

RECOVERY OF HCl FROM CHLORIDE LEACH SOLUTION OF SPENT HDS CATALYST BY SOLVENT EXTRACTION

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In the present work, amine based extractant and its mixture with cationic and solvating extractants were tested for the extraction of HCl from chloride solution containing Al(III). The chloride feed solution resulted from the leaching of spent HDS (hydro-desulfurization) catalysts. For this purpose, amine extractants, such as TOA (trioctyl amine), Alamine 336 (a mixture of tri-octyl/decyl amine), Alamine 308 (tri-isooctyl amine), and TEHA (tri 2-ethylhexyl amine) were used and the extraction and stripping behavior of HCl was compared. The extracted HCl was easily stripped from loaded TEHA phase, when compared with the other tested tertiary amine system. Solvent extraction reaction of HCl by TEHA was determined from the extraction data. Unlike TOA and Alamine 336, adding cationic extractant to TEHA had negligible effect on the extraction and stripping of HCl. In our experimental ranges, no Al was extracted by amines and pure HCl was recovered. McCabe-Thiele diagrams for the extraction and stripping of HCl by TEHA were constructed.

Keywords: HCl, extraction, stripping, recovery, TEHA

1. INTRODUCTION

In petroleum refining industries, catalysts are used for an effective generation of clean and pure oil products. After a certain period of processing, catalysts are contaminated with impurities (Jong et al., 1989) and become deactivated. A deactivated spent catalyst may pose significant environmental problems. Therefore it is extremely important to recycle the catalyst from an environmental point of view. Conventionally, in hydrometallurgical processes, it is quite common that mineral acids are generally used for the dissolution of desired metals (Marafi et al., 2008; 2011). Subsequently, a solvent extraction or ion exchange is employed for selective recovery of valuable metals and the resulting free acid contains base metals (Banda et al., 2012). Regeneration of this free acid in the leaching of the spent catalysts would produce less waste and improve the economics of the recovery process.

A survey of literature has shown that solvent extraction is one of the most effective methods for the recovery of mineral acids from solutions (Agarwal et al., 2007; 2008; Gotliebsen et al., 2000; Krirsch et al., 1996; Mikami et al., 1996; Sinha et al., 2010). Scibona et al investigated the extraction behavior of HCl, HBr and HI with diverse amines and the affinity constant values for acid-amine reaction was also discussed in terms of electrostatic and ion-water interactions in the organic and aqueous phases, respectively (Scibona et al., 1966). Eyal et al studied the extraction behavior of mineral acids such as H₂SO₄, HCl and HNO₃ with TEHA, TCA and N, N-dioctyl aniline in various diluent systems and reported that diluent and modifier provide a strong tool for an efficient reversible extraction of acids (Eyal et al., 1991). Furthermore, the same authors described that the ion pair and hydrogen bonding type of mechanism was involved in the extraction of mineral acids with amine based system and its

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extraction efficiency depended upon the aqueous phase pH, pKa of the amine based extractant and the properties of diluents (Eyal et al., 1995). The same authors already demonstrated that the binary extractant system comprising a strong basic amine and a strong acid, such as Aliquat 336/dinonyl naphthalene sulphonic acid, exhibited efficient and reversible extraction towards H₂SO₄ mineral acid (Eyal et al., 1986; 1989; 1990). Moreover, Tait also reported that a mixture of Alamine 336 and D2EHPA showed higher extraction ability towards H₂SO₄ than other tested binary systems involving cationic extractants (D2EHPA, PC 88A and Cyanex 302) with amine based extractants like Aliquat 336, Adogen 283 and JMT (Tait, 1993). Solvating extractants, such as TBP and TOPO, can also extract mineral acids efficiently (Alguacil et al., 1996; Apelblat et al., 1973; Sarangi et al., 2006; Wasniewski et al., 1996). The most recent review concerning studies on the recovery of acids was done with the waste stream of steel and electroplating industries, pickle liquor and spent bleed streams (Agarwal et al., 2009).

