



## Review

# An overview of the recovery of acid from spent acidic solutions from steel and electroplating industries

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## ABSTRACT

Every metal and metallurgical industry is associated with the generation of waste, which may be a solid, liquid or gaseous in nature. Their impacts on the ecological bodies are noticeable due to their complex and hazardous nature affecting the living and non-living environment which is an alarming issue to the environmentalist. The increasingly stringent regulations regarding the discharge of acid and metal into the environment, and the increasing stress upon the recycling/reuse of these effluents after proper treatment have focused the interest of the research community on the development of new approaches for the recovery of acid and metals from industrial wastes. This paper is a critical review on the acidic waste streams generated from steel and electroplating industries particularly from waste pickle liquor and spent bleed streams. Various aspects on the generation of these streams and the methods used for their treatment either for the recovery of acid for reuse or disposal are being dealt with. Major stress is laid upon the hydrometallurgical methods such as solvent extraction.

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## 1. Introduction

It is well known that a huge amount of water is used in various steps in a steel production industry such as washing, pickling, cleaning, rinsing, etc. Similarly in metal finishing process such as in electroplating unit, water is used in the electrolytic bath, washing and rinsing of the electroplated articles. Of these waste streams, waste pickle liquor from the pickling units and bleed streams from the electroplating units are of major concern due to the presence of high metals and acid contents which renders them highly corrosive and polluting in nature. Other pollutants such as cyanide, Cu(II), Ni(II), Fe(II), Fe(III), Cr(VI) and certain organic compounds such as degreasing solvents are also present in metal finishing wastewaters which are highly toxic even at low concentration in water. Mixed solution of metal wastes can be much more toxic than simple solution of corresponding metal of higher concentration. The formation of sludge deposits in stream by certain industrial waste can create a potential health hazard to prospective users of the stream and restrict its use for recreational or agricultural purpose. Industrial wastewater from industries such as electroplating, galvanising and steel industries is also a potential source of pollution if disposed untreated, into any natural water body such as river or lake due to the presence of suspended solids, biodegradable organics, pathogens responsible for water born diseases and trace metals. However, this article mainly focuses on the acid recovery from spent pickle liquor from steel industry and spent bleed streams from the plating baths which is normally disposed off after neutralization. Although the awareness regarding environmental pollution and the implementation of the strict environmental rules and regulations has alarmed all the metal producers for using safe technologies where all the wastes generated are to be taken care to ensure safe and eco-friendly disposal to land or water bodies.

Industrial wastewater are generally characterised in terms of conventional pollutants and priority pollutants. Conventional pollutants includes oil and grease, total suspended solid (TSS), pH and biological oxygen demand (BOD). Thus various permissible disposable limits have been fixed by various pollution controlling agencies depending upon the type of waste. Central Pollution Control Board [1], New Delhi, India has decided certain permissible limits for the discharge of metals in the wastewater from electroplating industries as given in Table 1.

The acidic and alkaline wastes generated during pickling and cleaning operation in iron and steel industries are considered as hazardous in nature, which can corrode metal and concrete sewage pipes. Thus the environmental health and safety guidelines for integrated steel mills have been given by International Finance Corporation which gives the permissible limits for various metals and other components for the effluents from the integrated steel mills sector [2] (Table 2).

**Table 1**  
Wastewater discharge standards for electroplating industry.

Parameter	Concentration not to exceed, mg/L (except for pH and temperature)
pH	6.0–9.0
Temperature	Should not exceed 5 °C above the ambient temperature of the receiving body
Cadmium(II)	2.0
Nickel(II)	3.0
Zinc(II)	5.0
Chromium(VI)	0.1
Total Cr	2.0
Copper(II)	3.0
Lead(II)	0.1
Iron(total)	3.0
Total metal	10.0

Source: [1].

**Table 2**  
Effluents levels for integrated steel mills sector.

Pollutants	Guideline value	Pollutants	Guideline value
pH	6–9	Nickel (mg/L)	0.5
TSS (mg/L)	35	Zinc (mg/L)	2
Oil and grease (mg/L)	10	Cyanides (free) (mg/L)	0.1
Temperature increase	>3 <sup>a</sup>	Cyanides (total) (mg/L)	0.5
COD (mg/L)	250	Total N (mg/L)	30
Phenol (mg/L)	0.5	Ammonia (mg/L) as N	5
Cadmium (mg/L)	0.01	Total P (mg/L)	2
Chromium (total) (mg/L)	0.5	Fluoride (mg/L) as F	5
Chromium (VI) (mg/L)	0.1	Sulphide (mg/L)	0.1
Cooper (mg/L)	0.5	Iron (mg/L)	5
Lead (mg/L)	0.2	PAH (mg/L)	5
Tin (mg/L)	2	Mercury (mg/L)	0.01
Toxicity	To be determined on a case specific basis		

Ref: [2].

<sup>a</sup> At the edge of a scientifically established mixing zone which takes into account ambient water quality, receiving water use, potential receptors and assimilative capacity.

Present review gives an overview on various aspects of the generation and treatment of industrial effluent/aqueous wastes from iron and steel industry and electroplating industries such as waste pickle liquor, copper bleed stream (CBS) and spent zinc electrolyte to recover acid for their reuse and recycling. Various processes have been discussed and more stress has been laid upon the solvent extraction methods.

## 2. Discussion

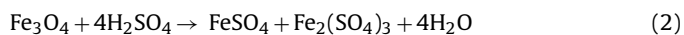
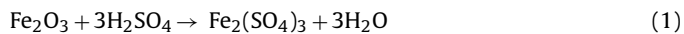
### 2.1. Generation of waste pickle liquor in steel industries

During the hot rolling or heat treatment of various kinds of steel, oxygen from the atmosphere reacts with the iron on the surface of the steel to form a crust that is made-up of a mixture of iron oxides. The presence of oxide (or scale) on the surface of the steel is objectionable when the steel is to be subsequently shaped or cold-rolled and coated. Numerous methods such as abrasive blasting, tumbling, brushing, acid pickling, salt bath descaling, and alkaline descaling and acid cleaning, have been used to remove iron oxide from metal surfaces. The removal of oxide scale from metal surfaces by cleaning with acid solution is one of the key steps in the metal finishing industries. This is usually accomplished by immersing the metal in an acid bath; a process called “pickling”. The various acids such as HCl, HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub> are used for this purpose as pickle liquor to remove surface oxide. The acid pickling method is preferred over all other above-mentioned methods to remove scale during steel production because of following reasons:

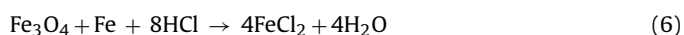
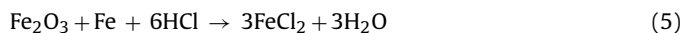
- Lengthens die life, eliminates irregular conditions and promotes surface smoothness of the finished products.
- Permits proper alloying or adherence of metallic coatings and satisfactory adherence when a non-metallic coating or paint is used.
- Prevents lack of uniformity and eliminates surface irregularities during cold reduction of steel sheet and strip.

