

STUDY ON THE PREPARATION OF ZINC SULFATE FROM CHLORIDE- CONTAINING HOT DIP GALVANIZING ASH

NGHIÊN CỨU QUÁ TRÌNH CHẾ TẠO KẼM SUNFAT TỪ XỈ MẠ KẼM NHÚNG NÓNG CHỨA CLO

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ABSTRACT

This study aimed to develop a zinc sulfate preparation process from chloride-containing zinc ash formed during the hot dip galvanizing. Zinc sulfate solution was formed by the hydrometallurgy of zinc ash in sulfuric acid. The main impurities included in the solution such as iron and aluminum were removed by pH-controlled precipitation using 10% NaOH solution as a neutralizing agent. In order to remove chloride, copper (I) oxide was used. The results showed that the hydrometallurgy of zinc ash achieved the highest yield (98.05% zinc was extracted) under the conditions: sulfuric acid concentration of 2 M, temperature of 55°C, liquid to solid ratio of 8/1 and leaching time of 90 min. Zinc sulfate with the purity of 98.37% was crystallized from refined - zinc sulfate solution.

Keywords: Chloride-containing hot dip galvanizing ash, zinc recovery, hydrometallurgy, zinc sulfate preparation.

TÓM TẮT

Nghiên cứu này hướng tới xây dựng và hoàn thiện quá trình chế tạo kẽm sunfat từ xỉ mạ kẽm nhúng nóng chứa clo. Trước hết thủy phân xỉ kẽm trong dung dịch axit sunfuric để tạo ra dung dịch kẽm sunfat. Các tạp chất chủ yếu trong dung dịch bao gồm sắt, nhôm được loại bỏ bằng phương pháp kết tủa điều chỉnh pH với tác nhân trung hòa là dung dịch NaOH 10%, đồng (I) oxit được sử dụng để loại tạp chất clorua. Kết quả cho thấy điều kiện thủy phân kẽm thích hợp là nồng độ axit sunfuric 2M, nhiệt độ 55°C, tỷ lệ lỏng/rắn 8/1, thời gian 90 phút. Ở điều kiện này, hiệu suất tách kẽm đạt 98,05%. Kẽm sunfat kết tinh từ dung dịch sau khi tinh chế có độ tinh khiết lên tới 98,37%.

Từ khóa: Xỉ mạ kẽm nhúng nóng chứa clo, thu hồi kẽm, thủy phân, chế tạo kẽm sunfat.

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1. INTRODUCTION

Hot dip galvanizing, which plays a very important role in zinc plating, it products a large amount of zinc- contained waste with hundreds of tons per year. These wastes called hot dip galvanizing ash or zinc ash is created by the oxidation of the molten zinc on the top of the bath [1]. Besides the mixture

of metallic zinc and zinc oxide, there are many such impurities in ash's constituent as iron, aluminum, especially chloride compounds from using NH_4Cl as an additive. Because of the presence of chloride with a quite amount (5 ÷ 20%), it is difficult to treat the ash to recover zinc [1].

There were two solutions of zinc recovery which were as follows: pyrometallurgy and hydrometallurgy. Nowadays, hydrometallurgy pays more attention of scientists than pyrometallurgy because hydrometallurgy not only makes it easier for conditions to carry out the process but it also reduces environmental pollution [1]. Thanks to hydrometallurgical recovery of zinc from zinc ash, many important zinc-containing compounds can be prepared, including zinc sulfate which is consumed in a large amount in Vietnam for such sectors as fertilizers, animal feed, toothpaste... However, the study on preparation of zinc sulfate from zinc ash is modest. Almost studies aimed to prepare zinc oxide or metallic zinc although zinc sulfate solution is the semi-finished product of hydrometallurgical process [2-6].

P. Dvorčák and J. Jandova [2] leached zinc ash in H_2SO_4 solution, the main impurities such as iron and alumina were removed from leach solution by pH-controlled precipitation using 10% NaOH solution as a neutralizing agent. Then chloride-free zinc hydroxy-carbonate was precipitated. Finally, metallic zinc was prepared by the electrowinning process with zinc sulfate solution. There were some other solutions to remove chloride offered in other work. For example, Steintveit et al [4] used organic amine as an extracting agent; Thorsen and Grislingas [3] leached chloride-containing zinc ash with a liquid organic phase containing cation exchanger, such as commercial carboxylic acid Versatic 9911.

In this study, a procedure to prepare zinc sulfate from hot dip galvanizing ash using hydrometallurgical solution were offered. Chloride was removed from leach solution by using copper (I) oxide instead of precipitation of zinc hydroxy-carbonate.

