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Resource reuse of spent pickle acid by mineralization process

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ABSTRACT

The spent pickle acid was collected from metal surface treatment factory. The pH of spent pickle acid was lower than 1.0, and the total concentration of ferrous ion was 186 g/L. Firstly, the lower activity of metal in the spent pickle acid solution was displaced by cementation process (pre-treatment). After cementation scraped iron, the coagulant agent (poly aluminum chloride (PAC)) was added to the solution. Then, the pH of the solution was adjusted to 4.5 by ammonia to remove SiO_2, P, and other impurities. Finally, the mineralization process was proceeded at pH 4.0 and 60°C with H_2O_2. X-ray diffraction (XRD) analysis shows that the mainly crystalline phase of the mineral product was γ-FeOOH. The high purity of Fe_2O_3 has been obtained by calcination from mineral product. Additionally, the economic evaluation results also show that the mineralization process was economic feasible. Therefore, this method could be applied to the metal surface treatment industry and printed circuit board manufacturing for recycling waste acid lotion.

Keywords: Spent pickle acid; Recovery; Mineralization; Fe_2O_3

1. Introduction

Hydrochloric acid has been used in pickling processes of metallurgical and metal surface treatment industries for decades. In Taiwan, as much as 3.5×10^5 metric tons of spent pickle acid is produced per year (Environmental Protection Administration, Republic of China). Thus, the reuse of spent pickle acid is an important environment issue in Taiwan. The spent acid contains great amounts of ferrous chloride [1–2]. The strict regulations for the treatment of heavy metal ion concentrations in waste effluents motivate the search for an efficient, cost-effective, and environmental friendly process to treat such waste acid.

In situ ferrite formation has been used for the treatment of heavy metal-containing wastewater from

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laboratories since the 1980s [3–5]. The process is based on the addition of Fe^{2+} ions into the wastewater, alkalization for the formation of ferrous hydroxide, and the partial oxidation of Fe^{2+} to Fe^{3+} by aeration [6]. A ferrite product with magnetic properties is thus produced which caused the co-precipitation of the other metal ions present in the wastewater [6,7]. Therefore, the filtrate could be discharged without risk for the environment. The dried solids could be disposed in landfills or employed in various applications, for example, magnetic recording media, magnetic inks, adsorbent for exhausted gases, pigment, etc. [8].

The crystalline structure of ferrite is the same as the cubic spinel structure AB_2O_4, with A^{2+} and B^{3+} being replaced by nonferrous metal M^{2+} and Fe^{3+}, respectively [9]. Thus, MFe_2O_4 is generally defined as ferrite's chemical formula [10]. Due to their high stability, ferrites are formed easily during the treatment of heavy metal-containing wastewater by wet oxidation [11,12].

In this study, the cementation process and mineralization process have been applied for the recovery of spent pickle acid from metal surface treatment factories in order to avoid waste of useful resources.

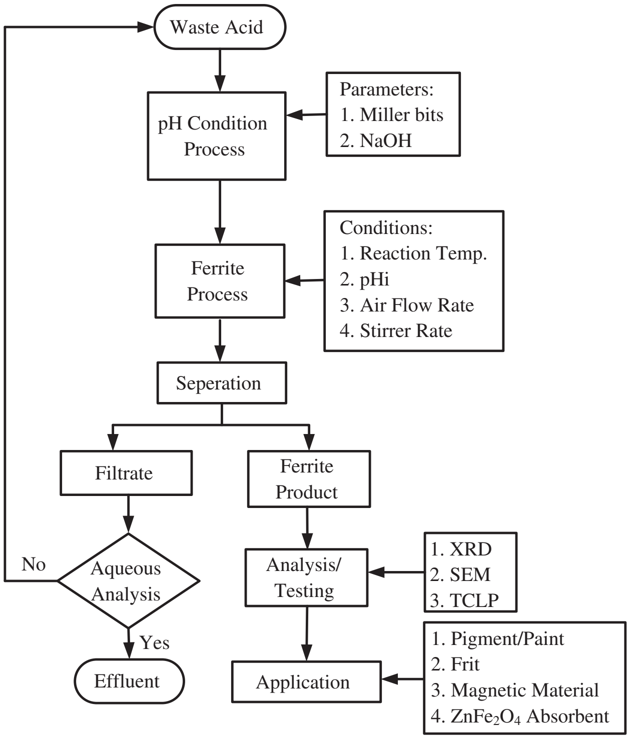

Fig. 1. Flow chart of experimental procedures.