While mild steel usually composed of wt.% 0.14% C, 0.35% Mn, 0.17% Si, 0.025% S, 0.03% P and rest Fe, are usually pickled by a solution of either hydrogen chloride (HCl) or sulphuric acid to treat carbon steel products, and a combination of hydrofluoric and nitric acids is often used for stainless steel. Normally steel is pickled in 15–20% hydrochloric acid at 60–70 °C or in 20–25% sulphuric acid at 95–100 °C, with the dissolution of the scale oxide to give iron

sulphates in sulphuric acid according to following reaction:



However starting in 1964, numerous steel pickling facilities changed from sulphuric acid to hydrochloric acid. Besides the advantage of lower cost, HCl pickling offers faster and cleaner pickling, lower acid consumption and greater utilization of the acid, less steam consumption and lesser quantities of waste pickle liquor, greater versatility and more uniform product quality than sulphuric acid pickling. But the only significant disadvantage of HCl acid is its volatility, which is greater than that of sulphuric acid. When iron oxides dissolves in HCl, the ferrous chloride is formed according to the following reactions:



hydrochloric acid also reacts with the base steel by the following reaction:



Therefore, an inhibitor is usually added to the acid solution to lessen acid attack on the steel itself while permitting preferential attack on the iron oxides only. The rate of pickling is affected by several variables, including the base steel constituents, the type of adherence of oxides, acid concentration and ferrous chloride concentration in the solution, temperature of the solution, agitation, time of immersion and the presence of inhibitors [3]. Pickling rate increases with temperature and acid concentration. As pickling continues, free HCl depletes and ferrous chloride builds up in the pickle liquor to an extent that pickling cannot be accomplished effectively and the quality of the treated metal surface deteriorates. At that point, the pickle liquor is discharged from the pickling tank to a storage tank, and the pickling tank is replenished with fresh acid solution. Acid transfer is done either continuously or in a batch mode and this discarded acid is to be treated for disposal/reuse/recycling/recovery.

The steel pickling operations are characterised by the form of metal processed and the type of pickling process used. The pickling processes are of following types:

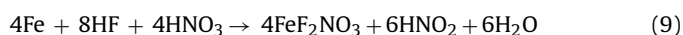
- Continuous pickling process: continuous pickling process is used for coils, rod, wire and pipe in the sense that the steel material is connected end-to-end and continuously run through the pickling tanks.
- Push–pull pickling process: the non-continuous process, also called push–pull, is usually used for coils and is an operation in which each coil is treated through the pickling tanks separately.
- Batch pickling process: the batch process is used for rod or wire in coils, pipes and metal parts in the sense that the material is dipped into the pickling tank for a certain period of time until the scale is dissolved. Every pickling process is followed by a rinse stage to remove acid residue.

Similarly during finishing of stainless steel, the metal is typically rolled and then annealed to achieve the desired structure and material properties. Because annealing is carried out in the presence of air, a film of oxide consisting mainly of chromium oxide ( $\text{Cr}_2\text{O}_3$ ), ferrous oxide (FeO) and manganese oxide (MnO) forms on the surface of the steel. Pickling is used to clean and condition the surface

of the metal after annealing. The pickling of stainless steel requires three distinct processes:

- Removal of the thermally grown scale for appearance purposes and to facilitate cold working of the steel.
- Enhancement of the corrosion resistance of the final product by dissolving the chromium-depleted zone that generally forms during annealing.
- Dissolution of a minimum amount of bulk steel, giving the desired brightening effect to the final product.

The first, scale removal step is often accomplished using shot blasting or electrolyte pickling in neutral salt. Recently, sulphuric acid pre-pickles have been commonly employed for scale removal. The remaining two pickling steps are normally carried out in mixed acid solution, which typically contain 90–160 g/L nitric acid and 10–40 g/L hydrofluoric acid. The basic reaction which occurs during stainless steel pickling can be expressed by equation:



The rate of pickling is principally dependent on the pickling bath temperature, the free hydrofluoric acid concentration and the dissolved iron and chromium concentration.

Steel pickling and the associated process of acid regeneration results in the emission of hazardous air pollutants (HAPs). Currently, the U.S. Environmental Protection Agency (EPA) is preparing National Emission Standards for Hazardous Air Pollutants (NESHAP) to apply to existing and new steel pickling facilities and associated acid regeneration plants under the authority of Section 112 of Clean Air Act.

Because of corrosive nature and high acid as well as metal content, the spent pickling solutions are considered as hazardous wastes. The pickling process generates two types of wastes:

- (1) Spent or waste pickle liquor (WPL) which is generated due to periodic discard of pickle liquor from pickling bath due to accumulation of highly concentrated iron (70–100 g/L).
- (2) Rinse water, containing 0.05–5.0 g/L acidic ferrous iron, generated during the washing of pickled iron.

The stainless steel pickling process also generates a considerable quantity of spent pickle liquor containing large quantities of nitrate, fluoride and heavy metals.

The permissible effluent discharge limit for the integrated steel sector as per EHS guidelines as on April 30, 2007 are given in Table 2 [2]. Hence the effluents have to be treated by suitable technique to recover and reuse both acid as well as the dissolved Fe(II) present in the spent pickling solution vis-a-vis prevent the environmental pollution.

According to the EPA Hazardous Waste list [4], spent pickle liquor containing 5–10% of free acid and 5–15% ferrous ions are considered hazardous and is designated as K062. The other hazardous constituents present in K062 are lead, nickel and hexavalent chromium. Average concentration of these constituents in K062 and the maximum allowable concentration of these constituents for safe land disposal of K062 are reported in Tables 3 and 4 respectively [5,6].

The steel producing industries and other metal finishing industries are now showing keen interest to treat WPL not only due to the implementation of strict rules by the Pollution Control Authorities but also to recover acid and valuable metals from it. Thus making the pickling process economical, non-polluting and to reduce the requirement of fresh acid with recycling of recovered acid.

The Environmental Law Institute and Innovative Technology working group for Iron and Steel Subcommittee of EPA Common Sense Initiative program, sponsored a workshop on the waste pickle

**Table 3**  
Average concentration of metals in spent pickle liquor.

Element	Concentration (ppm)
Cyanide	4.6
Arsenic	5.8
Cadmium	0.43
Chromium total	12,400
Hexavalent	19
Trivalent	6,690
Lead	1,500
Nickel	10,450

Source: Krishnan et al. [5].

liquor On 3rd December 1996. The workshop was convened to explore the possible innovative technologies that could be implemented to reduce or eliminate the use of pickling acid to clean steel. A wide variety of topics were covered [7] with main focus on ways of reducing the pickle liquor, opportunities for eliminating discharges of WPL, recycling and other alternative management approaches for WPL, and the regulating environment related to the overall pickling process, i.e. recycling and disposal.

About 6 million tons of spent pickle liquor are generated annually in the United States (Environmental Law Institute 1997). According to a workshop held on 1996, spent pickle liquor is generated by approximately 240 plants [8]. EPA estimates that these plants generate approximately 1400 million gallons of spent pickle liquor annually containing

Spent sulphuric acid pickle liquor: 500 million gallon.

Spent hydrochloric acid pickle liquor: 800 million gallon.

Spent mixed pickle liquor: 74 million gallon.

The U.S. had 103 operational steel pickling facilities in 1993 [9] and most of them were integrated into iron and steel manufacturing plants. In an ancillary process, spent HCl pickle liquor, which contains iron chloride is converted by a spray oxidation process into a marketable iron oxide product plus HCl solution that can be recycled for the pickling operation. According to the ICR database of USEPA in 1993, ten facilities perform acid regeneration in the U.S., of which two are independently operating plants and eight process lines operating in conjunction with steel pickling facilities [9]. Emission from most existing pickling and regeneration facilities are currently well under control.

Waste minimisation and reutilization lead to the consideration of a series of alternatives that range from separation of dissolved metallic ions (at least until levels that permits reutilization of the acid) to recovery of the acid itself in its pure states [10–14]. The concentration of pickling bath may be maintained by several ways:

- (1) hauling it away by a processing company that converts ferrous chloride to ferric chloride and sell the products as a precipitant to treat the wastewater in the treatment plants;
- (2) treating it on-site with caustics and hauling the resulted sludge away;
- (3) regenerating it by an acid regeneration process on site; or at an off-site facility and reusing the regenerated acid;

**Table 4**  
Maximum allowable constituent concentrations in K062 for land disposal (mg/L).

Regulated hazardous constituents	Concentration in wastewater	Concentration in non-wastewater
Chromium total	2.77	0.88
Lead	0.69	0.37
Nickel	3.98	N/A

Based on the Toxicity Characteristics Leaching Procedure (TCLP).

