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A review of acid recovery from acidic mining waste solutions using solvent extraction

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Abstract

The minerals industry is increasingly being forced by regulatory and cost pressures to reduce the amount of liquid acidic waste they produce. This requires a strong focus on waste reduction by recycling, regeneration and reuse. Four mineral acids were examined for recovery from waste acidic solutions including H₂SO₄, HNO₃, HCl, and H₃PO₄. The selection of the optimal extractant for acid recovery was based on extraction, stripping and scrubbing efficiencies. The extractants suitable for the recovery of H₂SO₄ and HCl are in the order of TEHA > Cyanex 923 > TBP > Alamine 336. TEHA has the highest degree of acid extraction and stripping compared to Cyanex 923 and almost 99% of the acid can be stripped. Alamine 336 can extract higher acid (for H₂SO₄ and HCl systems) than Cyanex 923 and TBP. However loaded acid for Alamine 336 system cannot be stripped using water at 60°C. For the recovery of nitric and phosphoric acids from acidic waste effluents, TBP was the best option. This work clearly demonstrates that extractant suitable for acid extraction may not be suitable for its recovery. However such extractant may be applied for the removal of acid from any waste acidic solution sacrificing the back extraction of the loaded acid. The effective implementation of options for acid recovery was examined to improve sustainability in the mineral industry.

Key words: Solvent extraction, Acid recovery, Waste solutions

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1. Introduction

1.1. Mineral acids and hydrometallurgical applications

Mineral acids such as H_2SO_4 , HNO_3 , HCl and H_3PO_4 are widely used in hydrometallurgical processes in various operations such as leaching, etching, electrowinning and electro-refining [1-8]. As a result, large amounts of acidic waste solutions are generated, causing environmental problems. These acidic waste streams sometimes contain heavy metals such as Ni, Co, Cu, Zn, Cd, Pb, etc. making it difficult to be disposed of [1-5]. Other acidic waste solution also considered is acid mine drainage (AMD), which is today the biggest environmental threat from mining activities [1]. Until recently, the practice for treatment of acid-containing effluents from waste solutions and metallurgical processes has been neutralization of which large amounts of alkaline reagents such as calcium carbonate; calcium oxide; calcium hydroxide; magnesium hydroxide and sodium hydroxide are used [1-3]. This also produces a sludge containing heavy metal compounds that must be disposed of [1-8]. Furthermore, valuable acid is lost during neutralization processes which could instead be recovered and reused. Industries are now giving serious consideration to acid recovery considering its economic and environmental benefits [1-3]. Acids are extensively used for hydrometallurgical treatment of minerals and metals. The recovery of acid will not only benefit the environment and the economics of the operation, it can also provide a secondary source of valuable metals, and extend the life of the acid used [1-4]. Furthermore, recycling of acid would mean elimination of the safety problems associated with its transport to the site. H_2SO_4 , HCl , HNO_3 , and H_3PO_4 are acids of interest because that they are commonly used in mineral processing and hydrometallurgical extractions [1-4]. Thus waste can be minimised by linking this acid demand to most hydrometallurgical applications which generally use acid. A closed loop process is the ultimate aim, where the resources such as acid and metals from hydrometallurgical waste streams are recycled and reused.

1.2. Technologies for acid recovery

Ion exchange (IX) and solvent extraction (SX) are well established technologies to separate and purify metals [1-7]. While research into acid recovery is a new area of application. Acid can be recovered using IX by selectively adsorbing the hydronium (H^+) ion on an anion exchange resin [1]. IX can recover some of the acids from discharge waters containing, for example, ferric chloride or ferric sulphate [1-3]. In most cases the acid can be reclaimed at least approximately half of the original concentration [1]. The economics of ion exchange is driven mostly by the cost of resin regeneration chemicals, which increases proportionately with the increase in the amount of dissolved salts in the water [1, 2]. However, the resin

regeneration costs decrease significantly when cheaper regeneration chemicals is used [1]. While IX is good for removing acids or metals for reuse, an additional concentration step is also needed. In comparison to SX, IX also requires the addition of chemicals to regenerate the exchange beds [1-3].

SX is a well-known treatment method which is used to purify and recover resources (metals) from waste solutions [1-8]. SX is the distribution of a solute or solutes between two immiscible liquids or phases. It commonly takes place with aqueous and organic solutions. The organic phase usually consists of extractant dissolved in diluent, but in some cases, a modifier, and a synergistic agent may be required [4]. The modifier is added to improve the physical properties of the system (e.g., to cause phase disengagement after mixing the two phases) while the synergistic agent is used for improvement and enhancement of extractant [1-7]. Nowadays, a very large number of stable solvents (extractants) are available for use in hydrometallurgy, with potential for excellent selectivity for a particular metal ion, coupled with advances in engineering and increasing demands for higher purity products and more environmentally friendly routes. The general requirements of an extractant suitable for use in commercial solvent extraction are as follows [1-7].

- Relatively inexpensive;
- Low solubility in the aqueous phase;
- Will not form stable emulsions with an aqueous phase when mixed, for example a mixer;
- Have good coalescing properties when mixed with a diluent (and modifier if necessary);
- High metal loading capacity; and
- Easily stripped of the loaded metal

SX is economically viable when both the solute concentration and waste water flowrates are high, but uneconomical when the concentration of the contaminant to be recovered is very low [1-4]. However, most acidic waste streams normally contain low concentrations of acids in the range of 10-20 g/L [1-3]. Furthermore, concentrating dilute acidic solution through evaporation faces a major challenge of consumption of large amounts of energy. To achieve a high concentrated solute, Membrane Distillation (MD) or other suitable techniques maybe applied.

MD is a thermally driven membrane process that can utilise waste heat or solar thermal energy more conveniently [8-11]. It is a new technology which offers advantages of low energy consumption and operating at low temperature with high efficiency to recover fresh water and concentrate the acid and metals [3, 8-11]. After concentrating the feed solutions, the acid and valuable metals could be recovered using SX as shown in Fig 1. The concept to combine SX and MD for H₂SO₄ and by-product recovery from acidic mining waste solution was examined in our previous work [1-3]. In bringing the two processes together, clean water is produced for reuse, and then acid is concentrated and recovered also for reuse leaving only concentrated brine rich in valuable metals.

Other technologies for acid recovery includes, electro dialysis, nanofiltration and biosorption. The selection of the optimal technology for acid recovery is complex and no single process fits all scenarios. The optimal solution might reside in the combination of different technologies resulting in a process able to exploit the respective advantages and overcome the weaknesses of each technology [1-3, 8-18]. However, this study is focused on solvent extraction for acid recovery.

A review of acid recovery using SX is not widely reported in the literature. A number of extractants including TEHA (tris-2-ethylhexylamine), Alamine-336 (a mixture of trioctyl/decyl amines), TBP (tri-butyl phosphate) and Cyanex 923 (a mixture of alkyl phosphine oxides) have been reported in the literature to be able to recover various acids [1-7]. However, there is no study in the literature comparing the performance of different extractants for the recovery of acids such as H_2SO_4 , HNO_3 , HCl , and H_3PO_4 . The extractants are compared taken into account the maximum workable concentration of each solvent for optimal recovery. Furthermore, for the development of a process for acid recovery from hydrometallurgical plants, a systematic study on the extractants is necessary to understand its viability to recover acid. This paper presents a comprehensive review of the current extractants suitable for acid recovery from acidic waste solutions. Particular attention has been given to the comparison of the performance of different organic systems with possible commercial applications.