2. Materials and method

2.1. Spent pickle acid

Spent pickle acid sampled from a metal surface treatment factory located in Jiali industrial area in Tainan City for this research work was characterized for composition, specific gravity and pH-value; the pH was lower than 1.0 and total concentration of ferrous ion was 186 g/L. Milling scraps (iron scrapings) were sampled from iron works.

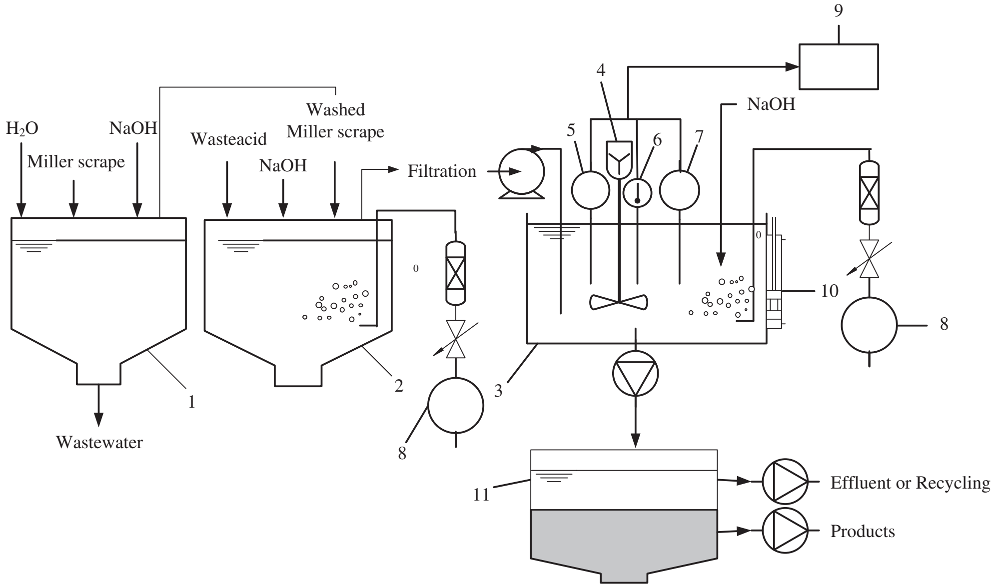

Fig. 2. Apparatus for waste acid treatment by ferrite process (1: NaOH rinse tank; 2: pH conditioning tank; 3: reaction tank; 4: stirrer; 5: pH meter; 6: thermometer 7: ORP meter; 8: air compressor; 9: data logger; 10: electric heater; 11: sedimentation tank).

2.2. Experimental methods

This study includes three main parts: (i) cementation on iron scrapings, (ii) removal of impurities by PAC, and (iii) mineralization reaction. The iron scrapings were washed with water and rinsed with 0.1 N NaOH to remove oil and impurities. The rinsed iron scrapings were then stirred into 3 L of spent pickle acid (ratio: 10 mL of spent pickle acid to 1 g of milling scraps) in a 5-L steel tank under aeration. The lower activity of metal in the spent pickle acid solution caused cementation on the iron scrapings, and the pH-value of the waste acid was thus raised to 2.5–3.0. The main purpose of this pre-treatment stage was to increase the pH of the solution so as to reduce the use of sodium hydroxide solution (NaOH). After the cementation, a coagulant agent (poly aluminum chloride (PAC)) was added to the solution. Then, the pH of the solution was adjusted to 4.5 by addition of ammonia to remove SiO_2, P, and other impurities. Finally, the pH of the solution was adjusted to 10.5–11.0 by adding 45% NaOH at the rate of 30 mL/min. Water was added to raise the volume of the suspension to 4 L. The suspension was then stirred continuously at 400 rpm, and reaction temperatures were set at 50, 60, and 70˚C. At each reaction temperature, aeration with flow rate of 5 L air/min/L liquid was initiated. The reaction time of the ferrite process was determined by monitoring oxidation-reduction potential (ORP) at about 3–4 h. After completion of the ferrite process, solid/liquid separation was achieved by filtration, and the residue was dried at 60˚C for 24 h. The flow chart of the whole process is shown in Fig. 1 [13,14].