Source: [6].

- (4) recovering the free acid and metal ion by several commercially available recovery system and
- (5) injecting it by deep well injection. In addition, chemical oxygen demand (COD), suspended matter, oil and grease, ammonium nitrogen ( $\text{NH}_4\text{-N}$ ), pH, cyanides, fish toxicity and several relevant metal ions such as Cd(II), Fe(II), Fe(III), Zn(II), Ni(II), Cu(II) and Cr(VI) have to be reduced below the maximum allowable limits.

The selection of the WPL management alternatives is determined by several factors such as the governing state or local regulations, the amount of WPL generated the proximity of processing or disposal facilities, space availability and the process cost. As state or local regulations become more stringent, deep well injection will phase out and will be replaced by other alternatives. In one of the WPL management alternatives, the acid regeneration process has a potential of emitting significant quantities of HCl and  $\text{Cl}_2$ . A brief description about the various options to treat sulphuric acid and hydrochloric acid containing waste pickle liquor for the mild steel pickling process are appended below followed by an extensive survey on the process which has been used by the author for detail studies.

## 2.2. Spent bleed streams from electroplating industries

Electroplating processes are one of the major industrial contributors of heavy metal-laden effluents into the environment as only 30–40% of all metals used in plating processes are effectively utilised (plated on the articles). A few metals that are generally used in electroplating are copper, nickel, zinc, chromium, etc. We have mainly concentrated on the wastewater/spent bleed streams from zinc and copper electroplating industries.

### 2.2.1. Spent zinc bleed stream (SZBS)

Waste effluents from zinc electroplating lines are responsible for high amounts of  $\text{Zn}^{2+}$  encountered in electroplating discharges [15]. Zinc concentration in the electroplating rinse effluent in some industries was found much higher than the regulated criteria (1–5 mg/L) [16]. Thus during the production of zinc by electrowinning, impurities are removed in a bleed from the spent electrolytic solution. A typical bleed composition is 15–16%  $\text{H}_2\text{SO}_4$ , 5–10%  $\text{ZnSO}_4$ , 4–5%  $\text{MgSO}_4$ , 1–1.5%  $\text{MnSO}_4$ , 200 ppm chloride, 300–400 ppm Ca and small amount of Fe, Ni, Co, Cu and Cd [17]. The main constituents viz.  $\text{ZnSO}_4$  and  $\text{H}_2\text{SO}_4$  are valuable and if separated from the impurities, can be recycled to the process. As the impurities are in relatively small amounts, one would prefer to remove them. However, different characteristics of various impurities would require several distinct separations, resulting in an expensive and complex treatment. Current practice to treat bleed stream of spent zinc electrolyte consists of controlled addition of lime to the bleed stream. After neutralization of acid,  $\text{Zn}(\text{OH})_2$  is precipitated, separated and recycled to the leaching stage. This treatment consumes a huge amount of lime, forms large volume of gypsum and entails loss of sulphuric acid [18], posing an important challenge to process development. Solvent extraction is a proven technique to recover zinc and acid from such a bleed stream. Zinc is not extracted by cation exchanger from the solution of high acidity. An alternative approach starts with  $\text{H}_2\text{SO}_4$  removal from the effluents followed by the zinc extraction by a liquid cation exchanger from the acid-depleted solution. Buttinelli et al. [19] studied  $\text{H}_2\text{SO}_4$  pre-extraction by alcohols. The low efficiency of these extractants at low  $\text{H}_2\text{SO}_4$  concentration imposes the choice between losing an important part of the acid and recovering it as a dilute solution. In addition, the alcohols studied are quite soluble in aqueous process solution which must be recovered by distillation. Eyal et al. [17,20] described the application of a mixed system consisting of an



acid-base couple extractant for treating zinc electrowinning bleed streams. These extractants are more selective, efficient acid extractant with a good stripping of loaded acid. Boucher et al. [21] studied the recovery of spent sulphuric acid from effluent generated in zinc hydrometallurgical industry by electro-dialysis (ED).

### 2.2.2. Copper bleed stream (CBS)

Copper is one of the important novel metals required for various applications in metallurgical, electric and electronic industries. It is mainly recovered from primary sulphide concentrates. A part of copper is also recovered from different secondary resources viz. electrical and electronic waste, brass smelting, automobile scrap, containing different level of impurities depending on their sources [22–24]. The mining and metallurgical industry generates and discards large volume of solid and liquid wastes which are found suitable for reuse. Effluents and waste streams from various copper surface treatment and electronic industries such as copper electrorefining, electroplating, electrowinning units, residual solutions from molybdenite concentrate processing, etc. are generated with a volume flow rate lower than 5 m<sup>3</sup>/day [25]. Acid mine drainage can have a moderate (0.35–0.55 g/L) to high (1.5–7.2 g/L) sulphate concentration [26,27] along with other metals constituents like copper, zinc, cadmium, arsenic, manganese, aluminium, lead, nickel, silver, mercury, chromium and iron, in a concentration that can range from 10<sup>-6</sup> to 10<sup>2</sup> g/L. The most important wastewater streams originate from the copper refining and the electrolyte regeneration stages as well as the sulphuric acid and the precious metals plants. These wastewaters are characterized by medium to high concentration of residual sulphuric acid and heavy metal ions such as Cu<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Fe<sup>2+</sup>, As<sup>2+</sup>, Sb<sup>2+</sup>, Bi<sup>2+</sup>, etc. all in mg/L Cu 6035.7, Ni 612.8, Fe 150.2, Pb 2.9, Zn 23.7, As 505.5, Sb 12.3, Bi 44.8, H<sub>2</sub>SO<sub>4</sub> 282.6, Cl<sup>-</sup> 60.8, pH of solution 0.2–0.3 [28]. Since these wastewaters contain significant amounts of metal values which can be recovered, they can be used as secondary sources. Moreover the reasons proposed for the desirability to the increased use of such discarded materials such as: energy saving, landfill space and environmental impacts are avoided. During the electrorefining [29] of copper anode, various impurities present in anode dissolve and/or settle as sludge in the cell. The dissolved impurities (nickel, iron, antimony, bismuth, and manganese) build up in the electrolyte with the recycling of the electrolyte resulting in the degradation of the quality of deposited copper cathode. Thus a part of the electrolyte is discarded as copper bleed stream and replenished with the fresh solution. A typical copper bleed electrolyte of modern copper refineries contains 40–50 g/L Cu<sup>2+</sup>, 170–200 g/L H<sub>2</sub>SO<sub>4</sub>, 10–20 g/L Ni<sup>2+</sup>, 5–10 g/L As<sup>3+</sup>, 2 g/L Fe<sup>2+</sup>, 0.5 g/L Sb<sup>3+</sup>, 0.2 g/L Bi<sup>3+</sup> and 0.03 g/L Cl<sup>-</sup>. This metal rich bleed stream is treated by various methods and a few of them are discussed in the following text.

## 3. Techniques applied for the regeneration/reclamation of acids from bleed streams/spent acids

### 3.1. Methods for the treatment of CBS

In the conventional practice a portion of the electrolyte between the electrolytic cell and circulation tank is bled to the liberator cell [29,30] where it is decopperised, purified and crystallized. In the decopperisation operation copper present in the electrolyte is deposited on the cathode up to a concentration level of 10 g/L of copper left in the solution. The decopperised solution containing other impurities is sent to the purification section, where the impurities co-deposit on the cathode with remaining copper. The purified solution is then crystallized to recover NiSO<sub>4</sub>·xH<sub>2</sub>O and black acid thus generated is recycled to the circulation tank. Alternative to the decopperisation, the copper sulphate (CuSO<sub>4</sub>·5H<sub>2</sub>O) could be

produced which is recycled to the circulation tank to maintain the copper content and quality of the electrolyte solution. But this process is difficult to operate due to high cost as reported by Shibata et al. [31]. Purification of crude nickel sulphate by precipitation method has recently been reported by Havlik et al. [32] involving cumbersome procedure and loss of acid.