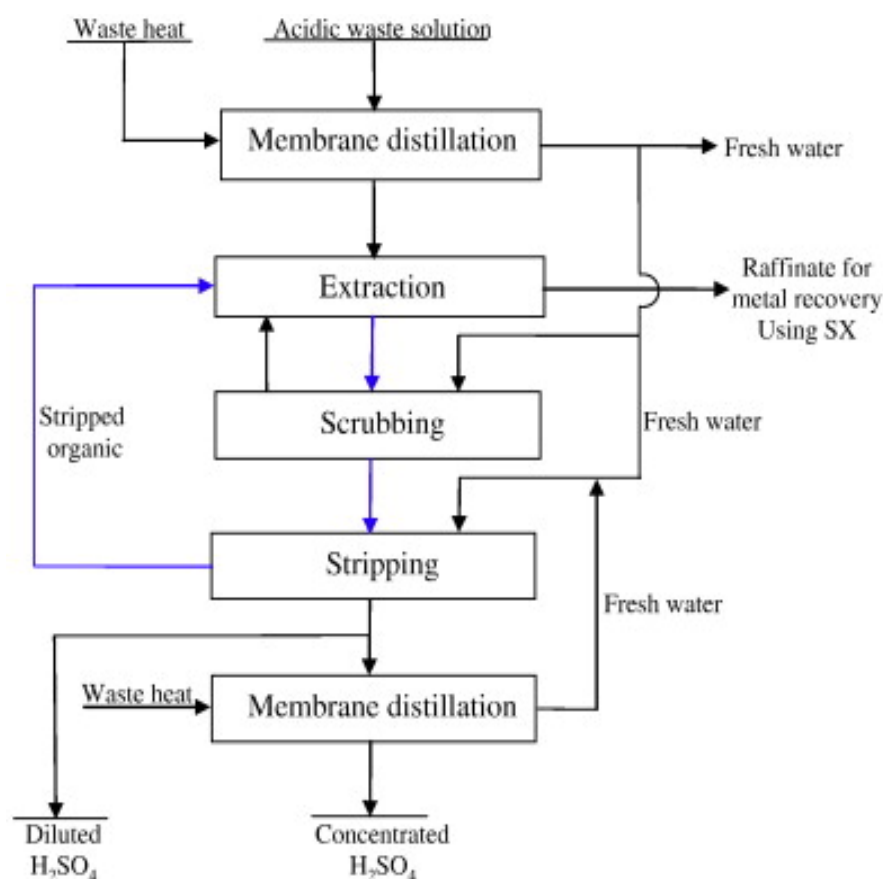


Fig 1: Flowsheet to recover water, H_2SO_4 and metal values from acidic mining waste solutions. Based on Kesime et al. [3]

2. Identifying acidic waste waters for acid recovery

The acidic waste solutions considered are acidic waste solutions from hydrometallurgical plant and acidic mine waters

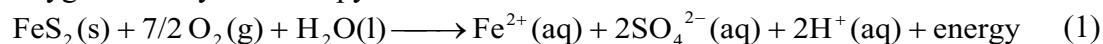
2.1. Generation of waste acidic mine waters

Acidic mine waters is defined as low pH, high metal and high sulphate-bearing waters, formed when rocks and sediments containing sulphide minerals are exposed to the atmosphere under an oxidising environment [1-4, 8-11]. Major occurring sulphide minerals, such as pyrite and pyrrhotite, produce sulphuric acid (H_2SO_4) when oxidised in the presence of certain metallogenic bacteria [1-3]. Pyrite oxidation can occur in both biotic and abiotic or inorganic chemical oxidation process. Biotic and abiotic degradation can be caused by oxygen (i.e. direct oxidation) or by oxygen and iron (i.e. indirect oxidation) [1]. Iron, both in its divalent and trivalent state, plays a central role in the indirect oxidation of pyrite. Different pyrite oxidation mechanisms can be summarized as follows:

- oxidation by oxygen (abiotic direct oxidation);
- oxidation by oxygen in the presence of microorganisms (biotic direct oxidation);
- oxidation by oxygen and iron (abiotic indirect oxidation);
- oxidation by oxygen and iron in the presence of microorganisms (biotic indirect oxidation)

Stoichiometric chemical reactions are commonly used to describe these different oxidation mechanisms. In the abiotic and biotic direct oxidation processes oxygen directly oxidizes pyrites.

Oxygen directly oxidizes pyrite:

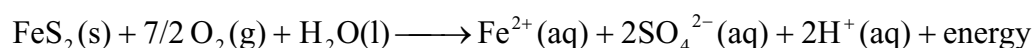


However, It is generally accepted, that pyrite oxidation is primarily accomplished by indirect oxidation. The indirect oxidation of pyrite involves the chemical oxidation of pyrite by oxygen and ferric iron (Fe^{3+}). The following chemical equations show the generally accepted sequence for such indirect oxidation of pyrite:

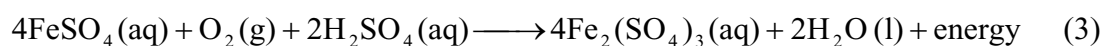
Oxidation of pyrite by oxygen (Step 1):



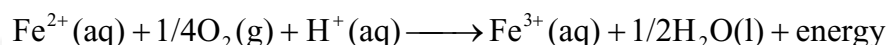
or



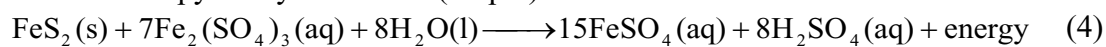
Oxidation of ferrous iron to ferric iron (Step 2):



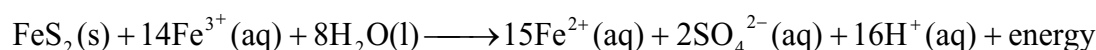
or,



Oxidation of pyrite by ferric iron (Step 3):



or,



Equations 2, 3, and 4 release energy. Indirect pyrite oxidation is exothermic. In the initial step (Equation 2), pyrite is oxidized by oxygen to produce dissolved ferrous iron (Fe^{2+}), sulphate and hydrogen ions. The dissolved iron sulphate ions cause an increase in the total dissolved

solids of the water. The release of hydrogen ions with the sulphate anions results in an acidic solution unless other reactions occur to neutralize the hydrogen ions. The second step (Equation 3) represents the oxidation of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}) by oxygen and occurs at a low pH. In the third reaction (Equation 4) pyrite is oxidized with the help of Fe^{3+} generated in Equation 3. Thus, Fe^{3+} acts as the oxidizing agent of pyrite. The oxidation of pyrite by Fe^{3+} in turn generates more Fe^{2+} . This Fe^{2+} can then be oxidized to Fe^{3+} by oxygen via Equation 3. The Fe^{3+} in turn oxidizes pyrite via Equation 4, which in turn produces more Fe^{2+} , and so on. Equations 3 and 4 form a continuing cycle of Fe^{2+} conversion to Fe^{3+} and subsequent oxidation of pyrite by Fe^{3+} to produce Fe^{2+} . The above reactions describe the weathering of pyrite, highlight the need for water and oxygen, and illustrate the production of H_2SO_4 . The oxidation of sulphide minerals does not only create acid, but it also liberates metals and sulphate into waters and accelerates the leaching of other elements from gangue (spent) minerals. An example of acidic mine waters is acid mine drainage (AMD).

2.2. Acid Mine Drainage (AMD)

The most acidic waters known, other than industrial solutions, are AMD. AMD can have a range of constituents, but the major cations are usually Fe and Al and the main anion is SO_4 [1-4, 12]. The pH can range from -2.5 to 5 [7-12]. Table 1 illustrates a broad range of pH (from -2.5 to 4) and solute concentrations of different acidic mine waters [1, 7-12]. The lowest-pH sample is from Iron Mountain, a massive sulphide deposit that was once the largest copper producer in California. The ultra-acidic mine waters from Iron Mountain are produced by the oxidation of large sulphide masses consisting of $\sim 95\%$ pyrite. A considerable amount of heat is also produced during oxidation, which drives evaporation of these waters, further concentrating them [12]. Another example of poor mine water quality that resulted to AMD is the waste rock dumps at the Mt. Lyell copper mine in Queenstown, Australia [1]. The waste rock dumps and mine workings are significant contributors to AMD, leading to waste leaching into the Queen River [1]. It is estimated that AMD in this region will continue for another 600 years with the present copper load being 2000 kg per day [1, 2]. In extreme cases, AMD may even continue for thousands of years [1]. Other effluent generated from mining and metallurgical processes includes tailing waters. When such acid-laden waters reach receiving water bodies, such as lakes, streams or aquifers, the waters can cause undesirable turbidity and sedimentation, or their chemical composition may have toxic effects on plants and animals.

