A Review on Spent Pickling Liquors Treatment

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Abstract. Spent pickling liquors is a hazardous waste because it is acidic and contains a large quantity of metal ions. It will cause severe environmental pollution and waste of resource if not properly treated. The traditional neutralization method will cause secondary pollutant. In this review, the latest development and research of spent pickling liquors treatment have been summarized, mainly including high temperature roasting, evaporation, ferric salt crystallization, ion exchange, membrane, chemical transformation, and electrolytic method. In the end of this review, there is outlook of spent pickling liquors treatment. It pointed out that the optimized way is to take the waste picking liquors as resource and combine the comprehensive utilization with the environment protection.

Introduction

Spent Pickling Liquors comes from the process of metal pickling. Acid is used as cleaning agents in pickling of metal surface and a lot of ground such as machinery industry and metallurgical industry. A lot of used acid which contains a large amount of metal ion especially ferric ion. Hydrochloric acid, sulfuric acid, hydrofluoric acid and nitric acid are mostly wildly used as cleaning agent for the process of steel pickling. In China, there are more than $1 \times 10^6$ m$^3$ spent pickling liquors produced each year. The waste water will cause environmental damage without proper treatment because of high concentration of ferric ion which is about 60-120g/L.

To reduce direct emissions of spent pickling liquors, the traditional treatment methods used by enterprises of China is to make use of lime, carbide slag or $\text{Ca(OH)}_2$ which is the reaction product of lime slaking reaction. Though pH can achieve the goal after neutralization, the rest of the indicators is difficult to achieve. The method produce a large amount of sludge containing metal salts, which is difficult to dry and after treated. It accumulates and takes up a lot of land, and it will cause secondary pollution of soil and groundwater.

In recent years, new spent pickling liquors treatment methods has gained widely attention. Researches on the recycling of the spent pickling liquors alleviate the current increasingly prominent environmental problems and resource shortage contradiction has very important practical significance. The review introduces several advanced treatment methods of spent pickling liquors.

High Temperature Roasting

High temperature roasting is a most thorough recycling method that burning and gasifying the spent acid in high temperature, and making the ferrous salt oxidation turns into acid ferric oxide and acid. This is the main chemical reaction mechanism...
(taking hydrochloric acid waste liquid for example):

\[
\text{HCl} \rightarrow \text{HCl}↑. \quad (1)
\]

\[
2\text{FeCl}_2 + 2\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 4\text{HCl}↑. \quad (2)
\]

**Evaporation**

The main process of evaporation is using the characteristics of some volatile acid, and evaporating acid by heating, then recovering acid by condensation. Distillation residue fluid is treated in different methods according to the way acid pickle is. This method is mainly used in liquid waste recycling of hydrochloric acid, hydrofluoric acid, and nitric acid.

The crystal of distilled liquor is easy to blocking device, needing to explore an appropriate heating temperature, vacuum degree and other conditions to reduce congestion.

**Ferric Salt Crystallization**

The mechanism of ferric salt crystallization is changing the physical and chemical properties of pickling waste liquor, and recycling the ferric salt from the waste liquid crystal precipitation, then turn it into regenerated acid.

**Concentration-filtration-spontaneous Nucleation Crystallization**

The method firstly puts Sulfuric acid full reacted with scrap iron in a reaction tank, then heat and concentrated and natural cooling to dissolve out the ferrous sulfate crystallization, finally dries it by dryer.

**Evaporation Concentration-freezing Crystallization**

The method is based on the change of ferrous sulfate solubility in acid solution, to improve the acidity of waste acid by the way of heating to promote evaporation and forced to cold the temperature (about -50°C) of the waste acid, solidify the supersaturated ferrous sulfate in the form of ferric sulfate heptahydrate, and centrifugal separate to obtain sulfuric acid and seven water ferrous sulfate respectively.