2. EXPERIMENTAL

2.1. Materials

Hot dip galvanizing ash used for this study was collected from An Viet Mechanical Company, Km 3, Phan Trong Tue Street, Tam Hiep, Thanh Tri, Hanoi.

Sulfuric acid, sodium hydroxide, hydrogen peroxide, copper (I) oxide made in China were collected from a local market.

2.2. Characterization of zinc ash

Zinc ash's chemical composition was analyzed by EDX method (Instrument: JEOL -JSM 6490) at Institute of Material Science, Viet Nam Academy of Science and Technology.

Zinc ash's phase composition was determined by X-ray diffraction analysis (Instrument: BRUKER X-ray Diffiactometer model 'Advanced D8') at Chemical Faculty, Hanoi University of Science.

2.3. Leaching tests

Leaching experiments were performed in a closed, stirred, thermostated glass reaction vessels provided with pH, temperature control and water cooler.

Based on previous studies [2], leaching conditions were as follows: the amount of zinc ash of 50 g, sulfuric acid concentration from 1 M to 3 M, reaction temperature from 25°C to 75°C, liquid to solid ratio (l/s) from 5/1 to 14/1, leaching time from 30 min to 150 min.

2.4. Purification of the leaching solutions

pH-controlled precipitation using 10% NaOH as a neutralizing agent was used to remove iron and aluminum from leach solutions. Precipitation was followed by an oxidation with H₂O₂ and KMnO₄ as agents. This process was performed at leaching test temperature and pH from 1.0 to 5.0, within 60 min.

Removing chloride was carried out by precipitating copper (I) chloride from the solution with copper (I) oxide as an agent following the European patent EP 2 504 459 B1 [7]. The conditions were as follows: the amount of Cu₂O from 10 to 50 g/l, room temperature, pH of 5,0 and reaction time of 60 min.

2.5. Crystallizing zinc sulfate

The refined - zinc sulfate solution obtained from the purification process was concentrated in the atmosphere. Then, zinc sulfate was crystallize by the natural cooling.

3. RESULTS AND DISCUSSION

3.1. Characterization of zinc ash

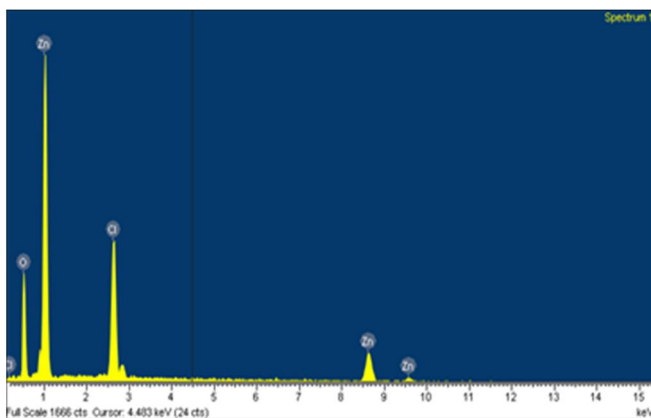


Figure 1. EDX spectrum of zinc ash

Table 1. Chemical composition of zinc ash

Elements	Zn	Fe	Cl	Al
% weight	58.57	0.98	19.50	0.12

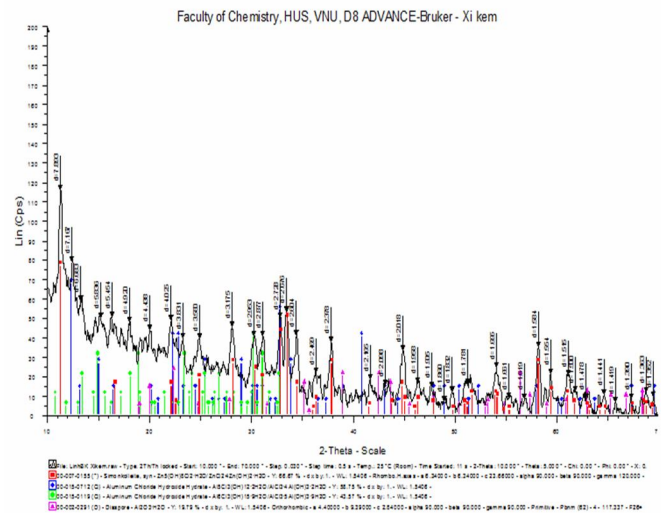


Figure 2. XRD pattern of zinc ash

Chemical composition of zinc ash given in Fig.1 and Table 1 is in line with a typical composition of zinc ash offered by V. Kumar et al (2000) but there is a higher amount of chloride compounds (19.5 wt %) for our zinc ash in comparison to typical one (2 - 12 wt %), making it more difficult for the purification.