The titration method was conducted for the determination of the chloride concentration in the dried residue. Metal concentrations in these samples were analyzed by atomic absorption spectrometry (Perkin Elmer AA 400). The solid products from the ferrite process were characterized with scanning electron microscope (SEM) (HITACHI S3000-N) and X-ray diffractometer (XRD) (BRUKER D8, Cu Kα radiation) [15]. The crystalline phases of the materials above were identified with database of the International Center for Diffraction Data (JCPDS-ICDD) and were further analyzed with XRD after drying at 50˚C; 2θ was set from 20 to 80°, and scanning velocity was 0.5°/min. The ferrite products after gold plating treatment were examined under SEM. Their stabilities were tested by standard toxicity characteristic leaching procedure (TCLP). TCLP test of samples was performed according to NIEA R201.12C (R.O.C., Taiwan). Apparatus for waste acid treatment by ferrite process is shown in Fig. 2. It can be divided into two stages:

Table 1
Characterizations of spent pickle acid before and after cementation on scraped iron

Item		Specific gravity (d)	Free acid (N)	Fe^{2+}/Fe^{3+} (mg/L)	Fe (mg/L)	Al (mg/L)	Cu (mg/L)	Cr (mg/L)	Zn (mg/L)	Pb (mg/L)	Ni (mg/L)	Cd (mg/L)	pH
Original spent pickle acid	A	1.35	0.80	98,600/20,300	118,900	162	3.27	18.7	99.5	2.3	18.4	0.26	<1.0
	B	1.34	0.71	182,200/4,100	186,300	140	4.52	81.3	267.2	26.5	32.2	0.08	<1.0
	C	1.34	0.77	134,200/5,200	139,400	147	3.12	25.3	155.8	12.2	25.1	0.05	<1.0
After cementation	A	1.37	0.10	122,200/42,800	165,000	53.9	2.01	15.7	78.0	1.5	12.40	0.13	2.80
	B	1.34	0.11	197,600/900	198,500	22.0	2.15	36.6	118.1	1.51	12.40	0.10	2.62
	C	1.36	0.10	148,700/10,100	158,800	36.2	2.33	12.6	98.2	4.22	14.50	0.06	2.69
Effluent standards		—	—	—	—	—	3.0	2.0	5.0	1.0	1.0	0.03	6.0–9.0

The first stage is the pre-treatment (NaOH rinse tank and pH conditioning tank), and the second is the ferrite process stage (reaction tank, meters, sensors and sedimentation tank).

3. Results and discussion

3.1. Characteristics of spent pickle acid

The characteristics of spent pickle acid before and after cementation on iron scrapings are shown in Table 1. The specific gravity and total Fe concentrations of spent pickle acid slightly increased after cementation. The concentrations of other heavy metals were reduced by the cementation process (lower activity of metal) or co-precipitation (higher activity of metal). A cementation process using iron powder for precipitating of Zn from spent pickle acid was impossible because Zn has a greater tendency to undergo oxidation than does Fe ($E^o_{\text{Cell}} = +0.32\,\text{V}$). The deposit of zinc results from the co-precipitation of the lower activity of metal by cementation processes [16]. However, the heavy metal concentrations of Cr, Zn, Pb, Ni, and Cd still did not meet the effluent standards. Notably, the free acid of spent pickle acid decreased after cementation on iron scrapings, and this resulted in an increase in pH. Thus, spent pickle acid after cementation on iron scrapings must undergo further treatment.

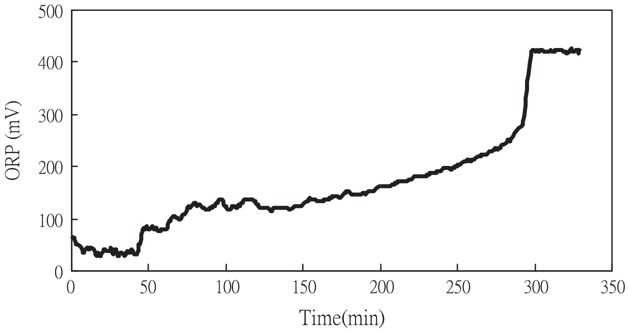

Fig. 3. ORP trends during mineralization process.

Fig. 3 shows the variation of ORP values in mineralization process with reaction time. The initial ORP value before the mineralization process was about 60 mV. The ORP value increased progressively and almost approached the state of equilibrium after 300 min (420 mV). Thus, the ferrite formation could be evaluated when the ORP values increased abruptly.

The spent pickle acid after the cementation process was subjected to the ferrite process at 50, 60, and 70℃ (Table 2). In general, the higher reaction temperature would enhance the mineralization completely and thus obtain the better crystallization of the solid product. However, the drawback of the higher reaction temperature is energy consumption. During the ferrite process, the heavy metal concentrations of spent pickle acid after cementation decreased obviously and met the effluent standards, regardless of reaction temperature. Thus, the combination of the cementation and ferrite processes may be combined to the recovering of spent pickle acid.