**Acid Added Freezing Crystallization**

By adding acid in the process of freezing crystallization, make the concentration of SO\(_4^{2-}\) of the spent pickling liquors increase, the balance of the dissolution of FeSO\(_4\) moving to the direction of the crystallization precipitation, so that Fe\(^{2+}\) dissolve out in the form of ferric sulfate heptahydrate. The waste liquors after precipitation can be applied back to steel pickling process, indirectly reduce the consumption of the new acid. This method has been widely used. The method has simple technological process, less investment, high reuse rate. It is suitable for acid spent pickling liquors that has little quantity and high concentration of FeSO\(_4\). C. J. Brown, etc. [2] studied acid added freezing crystallization. The results show that the recovery will have a part of sulfuric acid residue in hydrochloric acid, but it will not affect pickling effect, and can improve the rate to a certain extent, shorten the pickling time. In addition, inhibitor in the acid pickling process to protect the base metal is also effective.
Ion Exchange

Ion exchange refers to separating harmful ions from water by exchanging the exchangeable ions of ion exchanger with liquid ion. Some of the ion exchange resin has the property of adsorbing the strong acid ion or metal ion. The acid or metal ions adsorption is a reversible process, the strong acid or metal ion of which can be desorbed under the action of water or other elution agent from resin bed, thus metal ions and free acid can be separated. Since 1976, Eco-Tec company has successfully established hundreds of sets of APU (acid purification unit) ion exchange device treating stainless steel pickling wastewater in more than 30 countries. APU device can purify the spent pickling liquors by ion the exchange resin which can adsorb acid. When spent pickling liquors flows pass the APU device, the dissolved metal salts (iron, nickel, chromium) directly get through acid purification plant, meanwhile the acid will be adsorbed, achieving the purpose of separation. Recoflo Column is a patent ion exchange column in the APU.[3]

Many scholars use the property of some ion exchange resin that can adsorbing metal ions to remove the metal ion from the spent pickling liquors, to achieve the purpose of the acid recycle. A variety of strongly basic anion exchange resin, can be used to remove metal ions[4]. E. Maranon, etc.[5] has studied the effects of cation exchange resin, chelating resin and anion exchange resin in hydrochloric acid spent pickling liquors iron removal. Studies have shown that acid cation exchange resin and the chelating resin can remove the Fe (II), while anion exchange resin had good removal efficiency on FeCl$_3$, which is a negatively charged compounds formed by Fe (III) and chloride ion.

Membrane

Membrane treatment is to use ion selective permeability of the semipermeable membrane to separate the components in the solution. Currently membrane technology used in spent pickling liquors treatment takes advantage of ion selective permeability of membrane to separate ferric salt and acid, meanwhile recovers acid and iron salts. This method has high economic and environmental value without phase transformation.

Diffusion Dialysis

Diffusion dialysis takes differential concentration as driving force to separate salt from waste acid by using ion-exchange membrane. Bai-qing Zhou, etc.[6] separated waste hydrochloric acid by anion exchange membrane. The acid recovery rate was 90%, and the content of Fe$^{2+}$ of acid is less than 10 g/L. Mao-sen Zhu, etc.[7] used 3362 and DF120 anion exchange membrane to take diffusion dialysis experiment study for recycling hydrochloric acid from hydrochloric acid spent pickling liquors under laboratory conditions, meanwhile observing the effect of dynamic diffusion flow rate and flow ratio on the recovery and recycling acid concentration. The results show that acid recovery rates were 40% and 65% under proper conditions. Kun Wang, etc.[8] performed diffusion dialysis recycling spent pickling liquors of nitric acid, and observed the effect of waste acid concentration and acid flow rate on metal ions withholding rate and concentration of recycled acid. Result showed that acid recovery rate decreases with the increase of feed flow rate and acid concentration. The acid recovery rate was more than 80% and the interception of metal ion rate was more than 95% under the condition that material liquid and water flow rate was 160 mL/h.
Electrodialysis

The concentration of recovered acid of electrodialysis was low and cannot be directly used for pickling again. So, researchers make the anion and cation respectively move to the anion and cation using selective permeability of ion exchange membrane under the influence of external direct electric field separate acid from acid waste liquors. This method is called Electrodialysis. Mao-senZhu, etc.[9] adopted stainless steel as cathode and titanium base tin antimony metal oxide coated metal oxide as anode. They selected DF 120 homogeneous anion exchange membrane to perform recovery of acid and iron from hydrochloric acid spent pickling liquors using the static and dynamic electrodialysis technology. Fe recovery rate can reach 95% in proper conditions. E. Paquay, etc.[10] simulated the electroplating acid pickling wastewater treatment in electrodialysis in the laboratory, screened for a variety of anion and cation exchange membrane, and to quantify the relation between hydrodynamic condition of electrodialysis pool and the limited current density by using tracer technique.