Shibasaki et al. [33] reported a process for the treatment of copper bleed electrolyte at Naoshima Smelter and refinery at Japan, which involves two-step namely neutralization of the excess acid with lime and removal of iron, arsenic and copper as hydroxide. The remaining copper, zinc and calcium present in the filtrate is removed by solvent extraction using PC88A. Nickel is extracted from the solution using Versatic 10, leaving Na, Mg and ammonium in the solution. The loaded nickel is stripped using sulphuric acid which is concentrated to produce nickel sulphate crystals (NiSO<sub>4</sub>·6H<sub>2</sub>O). Here again all the acid is lost due its neutralization with lime.

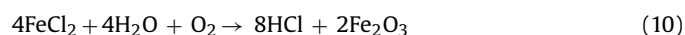
A number of processes have been developed by Japanese researchers [31,34] for the recovery of metals from copper bleed solution following SX and ion exchange and implemented in some plants. Other groups particularly Buttinelli et al. [35], Abishev and Stryapkov [36] and De Schepper [37] have also reported the treatment of CBS using solvent extraction (SX) techniques to recover sulphuric acid, arsenic, copper and nickel. SEC process described by Ritcey and Ashbrook [38] is based on SX–EW of Ni from the decopperised copper bleed stream at El Paso, USA. Baltazar et al. [39] studied the selective recovery and concentration of sulphuric acid from an acidic nickel sulphate stream containing copper, arsenic, bismuth and antimony in addition to nickel by electro-dialysis. Acid extraction rates of 170–450 g m<sup>-2</sup> h<sup>-1</sup> were achieved depending on the current density applied, resulting in the recovery of sulphuric acid solution up to 280 g H<sub>2</sub>SO<sub>4</sub>/L of a feed containing 150–180 g H<sub>2</sub>SO<sub>4</sub>/L with a total acid recovery of >80%. Nickel transferred into the recovered acid stream was <10%. Bartholomew [40] studied the recovery of sulphuric acid from spent pickle liquor. Palaty and Zakova [41] studied the transport of sulphuric acid through anion exchange membrane. Zhang et al. [42] investigated the recovery and concentration of sulphuric acid from solution containing non-volatile impurities using vacuum membrane distillation (VMD).

### 3.2. Methods for the treatment of waste pickle liquor

There are various methods for the treatment of waste pickle liquors. A brief description about various methods is given here.

#### 3.2.1. Pyrohydrolysis

In the fluidized bed acid regeneration process [43], the spent pickle liquor is thermally decomposed to convert the spent acid into hydrochloric acid and iron oxide at a high temperature in the presence of water vapor and oxygen as per equation (Eq. (10))



The spent pickle liquor is pumped into a separating vessel of the fluidized bed reactor (FBR) and then concentrated in a venturi loop by hot gases from the reactor. A part of the concentrated pickle liquor from this loop is continuously fed into the fluidized bed of the reactor. The fluidized bed consists of iron oxide granulates along with acid and water which are evaporated at about 850 °C resulting in the conversion of iron(II) chloride to iron(III) oxide and hydrochloric acid according to Eq (10).

Another regeneration option for hydrochloric acid is the spray roasting process. The principle of operation is similar for all roasting processes, but with some variation in equipments used. The pyrohydrolytic separation of iron(II) chloride and water is carried out at a temperature of about 450 °C in the spray roasting reactor. The

spent acid is fed to a venturi recuperator where the hot gases coming from the reactor are cooled and the acid is pre-concentrated. The concentrate is then sprayed directly into the fired reactor from above. Hot burn gases cause the fine droplets to evaporate as they descend [39]. The ferrous chloride is separated into hydrochloric acid and iron oxide by means of steam and oxygen in the air according to Eq. (10). The iron oxide thus formed is collected at the bottom of the reactor and conveyed pneumatically to an oxide bin. This oxide is a valuable raw material for the production of magnetic materials, i.e. hard and soft ferrites. Only one of the ten existing acid regeneration facilities uses a fluidized bed roasting process, which was built in 1974. These two acid regeneration processes are similar in chemical reaction principles but are different in roaster designs and the quality of iron(III) oxide produced [44]. Stocks et al. [45] reported that spray roasting requires a high energy input to produce a relatively low cost product, i.e. HCl which render the process non-viable. Kerney [10] pointed out that spray-roasting process commonly used to treat  $\text{FeCl}_2$  solution to recover HCl and iron oxide is disturbed by Zn, due to the formation of the compounds of low melting point sticking to nozzles and walls which contaminates the iron product. A process is described for treating waste from manufacturing  $\text{TiO}_2$  pigment by sulphate process. The spent acid is ejected into a spray dryer where acid and water are evaporated and anhydrous metal sulphates are collected in a cyclone. The condensed  $\text{H}_2\text{SO}_4$  is recycled to the manufacture of  $\text{TiO}_2$  [46]. The regeneration of spent  $\text{H}_2\text{SO}_4$  containing organic and inorganic impurities from different substances ( $\text{TiO}_2$ , dyes, PVC, etc.) was studied by Shenfel'd et al. [47]. In view of the above, there has been an increasing interest in developing processes for the recovery of acid and metal values from the secondary/wastes solutions and effluents. The process should produce a residue which could be recycled for further processing or safely disposed off without affecting the environment. Usually, pyrometallurgical and hydrometallurgical processes are employed for treating such secondary. A major drawback of the pyrometallurgical method is high energy requirement and need of dust collecting/gas cleaning system. The presence of chloride and fluoride salts in the dust causes severe corrosion problems and necessitates the use of expensive alloys as materials of construction. The hydrometallurgical processes are more environmentally suitable and economical for treating secondaries containing different impurities at small scale. Following hydrometallurgical methods are available for the recovery of free acid and metal ion from WPL and other electroplating bleed stream:

### 3.2.2. Neutralization/precipitation

In most of the cases, the desired removal of iron is achieved by precipitating this impurity as a solid jarosite or goethite product [48–50]. However, the disposal of these solid wastes may be a threat to the environment due to the presence of high contents of iron and other heavy metals as compounds in it. These metals may gradually leach under ambient condition to contaminate the soil and the groundwater. Furthermore, dumping of the solid waste in landfills takes up large surface areas and incurring costs related to the land and treatment of leachates. While purifying WPL and other bleed stream, investigations indicated that it was not possible to precipitate individual metals selectively from solution containing high  $\text{Fe}^{2+}$  content without contaminating the precipitate with Fe and leaving residual Zn or other single metal ion in the solution [10,51]. Dafour et al. [52] proposed oxy-precipitation method for the recovery of sulphuric acid from steel pickling liquor. Pourcelly et al. [53] studied the recovery of sulphuric acid by electro-transport using special anion exchange membrane (AEM). Lopez-Delgoda [54] studied the recovery of iron and acid from bio-oxidised sulphuric acid pickling waste by precipitation as basic sulphates. Thus acid is lost and the final products are of low value which needs further purification for its reuse.