3.2. Microstructure and TCLP of ferrite products

The XRD pattern of the solid product from the ferrite process is depicted in Fig. 4. This pattern

Table 2
Characterizations of spent pickle acid before and after mineralization process

Item		Heavy metal (mg/L)							pH
		Fe	Cu	Cr	Zn	Pb	Ni	Cd	
Ferrite process (50℃)	A	781.5	0.16	0.12	0.11	0.20	0.16	0.01	8.86
	B	1,002.3	0.23	0.10	0.16	0.22	0.11	0.01	8.95
	C	655.2	0.09	0.04	0.14	0.12	0.09	N.D.	9.12
Ferrite process (60℃)	A	805.5	0.22	0.07	0.24	0.15	0.14	0.01	9.02
	B	960.7	0.15	0.14	0.15	0.15	0.09	N.D.	9.11
	C	634.5	0.12	0.10	0.11	0.16	0.10	N.D.	9.21
Ferrite process (70℃)	A	682.6	0.17	0.05	0.18	0.11	0.12	N.D.	9.09
	B	998.3	0.22	0.10	0.17	0.10	0.08	N.D.	9.12
	C	455.2	0.10	0.09	0.12	0.23	0.02	N.D.	9.10
Effluent standards		—	3.0	2.0	5.0	1.0	1.0	0.03	6–9

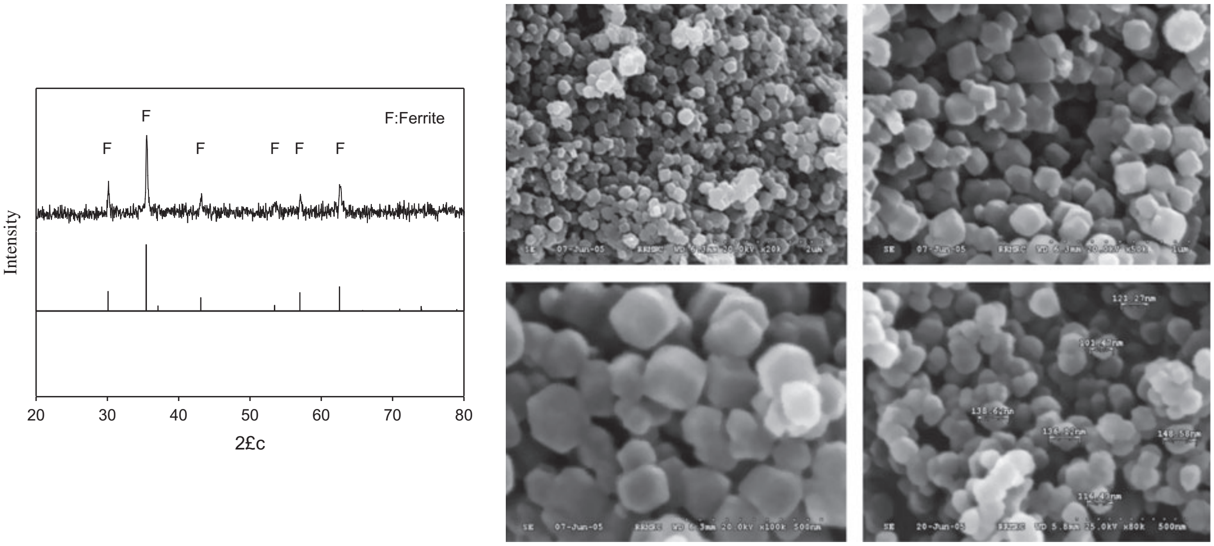

Fig. 4. XRD pattern and SEM micrograph of ferrite particle from spent pickle acid after cementation process and ferrite process.

Table 3
Leaching concentration of residues from spent pickle acid after cementation process and ferrite process

Heavy metals (mg/L)		Fe	Cu	Cr	Zn	Pb	Ni	Cd
Ferrite process (50˚C)	A	45.5	3.45	0.62	0.28	0.59	0.28	0.01
	B	56.2	4.35	0.78	0.42	0.67	0.24	0.02
	C	36.0	3.70	0.42	0.16	0.43	0.12	0.01
Ferrite process (60˚C)	A	35.8	1.40	0.06	0.14	0.39	0.08	N.D.
	B	69.2	1.62	0.12	0.18	0.45	0.10	0.01
	C	37.7	1.37	0.07	0.07	0.33	N.D.	N.D.
Ferrite process (70˚C)	A	48.2	0.94	N.D.	N.D.	0.29	N.D.	N.D.
	B	52.2	1.25	0.02	0.22	0.27	0.09	N.D.
	C	31.7	1.10	N.D.	N.D.	0.22	N.D.	N.D.
TCLP limitation		—	15.0	5.0	—	5.0	—	1.0

matches the pattern of magnetite (Fe_3O_4) and can be identified as a spinel structure. The high intensities of the reflections indicate the high crystalline structure of this ferrite product. Fig. 3 also shows the micrograph under SEM observation. It is evident that a single ferrite particle is smaller than 0.2 μm. It is interesting to note that these ferrite particles were mostly aggregates and highly crystalline, confirming the XRD results.