Table 1: Composition (in mg/L) of a range of acidic mine waters with pH -2.5 to 4 [1, 12]

Composition	Iron Mountain AMD, California	Leviathan mine AMD, California	Mount Lyell AMD Tasmania	Straight Creek, Natural Acid Rock Drainage, New Mexico	Cameron Mine, Coal Mine Drainage, Pennsylvania
pH	-2.50	1.85	2.40	2.98	4.0
Specific conduct(- s		12900		2920	389
SO ₄ (mg/L)	760000	11200	6430	1950	510
AL (mg/L)	1420	623	760	83.1	5.4
Ni (mg/L)	3.7	13.0		0.706	0.24
Cu (mg/L)	4760	9.64	82	1.55	0.0014
Fe (mg/L)	111000	2510	777	44.70	49.0
Mn (mg/L)	23	9.32	46.0	20.0	6.1
Zn (mg/L)	23500	2.62	728	7.30	0.36
Pb (mg/L)	11.9		27.4		
Co (mg/L)	5.3	5.07		0.301	0.18
Cl (mg/L)		9.2		7.5	5
Cd (mg/L)	211	0.338	3.71	0.038	0.0017

2.3. Acidic solutions from hydrometallurgical plant

HCl, HNO₃ and H₃PO₄ are also used commonly used in various hydrometallurgical applications. Some examples of industrial applications were HCl, HNO₃ and H₃PO₄ can be recovered are as follows (1) recycling of Platinum-group metals (PGMs) performed in hydrochloric acid media, (2) the reprocessing of used nuclear fuels performed in HNO₃

media, (3) Production of purified H_3PO_4 (e.g. Rayon process) by liquid-liquid extraction of phosphoric acid.

2.3.1. HCl industrial applications and case for acid recovery

The hydrometallurgical recovery of PGMs is usually carried out in acidic chloride solution, as these media dissolve PGMs well and allow high recovery performances [13]. PGMs are valuable and considered critical raw materials, mainly due to their scarcity in the Earth's crust, and also to their difficult replacement in most applications, such as fuel cells, electronics, and catalysis [13]. To allow the sustainable continuous supply for actual and emerging applications, recycling of HCl and PGMs-containing wastes is crucial. Furthermore, HCl is also used in other applications such as etching, electrowinning and electro-refining [1-4]. All these processes may generate and discharge effluents containing free HCl and precious metals. SX is one of the most successful unit operations that can be used for separating PGMs and HCl from chloride leach solutions, showing remarkable efficiency and selectivity patterns [4].

2.3.2. HNO_3 applications and case for acid recovery

HNO_3 is used as a dissolving agent in nuclear, chemical and metallurgical industries [14-17]. At the present time, all plants for reprocessing spent nuclear fuels use the Plutonium Uranium Redox Extraction (PUREX) process for recovering the uranium and plutonium that are present in these fuels [14]. HNO_3 is also in the manufacture of silicon wafer, where chemical etching methods use mixed acids to remove deterioration generated in wafer cutting and grinding process of single crystal silicon [1-4, 17-32]. All these processes may generate and discharge a huge quantity of effluents containing free nitric acid and different metal nitrates. Disposal of effluents containing high nitrate concentration is a serious and global problem. Nitrate contamination in drinking water causes methemoglobinemia, a disease in which oxygen-bearing capacity of blood is reduced, which is called Blue-Baby-Syndrome.

2.3.3. H_3PO_4 applications and case for acid recovery

Phosphoric acid (H_3PO_4) is an important industrial material and is widely used to produce phosphate fertilizers, food ingredients, and metal treatment products [16]. There are two common industrial techniques to produce phosphoric acid. These are called thermal and wet process technologies [16]. Generally, the thermal process technology results in a good product quality however at an expense of larger energy consumption and higher costs [16]. In the preferred wet process technology, the phosphate rock is leached using acid and the energy consumption of the process is lower. The Wet phosphoric acid (WPA) is produced by leaching phosphate rocks rich in calcium phosphate minerals such as apatite or francolite. About 75% of the global phosphoric acid production involves the use of sulfuric acid for leaching phosphate rocks [16]. Equation 5 is showing the leaching calcium phosphate minerals using H_2SO_4



During the leaching of phosphate rock, some other ore components also are dissolved in sulfuric acid, resulting in contamination of the phosphoric acid. Various techniques, some of which include adsorption, chemical precipitation, IX and SX, have been proposed to purify the phosphoric acid produced by wet process technology [1-4]. Because of the low cost and high quality output, SX is the most widely applied to purify the wet process phosphoric acid [16]. Phosphoric acid also used in semiconductor etching process [1-4, 17, 18]. All these processes generate large volume of acid which can be recovered and reused. The following section outline the rationale for the selection of extractants suitable for acid recovery.

3. Extractants for acid recovery

List of commercial extractants together with their manufacturers and common uses are given in the literature [19]. The extractants for the acid recovery were compared taken into account the maximum workable concentration of each solvent for optimal acid recovery. The selection of the optimal extractant for each acid is based on extraction, stripping and scrubbing efficiencies.

3.1. H₂SO₄ recovery using different extractants

The common extractants for H₂SO₄ recovery includes TEHA, Alamine 336, Cyanex 923, and Tributyl phosphate (TBP) [1-7].

3.1.1. TEHA

TEHA is a tertiary amine with a molecular formulae of (CH₃(CH₂)₃CH(C₂H₅)CH₂)₃N [1-4]. The physical and chemical properties of TEHA is well described in the literature [18]. Several authors have reported the use of TEHA for H₂SO₄ recovery from acidic mining waste solutions [1-7, 18-23]. Agrawal et al. [6] reported on recovery of H₂SO₄ from zinc electrowinning bleed stream containing 173.5 g/L of H₂SO₄ using 75% TEHA in kerosene. The results shows that TEHA had a very good acid extraction capacity even in the presence of a large amount of zinc. The extraction of H₂SO₄ increased with the increasing TEHA concentration. The plot of Log [H₂SO₄] vs. Log [TEHA] gave straight line with a slope value of 1.063, indicating that 1 mole of TEHA extracted 1 mole of sulphuric acid. Three extraction stages were required to extract 90% acid at an A: O ratio of 1:2 based on McCabe Thiele diagram. In a similar study, Kesime et al. [3] reported using 50% TEHA, 40% octanol in Shellsol A150. More 99% of H₂SO₄ was extracted after three successive extraction at room temperature and O: A ratio of 2 at 22 °C. The stripping and extracting kinetics results reported, shows that both were very fast and about between 1-2 mins [1-3]. It was reported that the TEHA can effectively recover H₂SO₄ even in the presence of metals in the waste solutions and only small amount of metals were entrained. After scrubbing the loaded organic solution using water in a single contact, almost all the entrained metals were removed [1-3].

Agrawal et al. [6] investigated the effect of TEHA concentration in octanol on acid extraction. It was reported that the acid extraction increased with the increase in the relative amount of TEHA in the organic solution and reached a maximum depending on the initial acid concentration in the feed solution. With the TEHA concentration of 64.5%, the highest

acid extraction of 58% was obtained at O: A ration of 1, but the organic solution started to separate into two phases. Therefore, 43% TEHA in octanol was considered better option with a maximum acid extraction of 49% at an initial acid concentration of 150 g/L [6]. Haghshenas et al. [24] reported that when octanol was added as a modifier in the organic solution containing TEHA, the acid extraction was significantly improved. The effect was more significant when the acid concentration was less 150 g/L [6, 24]. It was also reported that the presence of octanol in the organic phase improved acid extraction, and also prevented third phase formation although octanol itself did not extract sulphuric acid [3, 6, and 24]. Similar observation was reported in the work of Eyal et al. [22] and Gottliebse et al. [25].