### 3.2.3. Crystallization

In the 1920s, the first definition of crystallization as a unit operation appeared [55]. This concept was used until the 1960s, when Randolph and Larson [56] took population balance into account for the mathematical treatment for crystallization analysis and design. Many approaches appeared to establish the foundations of industrial crystallization [57–63]. A number of critical reviews [64–66] have been published describing various theories proposed on crystal growth. Kumari et al. [67] studied the effect of various parameters to produce copper sulphate, mixed crystals by crystallization from copper bleed solution. Nyirendra and Phiri [68] studied the removal of nickel salt from copper electrorefining bleed-off electrolyte by crystallization. Ozdemir et al. [69] suggested the recovery of metal from waste pickling acids by crystallization method. In case of sulphuric acid recovery from waste pickle liquor, crystallization is based on the solubility relations of water, sulphuric acid and iron sulphate. Iron sulphate is more soluble at increasing temperatures and crystallizes out of saturated solutions when being cooled. For the recovery of free sulphuric acid from spent pickle liquor from  $\text{H}_2\text{SO}_4$  pickling lines, the heptahydrate crystallization process yielding  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  is usually applied in industry. With respect to the type of cooling, the following heptahydrate crystallization processes for regeneration are available: crystallization with indirect cooling, cyclone crystallization and vacuum cooling crystallization. The treatment of spent pickle solution by crystallization avoids the need to neutralize free acid. Furthermore iron is precipitated as heptahydrate and does not have to be neutralized either. With crystallization processes a significant enhancement of the wastewater releases and a reduction of the salt load can be achieved. In this method Fe or other metal ions crystallizes as their sulphate or chloride salt by cooling waste acids. However, this method has the following disadvantage: (1) large amounts of energy are required for the crystallization. (2) The removal of heavy metallic ions such as Fe ion from the waste acids is difficult. (3) An economical method for treating the crystal removed is not available.

### 3.2.4. Thermal decomposition

Thermal decomposition is also a conventional method for treatment of acidic waste, which sprays the waste acids including metal ion into a furnace heated from  $600^\circ\text{C}$  to  $1000^\circ\text{C}$  [70]. HCl or  $\text{H}_2\text{SO}_4$  is recovered by absorbing the gases decomposed into  $\text{H}_2$  gas,  $\text{Cl}_2$  gas from chloride pickle liquor and  $\text{H}_2\text{SO}_4$  gas,  $\text{SO}_2$  gas,  $\text{SO}_3$  gas from sulphate pickle liquor and  $\text{Fe}_2\text{O}_3$  powder so formed is used for making magnetic materials. The recovered acids are reused for pickling and dissolution of material. The following disadvantages are found in this method:

- Loss of huge amount of energy during the thermal decomposition of waste acid containing low Fe ions.
- Loss of large amount of hydrochloric acid as HCl fumes unless the total  $\text{Cl}^-$  ion in the pickling process being increased.
- Beating of the pickling solution requiring an increased level of metal ions concentration in it.
- Difficulty in controlling the Fe concentration in practice.
- High maintenance cost due to the severe damage of the apparatus by wet  $\text{Cl}_2$  and HCl gases.

### 3.2.5. Electrolytic precipitation/deposition

Many researchers have worked on the recovery of HCl or  $\text{H}_2\text{SO}_4$  from waste acids by removing metal ion by electrolysis route [70,71,10]. In these methods the waste HCl or  $\text{H}_2\text{SO}_4$  along with Fe metal ions is introduced in the cathodic compartment of the electrolysis cell where metal ions electrodeposit on the cathode and  $\text{Cl}^-$  or  $\text{SO}_4^{2-}$  ions are transferred through the anion exchange membrane. Large amount of free acids in the waste acidic solution

is responsible for the low yields and a low Fe electrolysis efficiency due to the ionisation of HCl and H<sub>2</sub>SO<sub>4</sub> to H<sup>+</sup> and Cl<sup>-</sup> or H<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> ions. However, the above method cannot be used for the waste acid generated by the upcoming industries. Furthermore, since the waste acids often contain the heavy metallic ions along with Fe ions, deposited iron may be contaminated and consequently a valuable material may not be obtained.

### 3.2.6. Ion exchange technique/acid retardation method

The principle of the process is based on the adsorption of undissociated acid by ion-exchange resins as it passes through the resin bed. In backwashing with water, the adsorbed acid is released because of the difference in osmotic pressure. Thus acid retardation (i.e. ion exchange) is the most widely used process for the purification of mixed stainless steel pickle liquor because of its low cost, simplicity, reliability and superior performance [72]. Eco-Tec alone has installed hundreds of APU<sup>TM</sup> ion exchange system in 30 different countries in a variety of acid purification applications since the introduction of the process in 1978. Over 70 stainless steel pickling operations have installed APU systems [73]. The APU system utilises an ion exchange resin that has the ability to adsorb strong acids from solution while excluding metallic salts of those acids. The process is reversible in that the acid can be readily desorbed from the resin with water. It is thus possible, by alternate passing of the contaminated acid and water through a bed of this resin, to separate the free acid from the metal. A patented [74] ion exchange technique called Recoflo proved to be ideally suited to such an application. Through the use of short (60 cm) tightly packed beds of fine mesh resins and counter-current regeneration, Recoflo provides the necessary tool to achieve the required separation efficiency. Various other synthetic ion-exchange resins have long been used in commercial scale application for the softening or demineralisation of water. Again, while effective in reducing ionic contaminant levels to low levels, such resin have traditionally suffered from a lack of selectivity. Research has therefore been directed towards improving this selectivity and efficiency. Nenov et al. [75] separated arsenic from sulphuric acid using strong acid cation exchanger in the Na-form from aqueous solution containing arsenic. Kraus et al. [76], Sharitska et al. [77] Poluhina and Shamritska et al. [78] extracted sulphuric acid using some anion exchange resin. Brown et al. [79,80], Hatch and Dillon [81], Petkova et al. [82] studied the separation and recovery of H<sub>2</sub>SO<sub>4</sub> from metal cation coexisting in the waste plating solution by Wofatit SBW anion exchanger and pointed out that it is effective until the relative acid concentration in the effluents reaches  $C/C_0 = 0.55$ . The retardation technique based on ion exchange enables a partial acid recovery but lead to an increase of solution volume and a very dilute acid is obtained.

### 3.2.7. Electro-dialysis/membrane separation/diffusion dialysis

A membrane is a semi-permeable barrier through which only selected chemical species may diffuse. Historically, membrane technology has wide application in wastewater treatment and desalination through reverse osmosis. In this process, a pressure difference across a membrane is used to overcome the osmotic pressure gradient. The smaller water molecules are literally pushed through the semi-permeable membrane while the larger solute species are retained by the solution. Electro-dialysis is also a promising method of purification of the electroplating wastewater and extraction of non-ferrous metals from them. Greben et al. [83], treated dilute plating (rinsing) solution to recover their saline content as a concentrated solution, which can be used to replenish the operating bath of the plating process. Negro et al. [11] presented an alternative treatment method based on a diffusion dialysis process for the free acid recovery and neutralization process followed by a salt splitting process, for the chemical recovery. Rodrigues et al. [84] studied the possibilities of treating rinse water from chromating