In our work on the recovery of valuable metals from spent catalysts, we reported the optimum conditions to dissolve metals present in spent catalysts and to separate Mo and Co from the resulting leaching solution by solvent extraction (Banda et al., 2012). Solvent extraction of Mo and Co from the leaching solution resulted in hydrochloric acid solution containing Al. In this study, solvent extraction and stripping experiments were conducted to recover HCl from the solution containing Al after the separation of Mo and Co. For this purpose, amine extractants, such as TOA, Alamine 336, Alamine 308, Aliquat 336 and TEHA were used to investigate the possibility of recovering HCl from the solution. The effect of mixing these amines with cationic extractants was investigated to find an optimum condition. The extraction and stripping behavior of HCl with the amines was compared. McCabe-Thiele diagrams for the extraction and stripping of HCl were constructed.

2. EXPERIMENTAL

2.1. Materials and reagents

Asynthetic aqueous feed solution containing Al was prepared by dissolving metal salt (AlCl₃ Junsei Chemical Co. Ltd. Japan) in analytical grade 3 M HCl. TBP (Tri butyl phosphate, Yakuri pure chemical co., Ltd.), TOA (trioctyl amine, Sam Chun pure Chemical Co., Ltd.), TEHA (Tri 2-ethylhexyl amine, BASF Chem Co. Ltd.), Aliquat 336 (Tricaprylmethylammonium chloride, a quaternary ammonium salt) Alamine 308 (tri-isooctyl amine), Alamine 336 (mixture of tri-octyl/decyl amine) and Cyanex 272 (Bis (2,4,4-trimethylpentyl) phosphinic acid), D2EHPA (di-2-ethylhexylphosphoric acid), PC 88A (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester) were purchased from Cognis corporation USA and Cytec Canada Inc., respectively. 1-Decanol (Acros Organics) was used as a modifier. These reagents were used as such without any further purification. Kerosene was used as a diluent and all the other chemicals used were of analytical grade.

2.2. Solvent extraction procedure

The extraction and stripping experiments were carried out by shaking equal volumes of aqueous and organic phases in screwed cap bottles for 5 minutes with a wrist action shaker (Burrell, USA). After separation of the two phases, the concentration of Al in the aqueous phase was determined by ICP-OES (Spectro Arcos) and the metal concentration in the organic phase was determined from the mass balance. The concentration of HCl in the aqueous phase was analysed by acid-base titration as mentioned in Vogel (Vogel, 1989) and the concentration of HCl in the organic phase was determined by the difference between aqueous phases before and after extraction. In a majority of cases, two

replicate experiments were carried out simultaneously and the errors associated with the extraction and stripping percentages varied $\pm 5\%$.

3. RESULTS AND DISCUSSION

3.1. Effect of TOA, Alamine 336 and TEHA concentrations on the extraction of HCl

The initial screening experiments were conducted to evaluate the best extractant system for HCl. TOA, Alamine 308, Alamine 336 and TEHA were used as solvents for the extraction of HCl. The composition of the synthetic leach solution of spent HDS catalysts was Al-17.9 g/L and 3 M HCl. The results are described in Fig. 1.

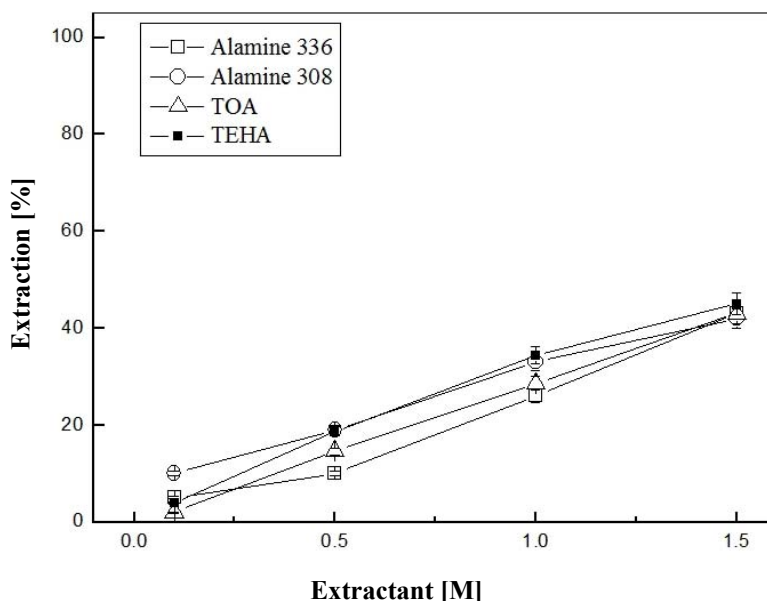


Fig. 1. Effect of tertiary amine based extractant concentration on the extraction of HCl