Kesieme et al. [3] examined the effect of diluents on H₂SO₄ extraction. The diluents are Shellsol A150 (100% aromatic), Shellsol2046 (19% aromatic and 81% aliphatic) and Shellsol D70 (100% aliphatic). It was found that in terms of diluents type, the acid extractions improved in the order of Shellsol A150 > Shellsol 2046 > Shellsol D70, indicating that Shellsol A150 performed best. In the case of a modifier, octanol achieved better performance compared to isodecanol. The effect of diluents such as n-dodecane, n-heptane, toluene and benzole on extraction conditions was examined by Haghshenas et al. [24]. It was reported that no significant effect was observed on the acid extraction when kerosene was substituted by other types of diluents.

Gottliebse et al. [25] reported that the increase in temperature slightly lowered the H₂SO₄ extraction. The temperature effect was more significant at lower acid concentrations in the feed solution. The acid extraction increased rapidly when the acid concentration in the feed solution increased to 1 M and then it remain constant when the acid concentration was over 1 M. In a similar study, Kesieme et al. [3] reported that with the increase in temperature from 22 °C to 60 °C the acid extraction decreased from 82% to 72%.

A comparison was made between TEHA and Cyanex 923 and also the feasibility of H₂SO₄ recovery using both extractants was considered in terms of thermodynamics [24]. It was reported that the relative amount of the reaction enthalpy is more sensitive with TEHA than Cyanex 923. Therefore, stripping of sulphuric acid from TEHA is more readily than from Cyanex 923 [24]. It was concluded that TEHA may be more feasible for recovery of H₂SO₄ from aqueous media than Cyanex 923 [1-3, 24-26].

Agrawal et al. [6] suggested that the extraction reaction of sulphuric acid by TEHA proceeded as in Equation 6:

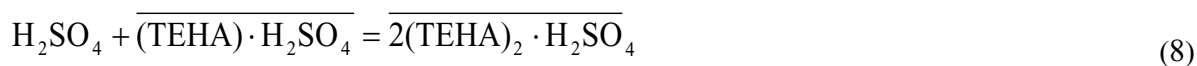


Where the top bar denotes compounds in the organic solution. The authors reported that the extraction was exothermic in nature and hence an increase in temperature decreased the uptake of acid by the solvent. Similar observations was reported by Gottliebse et al. [26]. When the acid concentration in the aqueous solution was below 1 M, the reaction between

TEHA and H₂SO₄ proceeded by the formation of amine sulphate complexes where 2 TEHA molecules combined with one H₂SO₄ molecule as shown in Equation 7:



However, when acid concentration was > 1 M, the final product would be amine bisulphate as shown in Equation 8:



Agrawal et al. [6] reported the stripping of acid-loaded organic solutions with different TEHA concentrations using distilled water as shown in Fig. 2. The loaded acid was stripped with hot distilled water at 60°C. Almost 99% of the acid was stripped from the loaded organic solution containing 50% TEHA and 50% kerosene after 4 contacts at 60 °C. When the strip O/A ratio increased from 0.2 to 5.0 the concentration of the acid in the loaded strip liquor increased from 32 g/L to 101 g/L, but the stripping efficiency decreases from 87% to 11%. Three stripping stages were required to strip 87% acid using an O/A of 2:1 based on the McCabe Thiele diagram plotted. Similar results was also reported by Gottlieben et al. [25]. The higher the strip O/A ratio was, the higher the acid recovery which approached the maximum at a strip O/A ratio of 2.1. However, as the strip A/O ratio increased, the acid concentration in the loaded strip liquor decreased.

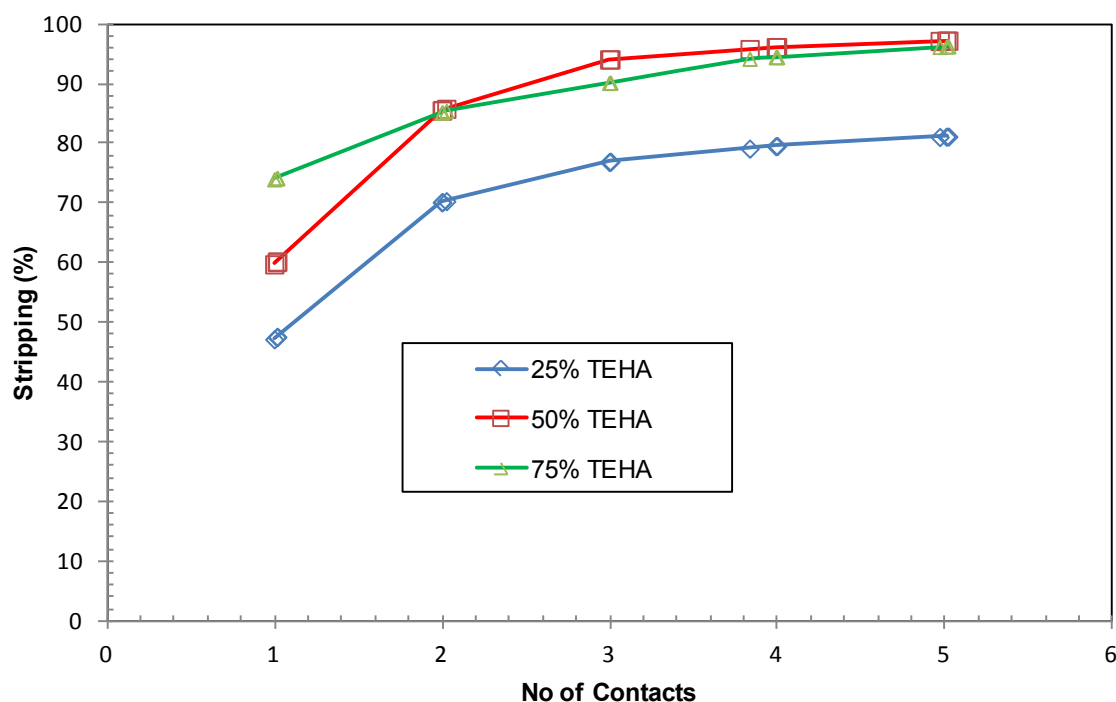


Fig. 2: Stripping of acid from the loaded TEHA in kerosene with different concentrations using A/O ratio of 1:1 at 60 °C. Based on Agrawal et al. [6].

3.1.2. ALAMINE 336

Alamine 336 is a mixture of tri-octyl/decyl amine [1-7]. Agrawal et al. [6] reported the extraction of H_2SO_4 using Alamine 336. It was reported that the extraction of H_2SO_4 increased with the increase in the Alamine 336 concentration. The acid extracted increased from 17 g/L to 37 g/L with the increase in the solvent concentration from 10% to 35% using A/O ratio of 1 in a single contact. After 4 contacts, the loaded acid concentration in the organic solution increased from 40.5 g/L to 80.8 g/L with the increase in the Alamine 336 concentration from 10% to 35%. Phase separation problem was reported when the concentration of Alamine is above 35% (v/v) in kerosene using 10% isodecanol as phase modifier. Similar observation was reported in the literature [1-4]. The author also reported that acid extraction was unchanged using tri-n-butyl phosphate or isodecanol as modifier when keeping other parameters constant, but the phase separation time was shorter using isodecanol [6]. The plot of $\log D$ vs \log (extractant concentration) gave a straight line with a slope value of 0.94, indicating that 1 mole of the extractant extracted 1 mole of acid [6]. The McCabe –Thiele diagram indicated that about 90% H_2SO_4 extraction could be reached with three counter current stages using an A/O ratio of 1:2. Fig 3 is showing the comparative equilibrium data for the extraction of H_2SO_4 using Cyanex 923, Alamine 336 and TBP [27]. Although Alamine 336 showed higher acid extraction than Cyanex 923, the acid extracted could not be stripped. The overall performance indicates that of the two extractant (Alamine 336 and Cyanex 923), Cyanex 923 would be the preferred extractant for H_2SO_4 recovery.