In term of phase composition, the results showed in Fig.2 are like previous studies (P. Dvorčák and J. Jandova) [2]. There are 3 main phase of zinc ash including simonkolleite (Zn₅(OH)₈Cl₂·H₂O), zincite (ZnO) and metallic zinc. This is an advantage of using hydrometallurgy method to leach zinc from ash.

3.2. Determining the appropriate conditions for the leaching process

3.2.1. Sulfuric acid concentration

Table 2. Effects of sulfuric acid concentration on the extraction yield (Zinc ash taken of 50g, room temperature, l/s ratio of 5/1, leaching time of 1h)

No. of expt	Sulfuric acid concentration (M)	Zinc initial amount (g)	Zinc extraction amount (g)	Extraction yield (%)
1	1	29.29	19.33	65.99
2	2	29.29	22.01	75.14
3	3	29.29	22.32	76.22

The effects of sulfuric acid concentration on the extraction yield is shown in Table 2. Following the increase of sulfuric acid concentration from 1M to 3M, extraction yield increases from 65.99% to 76.22%. The maximum yield was obtained at sulfuric acid concentration of 3M, however, the yield is insignificantly higher than that obtained at 2M. Therefore, the most appropriate sulfuric concentration of the leaching process was set to 2M.

3.2.2. Liquid to solid ratio

Liquid to solid (l/s) ratio is a parameter which plays a very important role in the leaching process. Basically, the higher l/s ratio is, the more extraction yield increases. This is caused by the increase of hydrogen ions in the solution. Yet, if l/s ratio further increase, the extraction yield will insignificantly develop. So, there is always an optimal l/s ratio of the process.

Table 3. Effects of liquid to solid ratio on the extraction yield (Zinc ash taken of 50 g, room temperature, sulfuric acid concentration of 2M, leaching time of 1h)

No. of expt	Liquid to solid ratio	Zinc initial amount (g)	Zinc extraction amount (g)	Extraction yield (%)
1	5/1	29.29	22.01	75.14
2	6/1	29.29	23.04	78.67
3	7/1	29.29	23.65	80.74
4	8/1	29.29	24.40	83.32
5	9/1	29.29	24.47	83.56
6	12/1	29.29	24.61	84.02
7	14/1	29.29	24.67	84.21

As shown in Table 3, with increasing l/s ratio from 5/1 to 14/1, the extraction yield rises from 75.14% to 84.21%. When l/s ratio reaches to 8/1, zinc was practically leached. After that, the increase of l/s ratio has no significant effect on the extraction yield. Hence, l/s ratio of 8/1 was recommended in the leaching process.

3.2.3. Leaching time

Fundamentally, there is a time which is suitable for the leaching process. This is the time at which the leaching reaction is close to equilibration.

Table 4. Effects of the leaching time on the extraction yield (Zinc ash taken of 50 g, room temperature, sulfuric acid concentration of 2 M, l/s ratio of 8/1)

No. of expt	Leaching time (minute)	Zinc initial amount (g)	Zinc extraction amount (g)	Extraction yield (%)
1	30	29.29	22.08	75.37
2	60	29.29	24.40	83.32
3	90	29.29	25.88	88.37
4	120	29.29	26.12	89.18
5	150	29.29	26.35	89.96

The results in Table 4 show that the extraction yield dramatically increases with the increase of the leaching time from 30 min to 90 min but not markedly in the later period (90-150 min) with a slight development in the extraction yield from 88.37% to 89.96%. Therefore, taking the leaching cost into consideration, the most favorable leaching time should be 90 min.

3.2.4. Temperature

Temperature affects almost chemical processes including leaching. It not only has an effect on the leaching

yield but also makes a difference to the cost of the process. For that reason, finding the appropriate temperature of the leaching process that plays a very important role.

Table 5. Effects of temperature on the extraction yield (Zinc ash taken of 50g, sulfuric acid concentration of 2M, l/s ratio of 8/1, leaching time of 90 min)

No. of expt	Temperature (°C)	Zinc initial amount (g)	Zinc extraction amount (g)	Extraction yield (%)
1	25	29.29	26.58	90.74
2	35	29.29	27.19	92.83
3	45	29.29	27.94	95.38
4	55	29.29	28.72	98.05
5	65	29.29	28.89	98.63
6	75	29.29	28.99	98.97

The effects of temperature on the extraction yield is shown in Table 5. As a result, in the temperature range from 25°C to 55°C, there is a significant increase in the extraction yield (from 90.74% to 98.05%). However, when it continues to increase from 55°C to 75°C, there is almost no difference in the extraction yield. Consequently, choosing the appropriate temperature of the leaching process was 55°C.