In all investigated cases, it can be observed that HCl extraction depended upon the extractant concentration and the extraction yield of HCl increased from $\sim 2\%$ to 45% as the extractant (TOA, Alamine 308 and TEHA) concentration increased from 0.1 to 1.5 M. However, under similar experimental conditions, it can be noticed that the tested tertiary amine based extractants such as TOA, Alamine 308 and Alamine 336 exhibited a similar extraction behavior towards HCl, whereas branched chain tertiary amine like TEHA showed somewhat greater extraction tendency towards HCl. Therefore, from these results, it can be said that the steric hindrance offered by the branched alkyl groups of tertiary amine system had no effect on the extraction of HCl at unit phase ratio.

3.2. Effect of O/A phase volume ratio on the extraction of HCl with various extractant systems

In order to attain the quantitative extraction of HCl into the organic phase, the organic to aqueous (O/A) phase ratio was varied with the aforementioned extractants including TOA, Alamine 336, Alamine 308 and TEHA in a kerosene diluent. In this system, the O/A ratio was varied from 1 to 4. The obtained results are displayed in Fig. 2. For TOA, Alamine 336 and Alamine 308 extraction systems, the protonation of the extractant was increased with increasing O/A ratio and attained a quantitative extraction of HCl at an O/A ratio of 4. By contrast, the results obtained by 1.5 M TEHA system showed

that extraction tendency towards HCl increased constantly from 45% to 85% with increasing O/ A ratio from 1 to 4. From these results, it is reasonable to assume that lower extraction efficiency of TEHA might be due to the fact that TEHA is a weaker base than the other tested amine based extractants such as Alamine 336, TOA and Alamine 308. Additionally, it is important to mention here that the formation of the third phase in an organic solution appeared at an O/A ratio of 4 in all extraction systems. As a result, 5% of 1-decanol was used as a modifier to prevent the formation of third phases in all the studied extraction systems. Finally, the obtained results suggest that a tertiary amine based system is effective for the separation of HCl over Al from synthetic chloride solution of spent HDS catalyst.

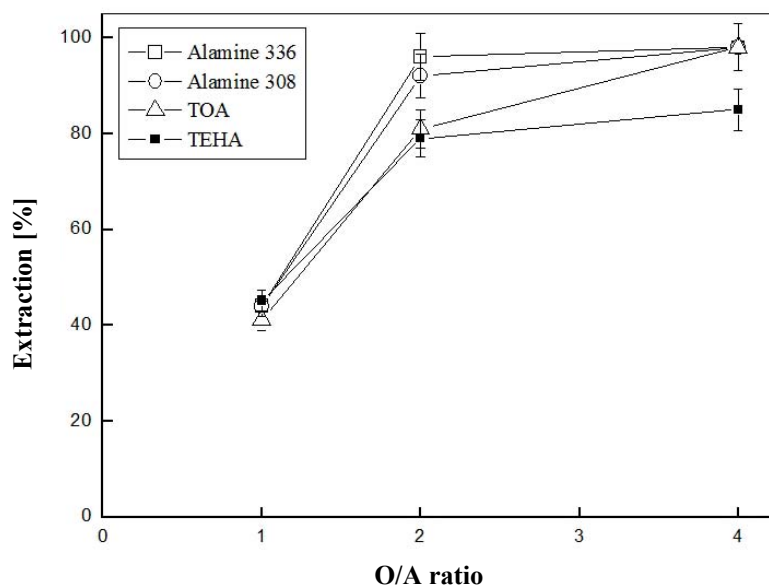


Fig. 2. Effect of organic to aqueous volume ratio on the extraction of HCl with Alamine 336, Alamine 308, TOA and TEHA