There is a technique to recycle hydrofluoric acid, nitric acid and other waste acid from metal spent pickling liquors using bipolar membrane electrodialysis. Its basis is the selective permeability ion exchange membrane and that ion directional move under the action of electric field, as well as the unique ability of bipolar membrane to produce $\text{H}^+$ and $\text{OH}^-$ by hydrolysis. Wisniewski, etc.[11] study the purification of acid and alkali using bipolar membrane electrodialysis. Results showed that concentration acid solution by bipolar electrodialysis was 51 times (in hydrochloric acid solution) and 63 times (sulfuric acid solution) of ordinary electrodialysis.

Nanofiltration

Nanofiltration membrane filtration technique developed in recent years is a new type of separation technology between reverse osmosis and ultrafiltration. It is a separation process with new membrane driven by pressure[12]. Jin-bao Wan, etc.[13] separated sulfuric acid and ferrous sulfate in sulfuric acid waste liquors using this technology, and successfully recovered ferric sulfate heptahydrate and 20% mass fraction of sulfuric acid from sulfuric acid spent pickling liquors by freezing crystallization of ferrous sulfate from concentrates. Bes-Piá, etc.[14] made industrial leather pickling wastewater treatment in the lab using spiral nanofiltration membrane component.

Chemical Transformation

Preparation of Poly Iron Flocculant

Some flocculant such as polymeric ferric chloride and polymeric aluminum chloride iron and polymeric ferric sulfate can be prepared using the hydrochloric acid, sulfuric acid and iron salt, aluminum salt in spent pickling liquors. Zhang Yun-hui, etc.[15] added industrial sulfuric acid to hydrochloric acid pickling wastewater to make it fully curing compound, and form compound ferrous coagulants. They applied it to electroplating, printing, dyeing wastewater, and simulation of wastewater treatment. The results showed that the coagulant has good flocculation and decolorizing function.

Material Preparation of Iron Series

Preparation of iron oxide pigments use spent pickling liquors is comparatively mature and has been widely applied. Taking the preparation of iron oxide from sulfuric acid pickling wastewater for example the process is: acid pickle adjust—crystal seed
preparation-crystal growth-product separation. Re-feiHuang, etc.[16]used this method to deal with industrial waste acid, producing iron inorganic pigments and ammonium sulfate, and has made the analysis of the market demand for products and thought high of the application prospects.

**Electrolytic Method**

The mechanism of electrolytic process is ferric ion moves to and precipitate out at the cathode under the action of electric field, achieving the purpose of purifying spent pickling liquors. But because there's some free acid and a large number of hydrogen ions in waste acid, and $E^0(\text{H}^+/\text{H}_2) > E^0(\text{Fe}^{2+}/\text{Fe})$, it is hard to precipitation of iron at the condition of acid pickling waste liquor without any cathode processing. Many scholars do the research in this field, put forward some measures in favor of electrolysis. Quan-yuDong, etc.[17] studied the electrolytic mechanism of acid spent pickling liquors contained hydrofluoric acid, and put forward to add one or several cationic surfactant liquid to make them cover in the cathode surface with the effect of electrostatic or physical absorption and form a layer of film, which can prevent or weaken the adsorption of H$^+$ and discharge process, and make the hydrogen evolution over potential increases, and dissolve out iron without hydrogen evolution, achieving the goal of recovery of hydrofluoric acid.

**Conclusion**

Nowadays in enterprises of China there are still a significant proportion of spent pickling liquors treated by slaking reaction which cause secondary pollution because sludge of this reaction containing a large amount of mental ion is classified as hazardous wastes. This review summarized several advanced methods treating spent pickling liquors, mainly including high temperature roasting, evaporation, ferric salt crystallization, ion exchange, membrane, chemical transformation, and electrolytic method. Each method has its own advantages and disadvantages.

The composition of spent pickling waste water is complicated, the treatment of which is strict. It is hard to get good treatment effect in just one method. In my opinion, we can study characteristics of each method and new methods, finding a proper method or a combination method to replace the traditional neutralization treatment gradually, in order to optimize the process system.

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**References**