TEHA and Alamine 336 are amine extractants and exhibit similar behaviour in terms of acid extraction while Cyanex 923 is a neutral extractant. Amines are bases that naturally react with and extract acids. Therefore, the extractability for acid with TEHA and Alamine 336 is expected to be stronger than that with the neutral extractant, Cyanex 923. Thus Alamine 336 extractant can certainly be used for the removal of H_2SO_4 from any waste solution sacrificing the back extraction of the loaded acid. TEHA and Cyanex 923 extractant can be stripped of its loaded acid using water at 60 °C and stripping efficiency >99% can be reached depending on the number of stripping stages[1-3]. The reason for the low stripping efficiency of H_2SO_4 using Alamine 336 maybe due to a strong interaction between the extractant and acid, in particular mainly due to increases in steric hindrances offered by the long R-chain structure. TEHA is a base and its bond strength towards H_2SO_4 is also weaker compared to Alamine 336. Therefore, TEHA can easily releases H_2SO_4 when contacted with water.

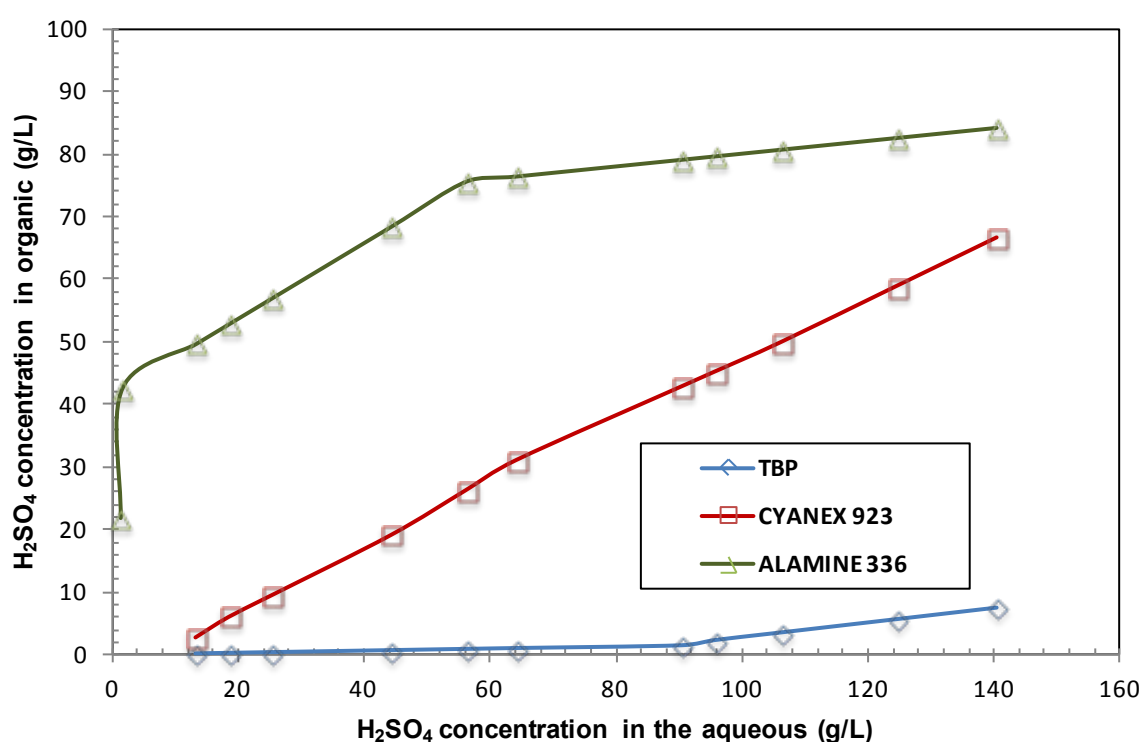


Fig.3: Sulphuric acid extraction distribution isotherms with Alamine 336, Cyanex 923, and TBP. Based on Anon, [27]

Tait [28] investigated the effect of different binary systems on acid extraction. These binary systems consist of amines and organic acids in a 1:1 molar ratio. The following six binary extractant systems were studied: Alamine 336/D2EHPA, Alamine 336/PC-88A, Alamine 336/Cyanex 272, Aliquat 336/D2EHPA, Primene JMT/D2EHPA and Adogen 283/D2EHPA

in Shellsol. The binary system consisting of 50% Alamine 336/D2EHPA in Shellsol AB with an O/A volume ratio of 5:1 was reported best amongst the binary systems tested in term of acid extraction, which reached almost 100% in the range of initial acid concentration of 0.2 – 0.4 M. However, the extracted acid could not be stripped from the loaded solvent using water. Instead, dilute base was required to strip the extracted acid, which made the application of these binary systems uneconomical and impossible.

3.1.3. CYANEX 923

Cyanex 923 is a mixture of four trialkyl phosphine oxides. The extraction of acid by Cyanex 923 has been investigated by several authors because of its desirable properties including low tendency to hydrolysis and low solubility in water [4, 29-31]. The advantage over other phosphine oxides is that it can be readily used without dilution [29]. Rickelton [32] proposed the use of Cyanex 923 as a potential extractant for recovery of H₂SO₄ because Cyanex 923 displayed a good compromise between its ability to extract sulphuric acid and to be stripped by water. Liao et al. [30] reported that when the acid concentration was less than 500 g/L H₂SO₄, third phase did not appear with the organic systems containing 40% and 50% (w/w) Cyanex 923. Haghshenas et al. [24] reported that H₂SO₄ extraction increased with increasing concentration of Cyanex 923. Kesieme et al. [3] also reported increases in H₂SO₄ extraction with increases in Cyanex 923 concentration and 100% Cyanex 923 concentration was reported as optimal for H₂SO₄ recovery.

Alquacil and Lopez [31] investigated the effect of diluents such as decane and toluene on the extraction equilibrium of sulphuric acid with Cyanex 923. It was found that diluent type did not affect the acid extraction. However, third phase formed with aliphatic diluents for 10-20% Cyanex 923 concentration when acid concentration was over 3 M. It was also found that the extraction of H₂SO₄ decreased with increase in temperature. Gottliebsen et al. [26] reported that the extraction of mineral acids by Cyanex 923 was generally represented by Equation 9:



Where X donates the dissociated acid anion and TRPO is Cyanex 923.

A similar equation was stated by Haghshenas et al. [24] as shown in Eq 10:



Wisniewski et al. [33] investigated the extraction of H₂SO₄ from solution containing hydroxylamine sulphate and ammonium sulphate using Cyanex 923 at 20 and 50 °C [Fig 4].

It was reported that the increase in temperature had no significant effect on H_2SO_4 extraction. In contrast, the phase separation time increased with increasing temperature. The author reported that the presence of hydroxylamine sulphate and ammonium sulphate did not affect both the rate and amount of sulphuric acid extracted with Cyanex 923. It was reported that the acid stripping kinetics was fast with the equilibrium being obtained after 4 - 5 minutes of mixing. Haghshenas et al. [24] reported that the extraction reaction of acid by TEHA and Cyanex 923 was exothermic and the enthalpy change was -6.34 kJmol^{-1} and -2.24 kJmol^{-1} , respectively, indicating that the acid extraction by Cyanex 923 was less sensitive to temperature compared to that by TEHA. It was reported that the time needed for equilibrium extraction of H_2SO_4 was 1.5 min indicating very fast separation [24]. Unlike other tertiary amines such as Alamine 336, the acid extracted by Cyanex 923 can be easily stripped using water at $60 \text{ }^\circ\text{C}$. This results demonstrate that composition and concentrations of TEHA and Cyanex 923 does not interfere with other cations and anions present in the acidic solutions during the extraction of H_2SO_4 and HCl .