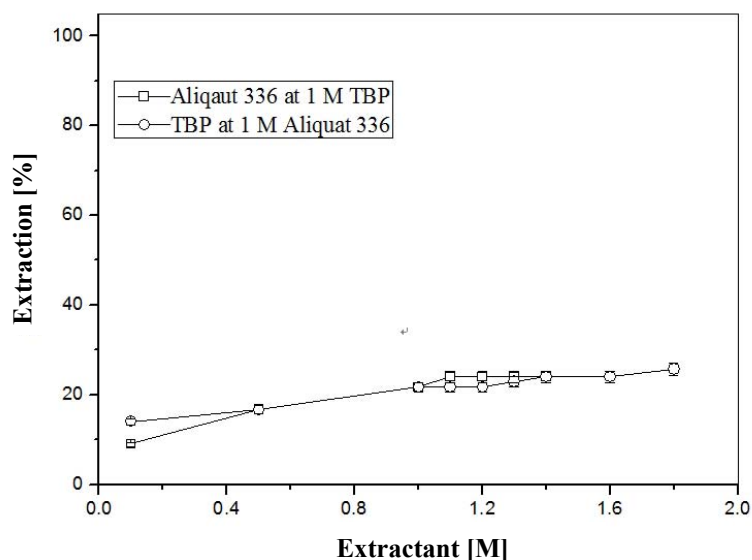


Fig. 3. Variation in the extraction percentage of HCl with the concentration of a constituent in the mixture of Aliquat 336 and TBP

3.3. Extraction of HCl with a mixture of Aliquat 336 and TBP

Literature survey indicates that quaternary ammonium salts can extract HCl from concentrated chloride solutions (Good et al., 1963). In addition, some studies reported that TBP was used for the extraction of

acid (Sarangi et al., 2006). Therefore, in the present study, the effect of the variation in the concentration of Aliquat 336 or TBP in the mixture of these two extractants was investigated. Fig. 3 shows that no significant increase of HCl extraction was observed by varying Aliquat 336 concentrations from 0.1 to 1.5 M at a constant proportion of TBP. By varying TBP concentration from 0.1 to 1.8 M along with 1 M Aliquat 336, a similar extraction behavior of HCl was noticed. Considering the results obtained in this study, it can be concluded that the mixture of Aliquat 336 and TBP system is not suitable for the extraction and separation of HCl from synthetic chloride leach solutions.

3.4. The dependence of HCl extraction on extractant concentration

It is well known that tertiary amines have the capability towards HCl extraction due to their strong interaction between the corresponding reagents (Sinha et al., 2010). However, the stripping of HCl from these organic phases is difficult. Therefore, TEHA, which has medium strength, could provide relatively effective extraction towards HCl and stripping from loaded organic phase. Additionally, Tait also reported that a mixture of tertiary amine and acidic cationic extractant could be efficient for HCl extraction and its recovery from loaded organic solutions (Tait, 1993). Therefore, in view of extraction and stripping of HCl, a mixture of TEHA with cationic extractants was analysed in order to investigate its extraction performance towards HCl. The results are summarised in Fig. 4. Under the given set of experimental conditions (see Fig. 4a), the extraction percent of HCl increased from 4 to ~50% with increasing TEHA concentration up to around 1.5 M even along with 0.1 M cationic extractants (D2EHPA, PC 88A and Cyanex 272) in all experimental cases. A similar type of experiment was carried out by varying cationic extractant concentration from 0.05 to 0.3 M at a constant concentration of TEHA as 1.5 M. As is shown in Fig. 4b, the percent extraction of HCl over Al was constant (~50%) in the studied concentration of cationic extractant along with 1.5 M TEHA. Based on these results, it can be said that the use of cationic extractant along with TEHA did not show any effect on the extraction of HCl. Therefore, the results clearly show that the TEHA extractant is the best for HCl extraction from acidic aqueous feed solutions.