3.3. Purification of the leaching solution

Table 6. Chemical composition of the leaching solution

Elements	Zn	Fe	Cl	Al
Concentration (g/l)	69.84	0.98	5.50	0.10

The concentrations of the main elements of the leaching solution are presented in Table 6. The results fit with the study of P. Dvorák and J. Jandova [2]. In order to remove the main impurities, there were many solutions suggested by previous studies. In almost these studies, removing iron and aluminum was solved by pH-controlled precipitation. There are some such solutions suggested to remove chloride as extracting with organic amine, using cation exchanger. Especially, a recent solution applied in many studies is forming precipitation of chloride-free zinc hydroxy-carbonate. However, this solution is only in line with preparing metallic zinc or zinc oxide from zinc ash, not with preparing zinc sulfate.

For the sake of finding the more appropriate solution to remove chloride, the European patent EP 2 504 459 B1 was applied [7].

3.3.1. Removing iron and aluminum

The main issue in removing iron and aluminum is to remove iron because the amount of aluminum in the solution is little. Therefore, it is necessary to treat the solution with 10% H₂O₂ to transform iron (II) to iron (III) before the precipitation with 10% NaOH solution. After that, with the purpose of completely transforming iron (II) to iron (III), the solution was continually treated with KMnO₄.

Table 7. The effects of pH on the removing iron and aluminum (Temperature of 55°C, time of 60 min)

No. of expt	pH	Initial concentration (g/l)		Remaining concentration (g/l)		Removing yield (%)	
		Fe	Al	Fe	Al	Fe	Al
Treated with 10% H₂O₂ solution							
1	1.0	0.98	0.10	0.98	0.100	0	0
2	2.0	0.98	0.10	0.72	0.078	26.12	21.56
3	3.0	0.98	0.10	0.52	0.061	47.09	39.15
4	4.0	0.98	0.10	0.33	0.042	65.87	58.03
5	5.0	0.98	0.10	0.22	0.040	77.31	60.47
Treated with KMnO₄							
6	5.0	0.98	0.10	0.02	-	98.00	-

Table 7 indicates the effects of pH on removing yield of iron and aluminum from the leaching solution. In the period of treating with H₂O₂, the maximum removing yield of aluminum and iron is 60.47% and 77.31%, respectively. After treated with KMnO₄, 98% of the amount of zinc was removed from the solution. Hence, the appropriate pH chosen for the process to be 5.0. Besides, the experiments indicated that the amount of 10% H₂O₂ solution and KMnO₄ needed for the process was 1% in volume ratio and 0.5g/l, respectively.

3.3.2. Removing chloride

Table 8. Effects of Cu₂O concentration on the removing yield of chloride (Room temperature, pH of 5, time of 60 min)

No. of expt	Cu ₂ O concentration (g/l)	Chloride initial concentration (g/l)	Chloride remaining concentration (g/l)	Removing yield (%)
1	10	5.50	1.53	72.15
2	20	5.50	0.81	85.21
3	30	5.50	0.25	95.38
4	40	5.50	0.11	98.05
5	50	5.50	0.07	98.67

The results in Table 8 indicates that there is a noteworthy increasing the removal yield of chloride from 72.15% to 98.05% following the increase of Cu₂O concentration from 10g/l to 40g/l, respectively. The yield little increases from 98.05% to 98.67% when further increasing Cu₂O concentration from 40g/l to 50g/l. For this reason, Cu₂O concentration of 40g/l was recommended in removing chloride.

3.3.3. Crystallizing zinc sulfate

As the results of the crystallization, the amount of obtained- zinc sulfate was 296.78g per liter of the solution with the purity of 98.37% corresponding to the yield of 96.24%.

4. CONCLUSIONS

The leaching process of hot dip galvanizing ash were studied. As a result, the appropriate conditions of the process are as follows: temperature of 55°C, sulfuric acid solution concentration of 2M, liquid to solid ratio of 8/1 and the leaching time of 90 min. In these conditions, 98.05% zinc was extracted from the ash;

The purification of the leaching solution was studied. 60.47% of aluminum and 98% of iron were removed from the solution by pH-controlled precipitation process with 10% NaOH solution as a neutralizing agent following transforming iron (II) to iron (III) by 10% H₂O₂ solution and KMnO₄. The process was carried out at temperature of 55°C, pH of 5, within 60 min, the amount of 10% H₂O₂ solution and KMnO₄ of 1% in volume ratio and 0.5g/l, respectively;

Precipitation of copper (I) chloride from the solution with copper (I) oxide as an agent was investigated to remove chloride. The results showed that 98% of chloride was removed from solution in the conditions which were as follows: room temperature, pH of 5, time of 60 min and Cu₂O concentration of 40g/l. The amount of obtained- zinc sulfate was 169.25 g per liter of the solution with the purity of 98.37% corresponding to the yield of 96.24%.

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