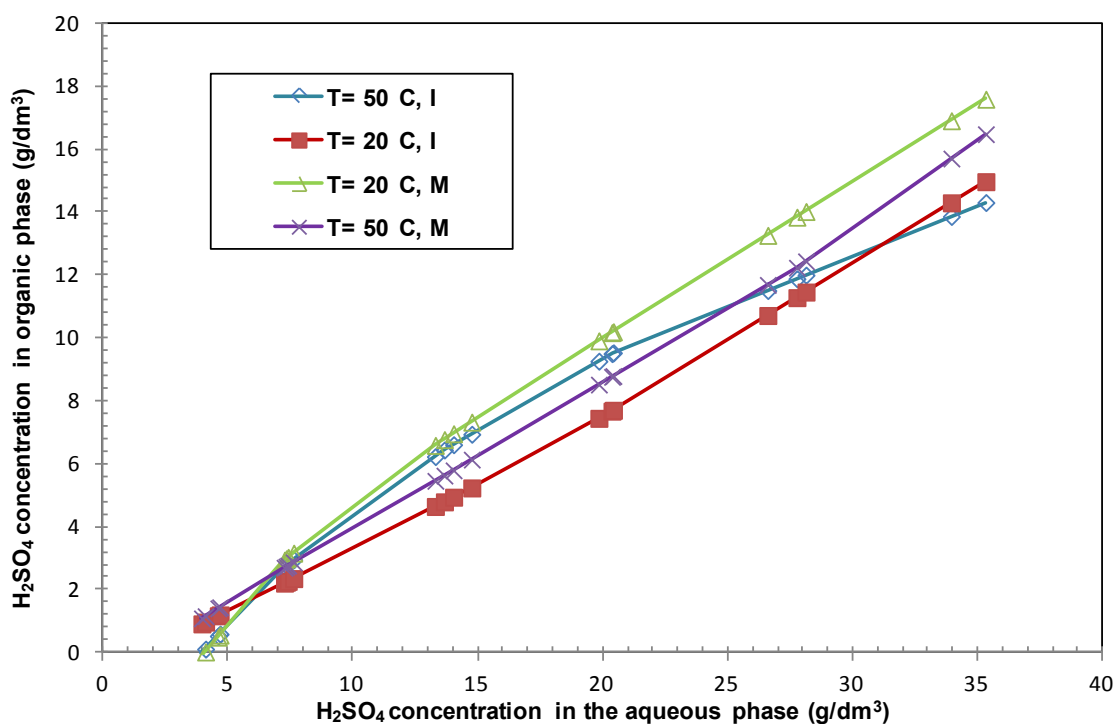


Fig. 4: Extraction distribution isotherms of sulphuric acid with 100% Cyanex 923 at $20 \text{ }^\circ\text{C}$ and $50 \text{ }^\circ\text{C}$. I donates aqueous phase containing only sulphuric acid and M aqueous phase containing sulphuric acid, 305 g/L hydroxylamine sulphate and 10 g/L ammonium sulphate. Based on Wisniewski et al. [33]

In summary, the extractants suitable for the recovery of H_2SO_4 in the order of TEHA > Cyanex 923 > Alamine 336.

3.1.4. Comparison of the extractants for sulphuric acid recovery

The extraction and stripping performance of the three extractants, TEHA, Alamine 336 and Cynaex 923 on H_2SO_4 recovery is summarised and compared in Table 2.

Table 2: Comparison of different extractants for the extraction of sulphuric acid

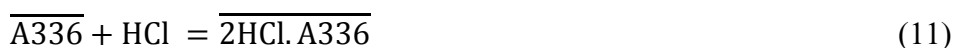
Name of extractant	TEHA	Alamine 336	Cyanex 923	References
Type of extractant	Tertiary amine	Tertiary amine	Phosphine oxide	
Diluents tested and effect	Kerosene and Shellsol 2046, Shellsol A150. Higher acid extraction	Kerosene.	Kerosene, Shellsol 2046, A150 and D70. Higher Acid extraction with 100% Cyanex 923	Eyal et al.[21-23]; Gottliebsen et al.[25, 26]; Fleet, [19]; Agrawal et al.[6]; Haghshenas et al., [24]; Kesieme et al.[3]
Modifier tested and effect	Octanol. Acid extraction improved by increasing the concentration of octanol	Isodecanol and TBP. No effect on acid extraction. Shorter phase separation time with isodecanol than with TBP.	Octanol. Acid extraction was higher with 100% Cyanex 923.	Tait, [28]; Wisniewski et al., [33] Gottliebsen et al.,[25]; Fleet [19]; Agrawal et al. [6]; Haghshenas., [24]; Kesieme et al [1-4]
H ₂ SO ₄ extraction and effect of reagent concentration	Good H ₂ SO ₄ extraction with 50% TEHA. Further concentration increases resulted in phase separation problem.	Good H ₂ SO ₄ extraction with 35% Alamine 336. Further concentration increase resulted in phase separation problem.	Good H ₂ SO ₄ extraction with 100% Cyanex 923 and no phase separation problem.	Tait,[28]; Eyal et al.[21-23] Gottliebsen et al. [25]; Alguacil and Lopez [31]; Agrawal et al.[6]; Agrawal et al.[7]; Haghshenas et al.[24]
Temperature effect on extraction	High extraction at room temperatures. Acid extraction decreased with increasing temperatures. In terms of H ₂ SO ₄ extraction: TEHA > Alamine 336 > Cyanex 923			Tait, [28]; Eyal et al.,[21-23]; Gottliebsen et al.[25], Alguacil and Lopez [31]; Agrawal et al.[6]; Haghshenas et al.,[24]
Extraction reaction	Exothermic. Enthalpy change -6.34 kJmol ⁻¹	Unknown	Exothermic. Enthalpy change -2.24 kJmol ⁻¹	Haghshenas et al., [20], Agrawal et al., [7]
Stripping using H ₂ O	Easy stripping using H ₂ O.	Not stripped completely using H ₂ O	Easy striping using H ₂ O	Agrawal et al.[6]; Haghshenas et al.[24], Kesieme et al. [1-4]

Temperature effect on stripping	Higher stripping at higher temperatures. 60 °C is the optimal stripping temperature >99% can be stripped	Poor stripping at higher temperatures	Higher stripping at higher temperatures 60 °C is the optimal stripping temperature >99% can be stripped	Agrawal et al., [6]; Haghshenas et al.[24]; Kesieme et al.[1-4]
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3.2. Solvent extraction of HCl

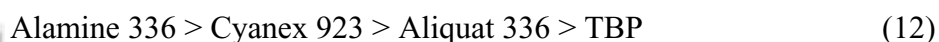
TEHA, Alamine 336, Aliquat 336, Cyanex 923 and TBP are the most common extractants used for HCl extraction and recovery [4, 21-24, 34]. Eyal and Canari [23] reported that HCl can be extracted using straight chain aliphatic amines diluted in alcoholic diluents due to ion pair formation. This mechanism may be represented by a two-step process of amine protonation and anion addition. Sarangi et al. [34] investigated the removal and recovery of HCl from a leach liquor of a secondary resource using extractants such as TBP (tri-butyl phosphate), Cyanex 923, Alamine 336 and Aliquat 336. It was reported that extraction of HCl increased with the increase in extractants concentration. When the Alamine 336 concentration increased from 10% to 100% (v/v) at an A/O ratio of 1:1, the extraction of HCl increased from 5.1% to 31.5%. The time for phase separation also increased with the increase in Alamine 336 concentration from 0.75 to 30 minutes. The logD vs. log (extractant concentration) plots (with all extractants) were straight lines with slope value ~1, indicating that 1 mole of extractant extracted 1 mole of acid. The McCabe–Thiele diagram constructed with Alamine 336 indicated > 99.5% HCl extraction in two counter current stages using an A/O of 1:4.

