]$_{aq}$ (g/L)	D	[HNO$_3$]$_{org}$ (g/L)	[HNO$_3$]$_{aq}$ (g/L)	D	$\beta(D_{HAc}/D_{HNO_3})$
1	161.3	117.7	1.37	214.9	298.1	0.72	1.90
2	97.0	85.0	1.14	144.7	223.7	0.65	1.76
3	77.7	45.9	1.70	123.1	143.6	0.86	1.98
4	59.4	41.3	1.44	100.5	110.8	0.91	1.59
5	48.5	36.3	1.34	83.1	97.5	0.85	1.57
6	41.5	30.1	1.38	71.1	86.2	0.83	1.67
7	36.5	23.4	1.56	62.3	77.0	0.81	1.92
8	32.1	22.3	1.44	55.1	71.8	0.77	1.87
9	28.7	20.9	1.37	49.6	66.7	0.74	1.84
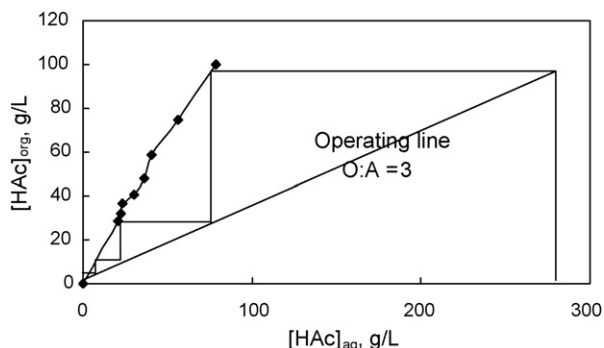
Fig. 6. Extraction isotherm of HAc with undiluted EHA and McCabe–Thiele analysis.

Fig. 8. Stripping efficiency of HAc from LO as a function of number of stages (strip feed = deionised water, contact time = 5 min, temperature = 22 °C).

tion efficiency was achieved, which resulted in a LO containing 92.5 g/L HAc. At the same time the LO also contain 141 g/L nitric acid which is undesirable in the process of getting high pure acetic acid. So, scrubbing of nitric acid was done using 2M acetic acid as scrub feed at an O:A phase ratio of 1. As shown in the Fig. 7, four scrubbing stages are required to quantitatively remove nitric acid from the loaded organic. It is possible to control the scrubbing stages either by increasing the scrub solution concentration or decreasing the O:A phase ratio. The loaded organic after nitric acid scrubbing contained 123 g/L acetic acid which was subsequently used for stripping studies. Acetic acid stripping from LO containing 123 g/L acetic acid was investigated using deionised water as stripping agent at an O:A phase ratio of 1. The results presented in Fig. 8 shows that similar to extraction, acetic acid stripping is also a slow process and at least 4 stages are required to quantitatively strip HAc from LO. The HAc concentration in the strip solution was found to be 119.7 g/L which is about 97.3% stripping efficiency. It is possible to enrich the acetic acid concentration in the strip solution by increasing the O:A phase ratio. It is concluded from the batch test results, 4 stages of extraction at an O:A ratio of 3, 4 stages of
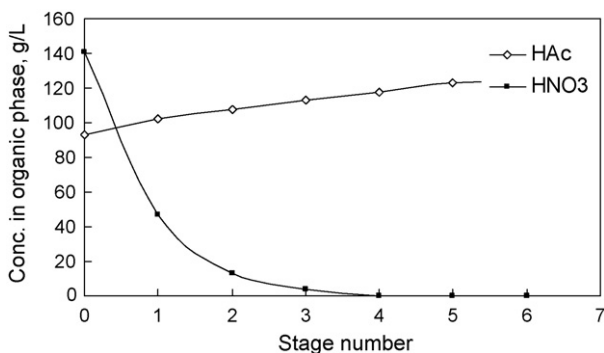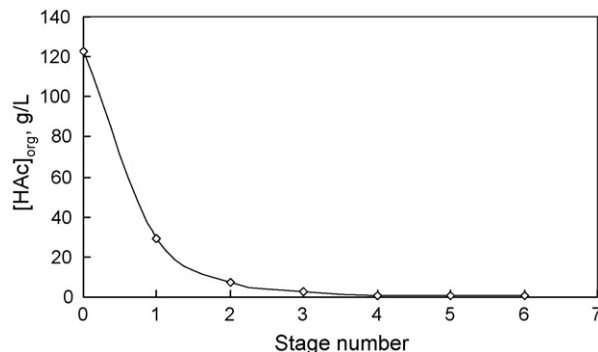
scrubbing and 4 stages of stripping at an O:A ratio of 1 is the best equilibrium condition for HAc recovery. The results demonstrated the feasibility of acetic acid separation and recovery using EHA as solvent in a batch process.