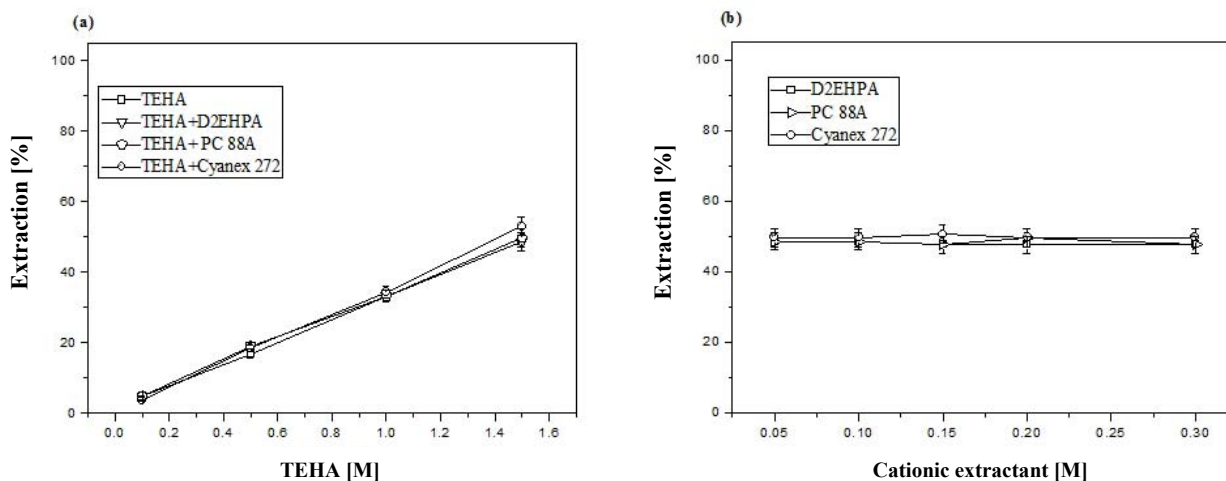


Fig. 4. Effect of mixture of extractants on the extraction of HCl. (a) Effect of TEHA concentration in its mixture with cationic extractants (0.1 M), (b) Effect of the concentration of cationic extractant along with 1.5 M TEHA

3.5. Extraction equilibrium curve of HCl

In order to determine the number of theoretical stages that are required in continuous experiments at a chosen volume phase ratio, an extraction isotherm was obtained by varying O/A volume ratios from 1 to 7 at a constant temperature (ambient temperature) with 1.5 M TEHA. The extraction equilibrium

curve results are presented in Fig. 5. The extraction equilibrium curve shows that 3 stages are necessary for maximum extraction of HCl to the organic phase at an O/A phase ratio of 4.8.

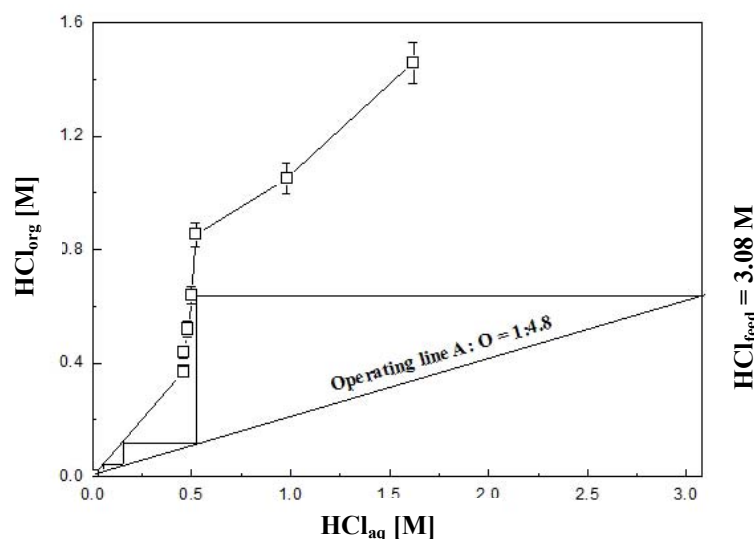


Fig. 5. Extraction isotherm of HCl with 1.5 M TEHA in kerosene diluent

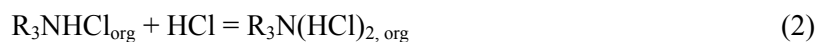
3.6. Identification of the solvent extraction reaction of HCl by TEHA

TEHA is a sort of tertiary amine. It was reported that tertiary amine (R_3N) forms a strong amine salt with hydrogen ions. The bonding between amine and hydrogen ions is so strong that amine salts remain protonated while exchanging anions. The solvent extraction reaction of HCl by amines can be represented as



where subscript org represents the organic phase.

When the amount of HCl is in excess to amine, a double amine salt can be formed as follows (Alguacil et al., 1997; Yakubu et al., 1987).