The results of TCLP are listed in Table 3. The leaching concentration of Cr from the spent pickle acid after the cementation process was higher than the regulatory standards stipulated by the EPA of Taiwan. However, the heavy metal ion concentrations of the leaching solution were below the TCLP limitation, especially for the ferrite process at 60 and 70˚C. This implies that the ferrite process is able to treat waste acid containing heavy metals and produce non-toxic ferrite products. The non-ferrous metals are immobilized in the spinel structure.

3.3. Economical evaluation

Table 4 gives the preliminary economic estimation for a recovery plant for spent pickling liquid

Table 4
Economical estimation for a recovery plant of spent pick liquid treatment by ferrite process

Item	Calculation	NTD $ 10^4	Month
(1) Capital cost		650	
(2) Operating and maintenance cost per month		82	
(3) Revenue from treatment fee and sales of resources per month		84	
(4) Net profit per month	60−(2)−(3)+(4)	62	
(5) Period of return	(1)/(5)		10.48

treatment by the ferrite process with a capacity of 12 tons per day. The capital cost would be NTD $6.5 million, annual operating and maintenance cost NTD $9.84 million, and annual amortization cost NTD $1.1 million. Annual profits from treatment fees and sales of ferrite products would be NTD $17.28 million. Consequently, the total investment could be reimbursed within one year.

3.4. Comparison with the published recent papers

To compare our results with those of other authors, we compiled data obtained from several studies (2008–2011) on the recycling of spent pickle acid to more valuable resources. Table 5 summarizes the results of this compilation. From the viewpoint of cost and benefit, the mineralization process for the recovery of spent pickle acid is always superior to the spray roaster process, fluidized bed process (Ruthner process), vacuum distillation process, and sulfuric acid replacement process (Tables 4 and 5). Additionally, the solid product (magnetite) could be applied to magnetic materials, absorbents for toxic gases (hydrogen sulfide), pigments, paints and frits [23,24]. Thus, recovery of spent pickle acid by the mineralization process could enhance the economic value of the waste acid.

Table 5
Comparison for resource recycling technology of spent pickle acid [1–2, 7–9,17–22, this study]

Regeneration techniques	Spray roaster	Fluidized bed (Ruthner process)	Vacuum distillation	Sulfuric acid replacement
Investment costs	High	High	Relatively low	Relatively low
Operation and maintenance costs per year	High	High	Relatively low	Relatively low
Economic benefit	High	Medium	Relatively low	Medium
Area required (m^2)	>500	>500	>100	>100
Operation condition	Continuous stirred-tank reactor (CSTR)		Semi-CSTR, Semi-batch	
Operating temperature (°C)	800		85	
Pollution	High air pollution (Emission of exhaust gases)		Relatively low air pollution	
Consumption of energy	High energy-consuming		Relatively low energy-consuming	
Recovery rate of regenerated spent pickle acid (%)	98	98	According to the concentration of free acid	98
Concentration of regenerated spent pickle acid (%)	16–18	16–18		16–18
Products	Fe_2O_3	Fe_3O_4 MFe_2O_4(Zn, Ni, Cd, Cr)	$FeCl_2$ (35%)	$FeSO_4 \cdot H_2O$
Application	Pigment, paint mordant, permanent magnet	Polishing agents, magnetic ink, magnetic tape coating	Waste water treatment agent, mordant, ferric chloride	Waste water treatment agent, reducing agents, preservatives

4. Conclusions

Based on the analysis results of heavy metal concentrations, XRD, SEM, and TCLP test, it is obvious that the heavy metal ion concentrations of the filtrate from the ferrite process lie below the regulatory effluent standards. The XRD pattern of the solid product matches the pattern of magnetite (Fe_3O_4). It is evident that a single ferrite particle is smaller than 0.2 μm. The results of TCLP test show that the heavy metal ion concentrations of the leaching solution were below the regulatory standards. The main advantages of the recovery of waste acid by the ferrite process are lower disposal costs, reclamation profits and stable and environmentally friendly ferrite products. It should also be emphasized that ferrite compounds containing heavy metals may have economically viable applications, such as for magnetic materials, absorbents for toxic gases (hydrogen sulfide), pigments, paints, frits, etc. Thus, research on the treatment of waste acid by the ferrite process is nowadays continuously being carried out.

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