3.3. Continuous process operation using mixer-settler

Continuous operations were carried out to examine the feasibility of the extraction system in a long run. For this purpose the best experimental conditions generated from the batch test were used to run a mixer-settler during 100 h. The organic solution coming out of the stripping circuit was redirected to the extraction circuit for continuous run. The extraction efficiency of HAc and concentration of EHA, the extractant, was measured as a function of time and the results are presented in Fig. 9. From this figure, extraction efficiency of HAc and EHA concentration was found to be gradually decreased with time. The HAc extraction efficiency decreased from 99 to 86% at the end of the 100 h run. At the same time the EHA concentration decreased from 98 to 95.6% due to the solubility of EHA in the aqueous solution. Although the solubility of EHA is negligible
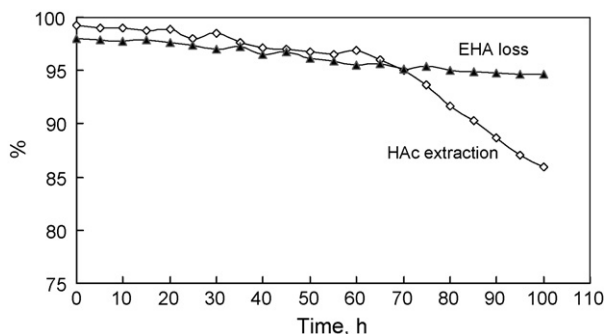

Fig. 7. Scrubbing efficiency of HNO$_3$ from organic phase as a function of number of stages (scrub feed = 2 M HAc, contact time = 5 min, temperature = 22 °C).

Fig. 9. Effect of time on EHA loss and HAc extraction efficiency in continuous operation using mixer-settler.
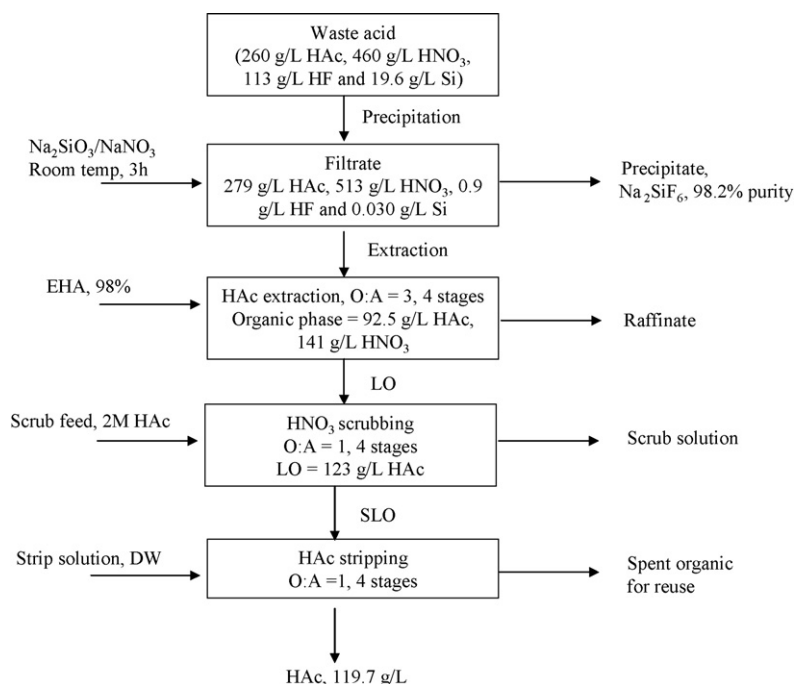
Fig. 10. Flowsheet of HAc recovery from the mixed acids containing HAc, HNO$_3$, HF and Si.

in water (0.1/100 g at 20 °C), there is no data available regarding the solubility of EHA in acidic medium. Such a loss is inevitable unless the feed and stripping solution are pre-saturated with the extractant solution. No problem of emulsification and phase separation in the settlers was encountered during continuous operation. It is necessary for this solvent extraction process to be examined by an economic analysis including the loss of extractant in the aqueous media. Finally, a complete process flowsheet with material balance to recover HAc from mixed waste acids is presented in Fig. 10.

4. Conclusions

An extraction system for the recovery of HAc was studied from the viewpoint of practical application by using 2-ethylhexyl alcohol as the extractant. In the first stage, HF and Si was removed from the waste acids by precipitation with an efficiency >99%. The precipitate, Na$_2$SiF$_6$ which formed during the process is a marketable product having good commercial value. From the batch test results, >99% HAc extraction was achieved using 98% undiluted EHA at 4 stages and an O:A ratio of 3. Four stages of scrubbing using 2 M HAc and 4 stages of stripping using deionized water at an O:A ratio of 1 was found to be optimum conditions for scrubbing and stripping, respectively. In the whole batch process 96.3% acetic acid recovery was achieved. A continuous operation to recover HAc from mixed waste acid was conducted during 100 h by using a mixer-settler. However, a decrease in HAc extractability was observed with the course of time. The HAc extraction decreased from 99 to 86% at the end of the 100 h run. This was attributed to the solubility of EHA in acidic medium there by decreasing the concentration of EHA in the extraction circuit. This is a problem in a continuous operation, which needs to be resolved before its commercial application. The economic feasibility of this extraction process depends on several factors such as availability and cost of the feed waste acids, infrastructure available, manpower cost, product cost, optimum parameters (number of stages and solvent to feed ratio, solvent loss), etc. All these items must be balanced to give maximum possible economy.

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