The extraction behavior of HCl by TEHA was investigated by varying the initial concentration of HCl to 7 M. In these experiments, the concentration of TEHA was kept at 1.5 M and the results are shown in Fig. 6. When the initial concentration of HCl was lower than 0.3 M, the extraction percentage of HCl was negligible. This indicates that some amount of HCl should be present in the aqueous phase for extraction to occur. The extraction percentage of HCl increased linearly with the increase of HCl concentration to 1.5 M and then decreased rapidly with a further increase of HCl concentration. From Fig. 1, it may be inferred that one mole of TEHA is necessary to extract one mole of HCl.

Extraction experiments were conducted by varying the initial concentration of HCl and TEHA and the results are shown in Fig. 7. The extraction percentage of HCl was increased with the increase of TEHA concentration when the initial concentration of HCl was fixed. When the initial concentration of HCl was 1.02 and 3.06 M, there was little difference in the extraction percentage of HCl with TEHA concentration. However, when the initial concentration of HCl was 5.18 M, the extraction percentage of HCl was reduced compared to the results obtained from 1.02 and 3.06 M HCl solutions. In order to identify the solvent extraction reaction of HCl by TEHA, the extraction data shown in Table 1 were analysed. Except the extraction data obtained from 1.02 M HCl, the concentration of HCl extracted into organic phase is equal to the initial concentration of TEHA. When HCl was in excess to TEHA, one

mole of HCl was extracted by one mole of TEHA. Therefore, it may be concluded that Eq. (1) is responsible for the extraction reaction of HCl by TEHA in the HCl concentration range to 5 M.

Table 1. Effect of initial extraction conditions on the concentration of HCl extracted into TEHA.(Unit:molarity)

TEHA, [M]	Initial HCl, [M]	HCl, [M] organic phase	Initial HCl, [M]	HCl, [M] organic phase	Initial HCl, [M]	HCl, [M] organic phase
0.3	1.02	0.02	3.06	0.26	5.18	0.28
0.5	1.02	0.08	3.06	0.46	5.18	0.56
0.7	1.02	0.22	3.06	0.64	5.18	0.72
1.0	1.02	0.34	3.06	0.92	5.18	1.08
1.5	1.02	0.5	3.06	1.42	5.18	1.5
2.0	1.02	0.62	3.06	1.86	5.18	2.06

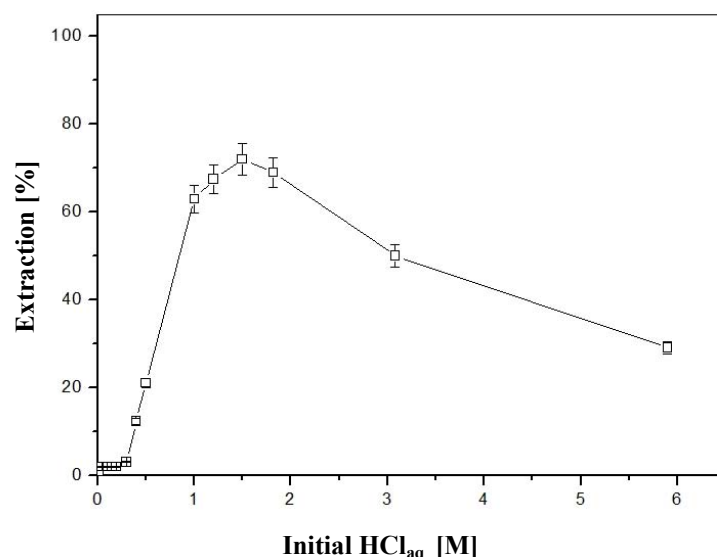


Fig. 6. Variation in the extraction percentage of HCl by 1.5 M TEHA with the initial concentration of HCl