bath by electro-dialysis and discussed the possibilities of optimising the treatment of waste reduction and reuse of water and chemical products. Industrial wastewater with high salinity and pH value can be treated with a combination of electro-dialysis and reverse osmosis (RO), while low-salinity wastewater with low pH value can be treated by reverse osmosis [85]. The use of electro-dialysis in the purification and re-concentration of spent acid has been limited by the deficiencies of commercial membranes: they suffer from an important proton leakage through the anion exchange membrane, limiting the re-concentration capacity [86], while a poor selectivity of the cation exchange membrane (CEM) affecting the proton/bivalent cation separation. In recent years, new AEM's with lower proton leakage have appeared in the market. It is now possible to concentrate mineral acids, such as sulphuric and phosphoric acids, from 2.6N up to 15N using these new membranes [85,87,88]. Waste sulphuric acid solution has been treated by diffusion dialysis [89–91], electro-dialysis [92,93], nanofiltration [94] and membrane separation [95]. Sulphuric acid recovery from rare earth (RE) sulphate solution by diffusion dialysis and its integrated membrane technique with vacuum membrane distillation have been studied by Tang et al. [96–98]. Trivedi et al. [99] studied the recovery of sulphuric acid and sodium hydroxide from aqueous solution of 0.5N, 1.0N and 1.5N Na<sub>2</sub>SO<sub>4</sub> solution using bipolar membrane. Results indicate that the process is able to produce concentrated chemicals with over 80% purity at a cell voltage of 10–25 V. Greben et al. [100] used electro-hydrolysis (EH) also known as 'electro-dialysis with bipolar membrane' or 'water-splitting electro-dialysis' to treat a solution originated from the electrolytic anodization of aluminium to obtain 140 g/L sulphuric acid with less than 1.2 g/L aluminium. Tzanetakis et al. [101] used a three-compartment EH cell to obtain sulphuric acid and sodium hydroxide from an aqueous sodium sulphate solution. The process produced high purity acid, but the operating cost was high compared to other methods. Negro et al. studied the recovery of inorganic acid from stainless steel pickling by electro-dialysis. Cifuentes et al. [102–104] carried out researches on the application of electro-dialysis to CuSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> based solution and also on the thermodynamic modelling of said electrolyte [105–107]. Cifuentes et al. [108] used two lab scale electro-dialysis (EH) cells to study the effectiveness of this method in the recovery of sulphuric acid from copper containing electrolytes such as those present in copper electrorefining. Winniewski et al. [109] studied the acid and base purification via bipolar electro-dialysis. Tongwen and Weihua [110] studied the simultaneous recovery of sulphuric acid and nickel from electrolysis of spent liquor of relatively low acid concentration by tuning the diffusion dialysis performance by surface cross-linking of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) anion exchange membrane. Tongwen and Weihua [111] also investigated the sulphuric acid recovery from titanium white (pigment) waste liquor using diffusion dialysis with a new series of anion exchange membranes. The effects of some important factors such as ion-exchange capacity, content of benzyl-halogen and the relative compositions of the liquor were experimentally investigated on the membrane dialysis process. It was found that the acid recovery rate was improved by bezyl substitution while the selectivity improved by aryl substitution. Sridhar and Subramaniam [112] examined the sulphuric acid recovery from sulphates of calcium, magnesium, sodium and potassium present in cation exchange regeneration waste by diffusion dialysis. Lin and Lo [113] employed the diffusion dialysis anionic ion exchange membrane to recover sulphuric acid from the waste acid solution of aluminium sulphate processing plant. Cherif et al. [86] investigated the yield of electro-dialysis transport of sulphuric acid under the same condition as in the zinc hydrometallurgy process involving an electro-dialysis cell divided by an anion exchange membrane. Metal ions were selectively separated from inorganic acid solution containing H<sub>2</sub>SO<sub>4</sub> and Cu<sup>++</sup> by reverse osmosis using



composite semi-permeable membrane prepared by forming thin layers of a multifunctional amino compound on a porous substrate [114]. In this process the spent  $\text{H}_2\text{SO}_4$  was mixed with technical grade  $\text{H}_2\text{SO}_4$  and HCl was separated by heating and blowing the air, adsorption, distillation and thermal decomposition. The resulting  $\text{SO}_2$  was reused for  $\text{H}_2\text{SO}_4$ . Metal ions were selectively separated from inorganic acid solution containing  $\text{H}_2\text{SO}_4$  and  $\text{Cu}^{++}$  by reverse osmosis using composite semi-permeable membrane prepared by forming thin layers of a multifunctional amino compound on a porous substrate.

Boudet-Dumy et al. [115] studied the transport properties of anion exchange membranes in contact with hydrochloric acid solution. The membranes used were commercially available AAV Selemion and ARA Morgane membranes, specially designed for the recovery of acids by electro-dialysis. Kameda et al. [116] studied the dehydro-chlorination of a chloride ion-intercalated hydrotalcite-like compounds at different temperatures in the nitrogen and water vapor atmosphere, for the recovery of hydrochloric acid. The degree of dehydrochlorination increased with increasing time, temperature and partial pressure of water vapor as compared to that in nitrogen atmosphere, however the concentration of HCl obtained under water vapor was lower than that under nitrogen. Kameda et al. [117–122] found that Mg–Al oxide was particularly effective for treating hydrochloric acid and chlorides in aqueous solution. The rehydration and subsequent combination of Mg–Al oxide anion in solution was accompanied by the release of  $\text{OH}^-$ . Thus Mg–Al oxide can neutralise and fix  $\text{Cl}^-$  during the treatment of hydrochloric acid. Kang et al. [123] applied the traditional neutralization method using alkali or recovered acid by diffusion dialysis from the strip HCl solution (usually 2–6 mol/L) used to strip rare earth. Harada et al. [124] recovered the HCl from RE stripped solution by high temperature evaporation. Kuppinger [125] studied the recovery and concentration of aqueous hydrochloric acid by electro-dialysis. Jian-Jun and Kang-Gen [126] investigated the hydrochloric acid recovery from rare earth chloride solution by vacuum membrane distillation. The results indicated that HCl separation from rare earth strip solution was possible using VMD method (vacuum membrane distillation) with the recovery ratio of 80%. Wisniewski et al. [109] studied the acid purification as well as base purification using bipolar electro-dialysis. Bipolar electro-dialysis yielded an acid solution having concentration up to 51-fold (in case of hydrochloric acid) and 63-fold (in case of sulphuric acid) as compared to that obtained by conventional electro-dialysis. The solution of the recovered acid was only slightly contaminated with iron salt (0.12 and 0.13%). The main application of bipolar electro-dialysis was found in the production of acids and bases from saline water. To achieve this goal, it was necessary to co-opt the bipolar membrane with monopolar membrane, for the production of base from an inorganic salt such as sodium chloride [127]. Kong et al. [128] developed a lumped-parameter model to predict the performances of diffusion dialysis using anion exchange membrane for hydrochloric acid recovery. The operating parameters investigated in their study included the feed concentration, the retention time and the ratio of feed to water flow rate. Palaty et al. [129] studied the recovery of hydrochloric acid by diffusion dialysis and presented a model for the transport of chloride ion through the anion exchange membrane. Urano et al. [130] proposed electro-dialysis for recovery of hydrochloric acid and sulphuric acid. Wisniewski and Wisniewska [131] investigated the acid and iron salts removal from rinsing water after metal etching by electro-dialysis. Dobrevsky et al. [132] proposed ion exchange method whereas Wisniewski and Suder [133] proposed an integrated method consisting of electro-dialysis with ion exchange to recover pure water from etching effluents, which could be reused for rinsing of a high-quality steel after etching. Results of earlier work by Tomaszewska et al. [134–136] showed that hydrochloric acid might be separated from the solution by membrane distilla-