The extraction equation of HCl using Alamine 336 is as shown in equation [11]:



Where A336 denotes Alamine 336.

The McCabe Thiele diagram constructed with Cyanex 923 indicated that the quantitative extraction of HCl could be reached using four counter current stages and an A/O ratio of 1:5. Sarangi et al. [34] reported on extraction of HCl and follows the order as shown below:



Although Alamine 336 was the most efficient extractant for HCl, the extracted acid could not be stripped from the loaded organic with water. In contrast, the acid can be readily stripped with water for other extractants including Aliquat 336, TBP and Cyanex 923. The author concluded that Cyanex 923 is the best option for HCl recovery in terms of extraction and stripping efficiencies.

In a similar study, Kesieme et al. [4] reported HCl extraction using TEHA, Cyanex 923, TBP and Alamine 336. The extraction tests was conducted using the organic extractants and a real leach solution from a hydrometallurgical plant at an A/O ratio of 1:2 at room temperature for 10 minutes of mixing. It was also reported that for all the extractants examined, acid extraction increased with the increase in the extractant concentration. The optimal extractant

concentration for extraction of HCl was reported to be 50% (w/w) of the extractants TEHA in an aromatic diluent ShellsolA150 as shown in Fig 5.

A phase separation problem was observed for the organic solution containing 50% Alamine 336 in Shellsol A150. However, it was reported that the phase separation was satisfactory using 35% Alamine 336 and 10% isodecanol as modifier in Shellsol A150, After the first stage of extraction, the HCl extracted using TEHA, Alamine 336 and Cyanex 923 are 96.74%, 78.35% and 63.12% of HCl respectively[4]. However, It was found that only 3% HCl was stripped from the loaded Alamine 336 organic solution [4]. There is a possibility of some interaction between the solvent and the acidic species. Hence the stripping of loaded acid was not complete and some amount of acid remained in the organic system.

TEHA and Cyanex 923 was further subjected to successive extraction for three times at an A/O ratio of 1:2 at room temperature for 10 minutes [4]. After three stages of successive extraction, the HCl extraction with the TEHA system reached 99% while Cyanex 923 organic system was 98%. In terms of stripping it was reported that after two stages of successive stripping, the HCl stripping with the TEHA system reached 94.85% while that with the Cyanex 923 system 100%, suggesting that both organic systems exhibited good performance in terms of acid stripping. However, in presence of metals and scrubbing TEHA performed best [4]. It is suggested that extractants suitable for the recovery of HCl are in the order of TEHA > Cyanex 923>Aliquat 336>TBP > Alamine 336 [4].

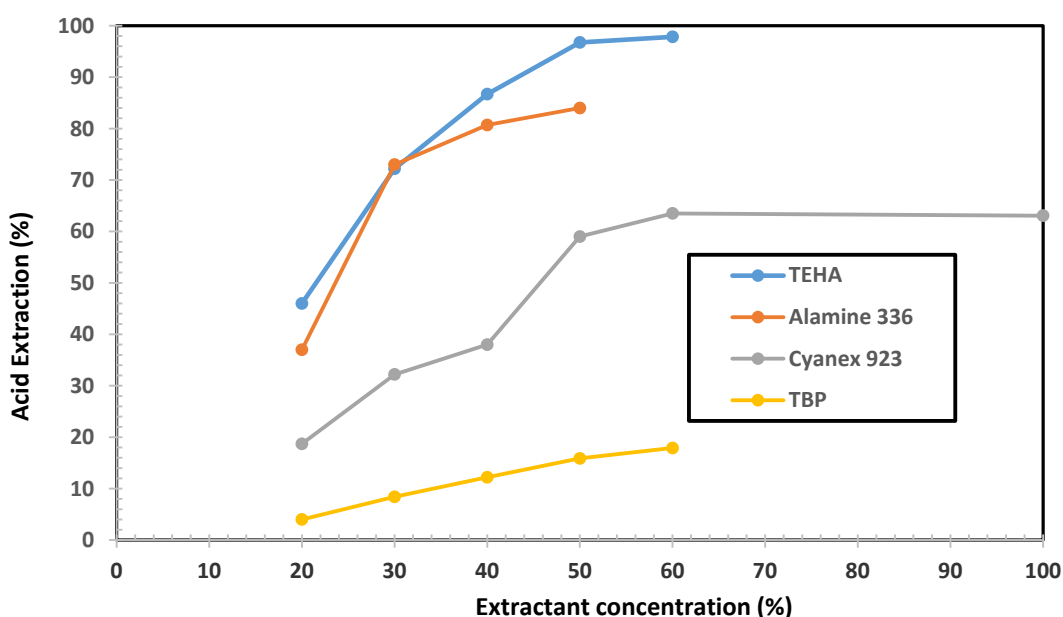


Fig. 5. Effect of extractant concentration on HCl extraction in a single contact at an O/A ratio of 2:1 and 22 °C. Based on Kesieme et al. [4].

3.3. Solvent extraction of nitric acid

TBP is a solvating extractant used at the industrial scale for the reprocessing of spent nuclear fuel [14]. TBP is generally used for purification of crude uranium, thorium and plutonium from nitric acid medium [14, 34-36]. PUREX process is, historically, the most studied solvent extraction system used to recover uranium and plutonium from used nuclear fuel [14]. In PUREX, an organic phase, consisting of TBP in a kerosene diluent, is contacted with an aqueous phase containing used fuel dissolved in concentrated nitric acid [14]. The TBP can selectively recover hexavalent and tetravalent actinides from the aqueous phase, leaving behind trivalent fission products and transuranics [14, 36]. TBP is also known to be effective for HNO₃ recovery from waste solutions such as leaching, etching, and electrowinning [35, 36]. Hoon-Shin et al. [36] investigated suitability of HNO₃ recovery from waste etching solution using different extractants such as TBP and TOP (Tri-octyl phosphate). The waste solution examined contain 260 g/L CH₃COOH, 460 g/L HNO₃, 113 g/L HF and 19.6 g/L. Preliminary results reported shows that solvents such as 2-ethylhexyl alcohol (EHA), decanol, octanol, heptanol and hexanol were more selective for acetic acid (HAc) over HNO₃ while Tri-octyl phosphate (TOP) and TBP showed more preferential extraction of HNO₃ compared to HAc. It was reported that the extraction of HNO₃ was about 46% against a co-extraction of 32% HAc in case of TBP in a single-contact and TOP were 35 and 22% for HNO₃ and HAc, respectively [36]. The high polarity of the phosphoryl (P=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.

The effect of the TBP concentration on the extraction efficiency of HNO₃ and HAc at O:A ratio of 1 and 22 °C was further examined [36]. It was reported that extraction of nitric acid increased from 19 to 46% ($D = 0.23-0.85$) 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% ($D = 0.10-0.47$). It was reported that more 99% acetic acid was scrubbed after four stages at an O: A ratio of 5[36].

The effect of HAc presence in feed solution containing HNO₃ was further examined and experiment was conducted using a synthetic solution containing only nitric acid [36]. It was reported that HNO₃ extraction efficiency increased by 12–14% in 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.

Kulkarni [37] reported using sing tri-*n*-octyl-phosphine oxide (TOPO) in emulsion liquid membrane to preferentially separate U⁶⁺ over Fe³⁺, Ca²⁺ and Mg²⁺ from a HNO₃ solution. Nevertheless for separating nitric acid, TBP has been found better due to its selectivity towards the extraction of HNO₃, overall high extraction efficiency, and favourable physico-chemical properties and low-cost [35]. Moreover, the solubility of TBP (in temperature range 25–60 °C) in nitric acid solution within the concentration range of 2.0 to 8.0 M has been investigated to be lower than that of with only water, and increases when using above 8.0 M HNO₃ in solution[39]

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It is known that TBP can extract nitric acid from aqueous solutions, and even the presence of metal ions in the aqueous phase [38]. Zhang et al. [38] reported that the nitric acid extraction improved in the presence of H_3PO_4 and nitrate salts in the aqueous phase. Liljenzin et al. [40] reported HNO_3 was selectively extracted from a solution containing in 18 g/L Cu, 2 g/L Fe and 148 g/L HNO_3 . More than 99% HNO_3 were recovered using 75% TBP in kerosene while Cu and Fe were not extracted. The nitric acid extraction decreased by increasing HF concentration in the feed solution [41].