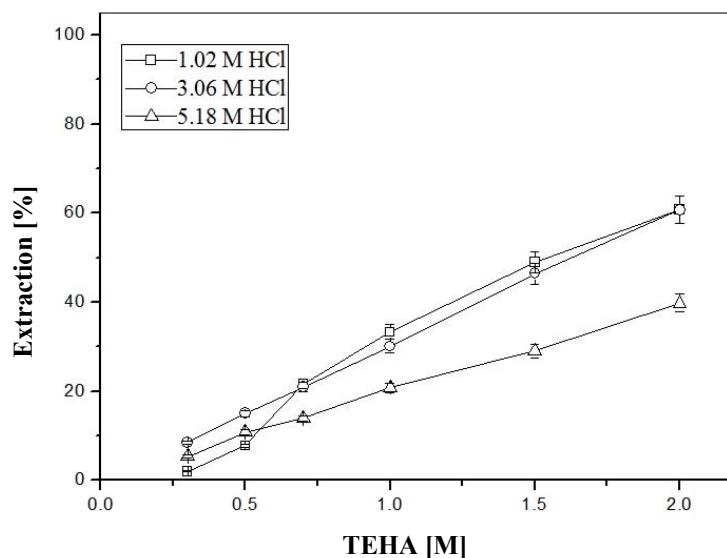


Fig. 7. Effect of TEHA concentration on the extraction of HCl from several initial concentrations of HCl

3.7. Stripping of HCl from loaded organic phases

Literature results show that water is the best option for stripping of HCl from loaded TEHA phase (Palant et al., 1973). Therefore, in the present study, the stripping of HCl was performed with distilled water from loaded Alamine 336, TOA, TEHA and Alamine 308. From the obtained results (see Table 2), it was observed that only 2% of HCl was stripped from the loaded TOA, Alamine 336, and Alamine 308. The reason for lower stripping efficiency of HCl from these amines is due to a strong interaction between these extractants and HCl. It was reported that adding cationic extractant to amines, such as TOA and Alamine 336, has a positive effect on the stripping of HCl from the loaded amines (Sinha, et al., 2010). Unlike TOA, Alamine 336, and Alamine 308, the stripping of HCl was higher from loaded TEHA phases. This phenomenon may be due to the fact that TEHA is an amine with weak and medium strength and its bond strength towards HCl is also weaker than the other tested amines. Therefore, stripping of HCl from loaded TEHA is easier than that from loaded TOA and Alamine 336.

Table 2. Variation in the stripping percentage of HCl from the loaded organic phase

Extractant	Stripping, %
TOA	1.6
Alamine308	2.0
Alamine336	1.2
TEHA	55.0

In order to investigate the effect of adding cationic extractant to TEHA on the stripping of HCl, stripping experiments were carried out for the loaded TEHA alone and TEHA mixed with cationic extractant. In these experiments, the aqueous to organic volume ratio was varied from unity to 3 by using water as a stripping agent. Fig. 8 shows that adding cationic extractant to TEHA has little effect on the stripping of HCl. At the A/O ratio of 3, most HCl was stripped from the loaded TEHA. It may be concluded that among the tested amines in this study, TEHA is the best extractant for the separation of HCl from the chloride leach solution. Moreover, HCl can be stripped from the loaded TEHA even in the absence of cationic extractant.

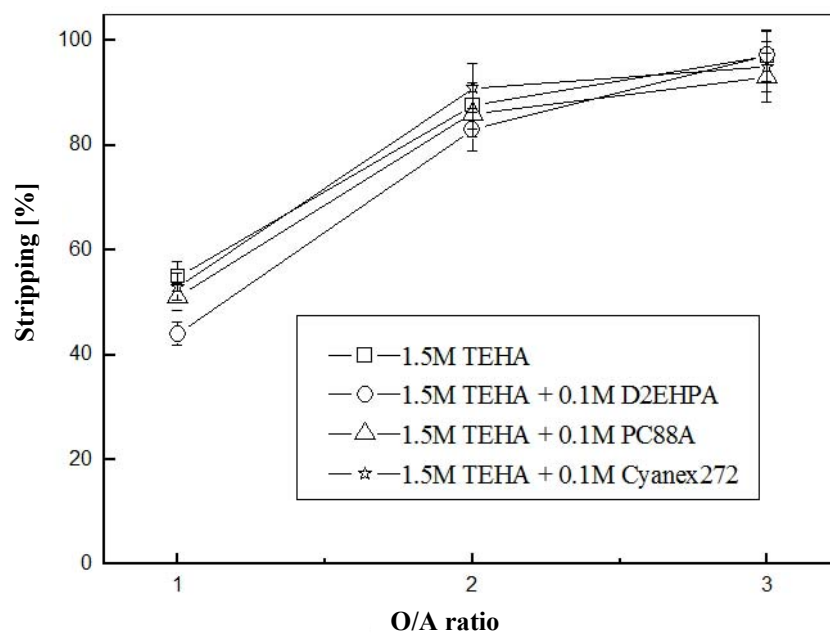


Fig. 8. Effect of aqueous to organic volume ratio on the stripping of HCl from the loaded organic by water