tion (MD). MD is the process in which a hydrophobic membrane separates the two aqueous solutions at different temperature and composition to get a concentrated solution containing hydrochloric acid and salts. It was found that both water vapor and hydrogen chloride are transported through the pores of a hydrophobic membrane. This effect was utilized for the recovery of HCl from acidic spent solution. Boucher et al. [137] recovered the spent acid by electro-dialysis using different cation exchange membranes from waste generated in zinc hydrometallurgy industry. Sista et al. [138] investigated the acid recovery from the effluents containing metallic divalent salts by dialysis using cation exchange membrane modified in situ. Wisniewski and Wisniewska [139] studied the recovery of water and acid from the effluents generated during the rinsing of etched metal with hydrochloric acid by a combination of conventional electro-dialysis, ion exchange and mono selective electro-dialysis. Elmidaoui et al. [140] studied the competitive diffusion of hydrochloric acid by diffusion dialysis. Stachera et al. [141] studied acid recovery using diffusion dialysis with poly (4-vinyl pyridine) filled microporous membrane. Two series of membranes were produced by photoinitiated polymerisation of 4-vinylpyridine (4VP) and divinylbenzene (DVB) within the pores of polypropylene microfiltration membranes. The membrane were tested by diffusion dialysis of acid/salt solution ( $\text{HCl}/\text{NaCl}/\text{MgCl}_2$ ) in order to determine the effects of both mass gain and degree of crosslinking on dialysis co-efficient and acid/salt separation. Tomaszewska et al. [142] studied the influence of acid concentration and salt present in feed, on molar flux through the membrane. The study showed that when the feed solution contained a low concentration of HCl, the permeate was practically pure water. The increase in temperature and acid concentration of the feed solution and the presence of high amount of  $\text{FeCl}_3$  caused a substantial increase in HCl molar flux through the membrane. Electro-dialysis was not commonly used for the extraction and re-concentration of acids, because the standard anion exchange membranes are highly permeable to proton. Recently, special AEM showing a reduced proton leakage was developed for the recovery of acids by electro-dialysis. Lindheimer et al. [143] studied the electro-dialysis of hydrochloric acid solution using one of these membranes. Two main parameters quantifying the performance of the process were the current efficiency of HCl removal and the maximum re-concentration level of the acid which were analysed on the basis of a transport model. The current efficiency was determined by proton leakage through the AEM while the maximum re-concentration level was determined by the water transport through two ion exchange membranes. Mrochek and Banks [144] presented a comparative partition data for the solvent extraction of mineral acids, Uranium (VI) and some lanthanide elements by bis-(di-n-hexylphosphinyl)-alkane as a function of the aqueous concentration of nitric, hydrochloric and perchloric acid extractions. A method of recovering hydrochloric acid from spent hydrochloric acid pickle liquor was patented by Beecher [145]. In this process the waste pickle liquor from the pickle line was first concentrated before the liquor is reacted in a double exchange process with strong sulphuric acid. The overhead from the reaction process consisting of hydrogen chloride and water vapor was condensed and made available for addition to the fractionated hydrogen chloride. The remaining products of the double exchange reaction were filtered to form ferrous sulphate monohydrate crystals. Wolfgang [146] reviewed the pickling technology using acids such as sulphuric and hydrochloric as well as mixed acids for high alloyed steel. They presented a new technological approach to regain spent mixed acid. Gineste et al. [147] investigated the use of bipolar membranes for the recovery of hydrochloric acid and sodium hydroxide from NaCl solution. These authors proposed a mathematical model of the process, which allowed the prediction of the concentration of acid and base as a function of water transport rate, cell current density and ion flux through membranes. A spent





**Table 6**  
Processes for recovery and regeneration of spent acids from HCl pickling plants.

Principle of process.	Pyro-hydrolysis	Retardation	Dialysis	Electrolytic oxidation	Electrolytic Fe-ppn	Chemical oxidation	Ion exchange
Other products	Regeneration	Recovery of free HCl	Recovery of free HCl	Transformation of FeCl <sub>2</sub> to FeCl <sub>3</sub>	Regeneration of HCl	Transformation of FeCl <sub>2</sub> to FeCl <sub>3</sub>	Recovery of free HCl
Waste for disposal	Iron-oxides	–	–	FeCl <sub>3</sub>	Ferrous shots	FeCl <sub>3</sub>	FeCl <sub>3</sub>
Regeneration	>99%	Acidic FeCl <sub>2</sub> solution For neutralization	Acidic FeCl <sub>2</sub> solution For neutralization	>95%	>95%	>95%	
Free acid	Electrical energy, natural gas fresh and wastewater	75–90% VE–water	75–90% VE–water	Electrical energy	Electrical energy	Electrical energy HCl + air or Cl <sub>2</sub> or HCl + H <sub>2</sub> O <sub>2</sub>	50–70% Electrical energy, VE–H <sub>2</sub> O, oxidizing agents
Input for regeneration	High	Low	Medium	Low	Medium	Medium	High
Complexity of installation	Large	Small	Medium	Small	Small	Medium	Medium
Required space	High	Medium	Medium	Medium	Medium	Low	Low
Benefits/cost ratio							

represented by the expression:

$$K_D = \frac{[H_2SO_4]_o}{\alpha_{(H_2SO_4)A}} \quad (13)$$

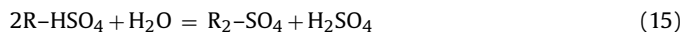
where  $[H_2SO_4]_o$  is the molar concentration of sulphuric acid in the organic phase.

A technique was developed for the recovery of pure sulphuric acid from a metal sulphate solution generated during acid cleaning of the titanium(IV) oxide production process wherein titanium present in the waste solution was removed by a solvent extraction process and the raffinate obtained after the solvent extraction was subjected to diffused dialysis treatment [158,159]. Apelblat [160] studied the extraction of sulphuric acid by methyl-diphenyl phosphate and TBP. The extraction equilibria in sulphuric acid-methyl diphenyl phosphate-water and sulphuric acid-tributyl phosphate-water system were investigated. The activities of methyl diphenyl phosphate and tributyl phosphate were calculated in the range of aqueous 0–10 M H<sub>2</sub>SO<sub>4</sub> with the aid of Gibb's–Duhem relationship. Wisniewski et al. [161] studied the extractions of As(III) and As(V) from sulphuric acid solution of various concentrations (50–200 g/dm<sup>3</sup>) with Cyanex 923 dissolved in Exxsol 220/230 and regenerated sulphuric acid in raffinate. Wisniewski et al. [162] studied the extraction of sulphuric acid from solution containing hydroxylamine sulphate and ammonium sulphate with Cyanex 923 at 20 °C and 50 °C. They also discussed about the number of extraction and stripping stages and the effect of volume phase ratio on the extraction and stripping of sulphuric acid. Buttinelli et al. [163] studied H<sub>2</sub>SO<sub>4</sub> pre-extraction by alcohols. The low efficiency of these extractants at low H<sub>2</sub>SO<sub>4</sub> concentrations imposes the choice between losing an important part of the acid and recovering it as a dilute solution. In addition, the alcohols used were quite soluble in the aqueous phase and must be recovered from them by distillation. Petkovic et al. [164] studied the extraction of mineral acids such as hydrochloric acid, nitric acid and sulphuric acid using tri-n-octylphosphine oxide with carbon tetrachloride as the diluents. Rickelton [165] proposed Cyanex 923 (a mixture of four trialkylphosphine oxide) as a possible extractant for recovery of sulphuric acid. He found that Cyanex 923 displayed a good compromise between its ability to extract sulphuric acid and strip out the extracted acid by water. Rickelton's experiments also showed that Cyanex 923 had a very high selectivity for acid in preference to both copper and nickel. Alguacil and Lopez [166] looked at the effect of diluents such as decane and toluene on the equilibrium of the Cyanex 923 extraction system. They found that diluent did not seem to influence the acid extraction although they observed the formation of a third phase with aliphatic diluents with 10–20% Cyanex 923 and above an aqueous acid concentration of 3 M. They also found that the extent of extraction decreased with the increase in temperature. While working with tris-2-ethylhexylamine (TEHA), Eyal et al. [167–169] and Gottlibsen et al. [170] showed that absence of a modifier gave poor extraction of acid by TEHA. When octanol was added as a modifier, the extraction was significantly improved. The ability of the solvent to extract the sulphuric acid decreased as the concentration of the modifier decreased. A similar effect was observed with temperature change. At each octanol concentration, an increase in temperature lowered the ability of the solvent to extract the sulphuric acid. The temperature effect was more significant at lower octanol concentration. Thus acid extraction from wastewater was either by anion or cation exchange mechanism. The anion exchange mechanism was based on the phenomenon described by Kraus et al. [76] and developed by Shamritska et al. [77] and Poluhina and Shamritska [78], according to which an anion exchanger was converted initially to its SO<sub>4</sub><sup>2-</sup> form, so that it could adsorb an additional amount of sulphuric acid from highly acidic sulphate containing solutions shown by

Eq. (14)

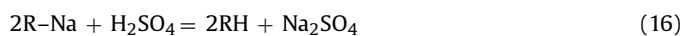


Since hydrolysis of the hydrosulphate form could easily occur in contact with water:

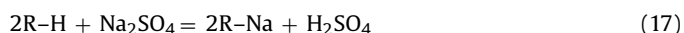


this reaction could be used as an acid stripping step.