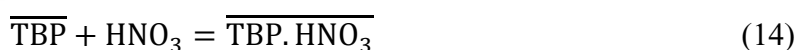
Jaiswal et al. [35] examined the effect of various metal nitrates: Na^+ , Mg^{+2} , Ca^{2+} , Al^{+3} , etc. of different concentrations on HNO_3 extraction using TBP. It was found that the percentage of extraction of nitric acid in the presence of $\text{Al}(\text{NO}_3)_3$ was higher than that of other metal nitrates. It was reported that 69–76% of nitric acid may be recovered in a single stages extraction. It was reported that the percentage recovery of nitric acid decreases by using higher concentration TBP, as the concentration of TBP increases percentage recovery decreases which can be enhance by increasing the O/A ratio and mixing time. Moreover, by using multistage extraction the complete extraction of nitric acid is possible [35].

Hesford and Mckey [42] reported the extraction order of mineral acids by TBP followed the following order:



In a similar study, Lee et al. [43] conducted experiments to recover valuable metals and regeneration of nitric acid from the spent nitric acid solutions. It was reported that 95% extraction of nitric acid was possible by using 50% TBP in five counter-current stages at the volume ratio of organic (O) to aqueous (A) of three, from a feed solution containing 250 g/L nitric acid.

Theory of extraction of nitric acid from aqueous solution using TBP is shown in equation 14. TBP form a complex, $\text{TBP}\cdot\text{HNO}_3$ with nitric acid during the extraction from aqueous solution as shown in Reaction

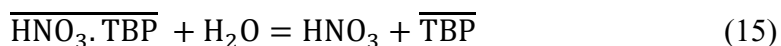


The top bar denotes compounds in the organic solution. Where $[\text{TBP}]$ and $[\text{HNO}_3\cdot\text{TBP}]$ are the concentration of free and bound TBP in the organic phase.

The stripping of HNO_3 using distilled water at 60 °C was investigated by Hoon-shin et al. [36]. Over 94% stripping efficiency was achieved in a five stage counter-current test at an O/A ratio of 1.5. High purity product of 99.8% HNO_3 was reported after stripping [36]. Lee et al. reported similar results using distilled water as a stripping agent, and they found that nitric acid was stripped from the loaded organic phase containing 80 g/L nitric acid.

Recovery of nitric acid (>99%) back in the aqueous phase was prominent with water stripping after five contacts [35-43]

The stripping of nitric acid from organic phase by using water can occur as shown in the reaction equation 15



3.4. Solvent extraction of Phosphoric acid

Several authors reported the using various extractants such as methyl isobutyl ketone (MIBK) and TBP for recovery of H_3PO_4 from various waste solutions [16, 17, 44-47]. TBP is an effective extractant for extracting phosphoric acid because of its immiscibility with the aqueous solution, good selectivity to phosphoric acid, and easy recovery [16]. Yagodin et al. [44] used TBP as the extractant for H_3PO_4 extraction and found that the extraction increased with the increase in the concentration of H_3PO_4 . From 15 to 82% H_3PO_4 (by weight) in the aqueous feed, the distribution coefficient D increased from 0.20 to 0.52 with undiluted TBP at 20 °C [45]. At temperature of 20 °C, extraction of H_3PO_4 involved the formation of hydrated mono- and di-solvates. At low H_3PO_4 concentration, the di-solvated compound $\overline{2\text{TBP} \cdot \text{H}_3\text{PO}_4}$ is the predominant species, while the mono-solvated form, $\overline{\text{TBP} \cdot \text{H}_3\text{PO}_4}$ dominated with increased feed H_3PO_4 concentration [44].

Ahmed et al. [46] reported using methyl isobutyl ketone (MIBK) and TBP for phosphoric acid recovery. It was reported that phosphoric acid extraction with MIBK could be carried out at room temperature, while TBP extraction should be conducted at higher temperatures because of its relatively high viscosity. However, TBP has a better selectivity in phosphoric acid extraction than MIBK. The purification process consisted of an extraction, a washing and stripping operations.

The purification of the wet process phosphoric acid (WPA) with mixtures of methyl isobutyl ketone (MIBK) and tri- butyl phosphate (TBP) was reported in the literature [17]. It was reported that P_2O_5 recovery increased with higher solvent MIBK content whereas the impurities' contents were lower for near equal TBP and MIBK weight fractions in the solvent mixture. Purification of WPA with mixtures of MIBK and TBP gave the greatest recovery of P_2O_5 with 55% MIBK-45% TBP [17].

Assuncao et al. [16] reported on the extraction of phosphoric acid from concentrated aqueous feeds (3 to 14 M H_3PO_4) by TBP at 25 C. It was reported that acid extraction increased with increase in the extractant concentration. The acid extraction exceeded 97% and most of the acid was stripped using water at 60°C. Various solvents based on functionality are used either individually or in synergetic mixtures, have been patented [16]. These systems are listed in Table 3. All of these solvents can extract more or less efficiently phosphoric acid as a result of the formation of hydrogen bonds between the extractant and phosphoric acid molecules [16]. Water is co-extracted as well because hydrogen bonding can take place. Among these

systems, the Prayon Process, based on the mixture of 90 wt% di-isopropylether (DiPE) and 10 wt% tri-nbutylphosphate (TBP) is the most used at the industrial scale. [16].

Table 3: Main patented processes industrially deployed for purification of H_3PO_4 [16]

Process	Patent	Extractant	Feed solution (% P_2O_5)	Feed solution (M)
Prayon	US3970741	DIPE +TBP	61	14.2
Rhone-Poulenc	US4769226	TBP	< 40	7.6
IMI	US3304157	Ethers + Alcohol	>35	6.4
Budenheim		Iso-propanol	20–55	3.2–12
Toyo-Soda	US3920797	Butanol or iso-butanol		
Albright & Wilson	US3947499	MIBK	<62	14.2

4. Summary

Solvent extraction is a very important technique to recover mineral acids from hydrometallurgical processes and acidic waste solutions. The extractants suitable for the recovery of H_2SO_4 and HCl are in the order of TEHA > Cyanex 923 > TBP > Alamine 336. TEHA has the highest degree of acid extraction and stripping compared to Cyanex 923 and almost 98% of the acid can be stripped from the loaded organic. The acid stripping using water was difficult for Alamine 336 while that for TEHA and Cyanex 923 was easy at a high temperature such as 60 °C. The presence of octanol as a modifier for the TEHA organic systems prevents third phase formation. No phase separation problems were reported for Cyanex 923 organic systems even without dilution. Phase separation problems were reported for Alamine 336 when the concentration is above 35% in the presence of a diluents and modifier.

Alamine 336 and being anionic in nature, there is a possibility of some interaction between the solvent and the acidic species. Hence the stripping of loaded acid is very low and some amount of acid will remain in the organic system. Thus Alamine 336 could be used for the removal of acid for the recovery acid from any acidic waste solution

TBP is a good extractant for recovery of nitric and phosphoric acid from acidic waste effluents. TBP extracted acid in the following order: HF ~ $HClO_4$ > HNO_3 > H_3PO_4 > HCl > H_2SO_4 .

The stripping of acids from the loaded organic is done with water and the stripped acid will be diluted. However when the stripping is done in a counter current mode a concentrated acid is obtained which could either be recycled back into the system after adding a small amount of acid to make up the desired concentration.

In this work we have stressed upon the solvent extraction of acid because direct neutralization of the any spent acidic solution leads to the generation of a huge amount of solid waste which creates a disposal problem.

Acknowledgements

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