3.8. Stripping equilibrium of HCl

In order to determine the number of stages required to strip HCl from the loaded TEHA at a chosen volume phase ratio, stripping equilibrium curve was constructed. For this purpose, an experiment was performed by using water as a stripping reagent at different O/A ratio from 1 to 5. The obtained stripping equilibrium curve was described in Fig. 9. As can be seen from this figure, three stages are required for maximum stripping of HCl from loaded 1.5 M TEHA phase.

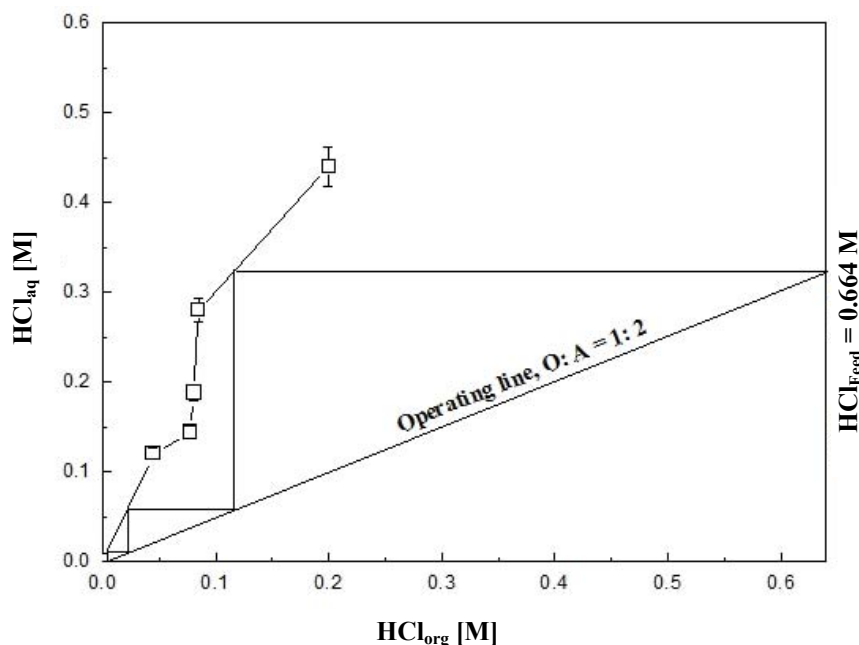


Fig. 9. Stripping isotherm for recovery of HCl from loaded TEHA phase

4. CONCLUSIONS

In order to recover HCl from chloride leach solutions of spent HDS catalysts, solvent extraction and stripping experiments were performed. For this purpose, several amine based extractants (TEHA, Alamine 336, Alamine 308 and TOA) and their mixtures with solvating (TBP) and cationic extractants (Cyanex 272, D2EHPA and PC 88A) in kerosene were investigated. In all extraction systems, the percent extraction of HCl increased with increasing extractant concentration and O/A ratio. All tertiary amine based extractants exhibited more or less similar extraction behavior towards HCl. By contrast, a mixture of Aliquat 336 and TBP showed lower extraction tendency towards HCl, when compared with tertiary amine based system. The stripping percentage of HCl from the loaded amines except TEHA was too low and consequently complete stripping of HCl was difficult. However, HCl was easily stripped from the loaded TEHA compared with other amine extractants tested in this study. Adding cationic extractants to TEHA was found to have a negligible effect on the extraction and stripping of HCl. Solvent extraction reaction of HCl by TEHA was identified from the extraction data which were obtained by varying the concentrations of HCl and TEHA. McCabe-Thiele diagram for the extraction and stripping of HCl by TEHA was constructed.

This work was supported by a grant operated by KEITI of the Ministry of Environment of Korea. The authors would like to thank for the financial support.

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Received 23 December 2012

Received in revised form 06 February 2013

Accepted 14 February 2013