On the other hand cation exchange mechanism could be performed using strong acid cation exchanger. The sodium form of the cation exchanger was suitable as an initial ionic form. The acid accumulation step could be expressed by:

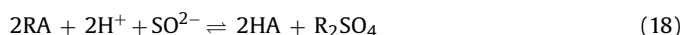


$Na_2SO_4$  could be used to strip the loaded acid as shown by Eq. (17):



The acid recovery was not possible if the cation exchanger was weakly acidic because of absence of the salt-splitting capacity as seen in strong cation exchanger.

Organophosphorus compounds containing P=O functional groups have been used as a favourable acid extractants for many years. Among these solvents, tri-*n*-octylphosphine oxide (TOPO) plays a noticeable role. A good review on the solvent extraction of uranyl compounds with TOPO was published by Kolarik [171]. Due to remarkable extraction ability of TOPO a detailed investigation on the thermodynamics of extraction of nitric, hydrochloric and sulphuric acid and corresponding uranyl salts was carried by Petkovic et al. [164]. Eyal et al. [17,172,173] studied the extraction of sulphuric acid by some binary extractants. They concluded that a binary extractant comprising of a strong basic amine and a strong acid, such as Aliquat 336/dinonyl naphthalene sulphonic acid should be used for efficient and reversible extraction. Tait et al. [174] investigated the effect of the class of amine (primary, secondary, tertiary or quaternary) and organophosphorous acid (phosphoric, phosphonic or phosphinic) present in a binary mixture, on their extraction properties. The extraction of sulphuric acid by binary extractant, RA, could be expressed as:

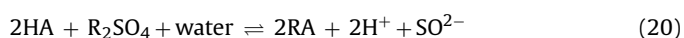


The reaction stoichiometry was two extractant molecules per sulphuric acid molecule. Thus, relatively high extractant concentrations were necessary to achieve efficient acid extraction. The binary extractant systems studied had a concentration of 1.4–1.6M when undiluted. However, these mixtures were viscous and required dilution. Consequently, to obtain effective extraction at relatively high acid concentrations, high organic to aqueous phase ratio was required.

In strongly acidic media the bisulphate anion will predominate over “free” sulphate. The extraction equilibrium in such a case may be expressed as:



The stripping of the loaded organic phase by water results in the transfer of the acid into the aqueous phase:



Agrawal et al. [175] studied the extraction of acid from the zinc bleed stream using tris-2-ethylhexylamine (TEHA). They found that this solvent had a very good acid extraction capacity even in the presence of high amount of zinc. Extraction of  $H_2SO_4$  was found to increase with increasing solvent concentration. There was no extraction of zinc in dilute TEHA solution, however with the increase in TEHA concentration to 75%, about 1–2% of zinc

was found to be extracted. Plot of  $\log D$  vs.  $\log [TEHA]$  indicated that 1 mol of the TEHA was involved with 1 mol of the extracted acid. About 90%  $H_2SO_4$  was extraction in three counter-current stages at the A:O of 1:2. Loaded acid was stripped with hot distilled water at 60 °C. McCabe Thiele plot showed that at O/A of 1: 2.11, the loaded acid was stripped in three stages. Hence TEHA could be a prospective acid extractant. In another study alamine 336 [176] was used to extract sulphuric acid from the spent pickle liquor. Here also extraction of  $H_2SO_4$  increased with increasing solvent concentration. Involvement of 1 mol of the extractant with 1 mol of the extracted acid was indicated by the plot of  $\log D$  vs.  $\log [\text{extractant}]$ . Although alamine 336 was found to be a good acid extractant but acid could not be stripped completely from the loaded organic phase with water. Iron (II) present in the raffinate was oxidized to Fe (III) and was then subjected to the solvent extraction of Fe (III) with an appropriate mixture of D2EHPA and MIBK behaving as a binary extractant. MIBK was found to enhance the D value showing a synergetic effect.

### 3.4. Recovery of hydrochloric acid from waste solutions

In continuation of earlier works, liquid–liquid phase equilibria were studied with a single carboxylic acid or binary mixture of carboxylic acids and an organic solution of tri-*n*-octylamine [177–184] as an effective and efficient solvent for acid extraction. Schunk and Maurer [185] studied the acid extraction using a liquid–liquid equilibrium of systems inorganic acid + water + toluene + tri-*n*-octylamine. Schunk et al. [186] investigated the extraction encountered in the reactive extraction of a single mineral acid (nitric, hydrochloric or sulphuric acid) from water with a mixture of tri-*n*-octylamine and methylisobutylketone or toluene which was characterised by the formation of water-insoluble complexes of amine, acid and water. Baerhold et al. [187] studied the recycling of hydrochloric acid from the pickling of mild steel using pyrohydrolysis. Recent developments have focused on the production of a high value iron oxide by-product, where the chemical purity and physical properties are the main issues. New processing routes, especially for  $TiO_2$  and Ti production, use leaching operation with hydrochloric acid. Feasibility of those processes depends on the availability of an economic and reliable process for the recovery of the acid. Brown and Olsen [188] studied the regeneration of hydrochloric acid pickle liquor by crystallization. The low-temperature crystallization of ferrous sulphate, which is a standard technique for regeneration of sulphuric acid pickle liquor, is applicable to any size operation. A similar technique has recently been developed to regenerate hydrochloric acid. Sulphuric acid is added to the ferrous chloride bearing spent HCl pickle liquor. The temperature is then reduced below 0 °C, resulting in the crystallization of ferrous sulphate heptahydrate and liberation of free hydrochloric acid. Due to remarkable extraction ability of tri-*n*-octylphosphine oxide (TOPO), Petkovic et al. [164] carried out a detailed investigation of the thermodynamics of extraction of nitric, hydrochloric and sulphuric acid and the corresponding uranyl salts. Alguacil and Lopez [166] studied the extraction of the minerals acids:  $H_2SO_4$ , HCl,  $HClO_4$ ,  $HNO_3$  and  $H_3PO_4$ , commonly found in hydrometallurgical processes, by Cyanex 923 to obtain information about the behaviour of this reagent and to help in understanding its probable future applications in the recovery of metals and/or acids from acidic aqueous solution or effluents. Sarangi et al. [189] carried out the removal/recovery of hydrochloric acid from a leach liquor of a secondary waste, using extractants such as TBP, Cyanex 923, tri-*n*-octylphosphine oxide and tris-(2-ethyl hexyl) amine.

#### 4. Conclusion

Based on the review made on hydrometallurgical processing of waste streams/solutions containing acid, the following points may be highlighted.

Waste streams such as waste pickle liquor from steel industries and spent bleed streams from copper and zinc plating/electrowinning industries are considered as hazardous materials due to the presence of high concentration of acid and metal such as Fe, Cu, Ni and traces of other impurities. The commonly used method of lime neutralization of the acid content and precipitation of the metal content from such waste streams leads to the loss of acid and metal values along with the generation of a huge amount of sludge due to the precipitation of metals as hydroxides. However this treatment method of a waste stream seems to be objectionable due to the burden of sludge disposal in a secured land fill and pollution due to the disposed sludge. Hence the concept of recycling/recovery/reuse of these wastes is stressed upon so as to convert these streams as a secondary source of acid and metal content in it. Various hydrometallurgical processes were considered which are ecofriendly and produces residues suitable for safe disposal. This review highlights all the possible hydrometallurgical options for the recovery of acid from these streams. Major stress is given to solvent extraction methods.

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