Available online at www.sciencedirect.com
SciVerse ScienceDirect
Procedia Environmental Sciences 16 (2012) 674 – 682
Procedia Environmental Sciences

The 7th International Conference on Waste Management and Technology

Optimized hydrometallurgical route to produce ultrafine zinc powder from industrial wastes in alkaline medium

Qiang Li[a], Youcai Zhao[a,*], Jiachao Jiang[b], Chenglong Zhang[c]

[a]*The State Key Laboratory of Pollution Control and Resource Reuse, Tongji University, Shanghai 200092, China*
[b] *School of Environment Science and Spatial Informatic, China University of Mining and Technology, Xuzhou 221116, China*
[c]*School of Urban Development and Environmental Engineering, Shanghai Second Polytechnic University, Shanghai 201209, China*

Abstract

A hydrometallurgical process for producing ultrafine zinc powder from industrial wastes containing zinc was proposed. This process consists of alkaline leaching, purification stage, and electrowinning section. Firstly, affecting factors, such as leaching condition and waste sample composition were studied. In the alkaline medium, the leaching extractions of Zn and Pb are above 80% and 90%. Moreover, the residue was detoxified completely. In the purification section, the Pb, Sn and Al were separated by adding Na_2S, Zn and CaO, respectively. Experiments were performed to obtain the optimal condition. Hence, more than 90 % of metal impurities could be removed. Finally, zinc electrowinning was undertaken with addition of the Pb, Sn and Al. Morphology and size distribution of Zn particles were characterized by Scanning Electron Microscopy and Laser Particle Size Analyzer. The electrowinning results show that metal impurities could evidently reduce the size of zinc particle under optimum condition. Through this process, ultrafine zinc powders with a mean diameter of around 10 μ m, containing less than 100 ppm of metallic impurities, could be obtained.

Keywords: Hazardous wastes; Alkaline leaching; Electrowinning; Ultrafine Zn powder

Corresponding author. Fax: +86 21 65982684
Email address: zhaoyoucai@tongji.edu.cn

doi:10.1016/j.proenv.2012.10.093

1. Introduction

In china, a large amount of industrial wastes containing zinc are generated per year, especially from metal fusing process [1, 2]. These wastes are commonly classified as hazardous wastes, due to their metal leaching potential. Accordingly, their disposal and utilization attract increasing interest.

In view of low energy consumption and gas emission, the hydrometallurgy is frequently employed to recover metal from wastes [3]. However, a major problem corresponding to this process is the detrimental effect exerted by metallic impurity [4]. Elements such as Pb, Ca, Fe, Mg, Al, Cu, etc. may also dissolve in the acid leaching agents [5, 6]. As a result, a large quantity of extra leaching agents will be consumed and a leach solution with complex components will be obtained. Therefore, leaching with alkaline solution is gaining importance in hydrometallurgy process to treat wastes. In this method, Fe, Mg, Ca, etc. will not be dissolved in alkaline solution. Moreover, current efficiency of 100% can be reached when high current densities are applied, owing to the impeded hydrogen evolution in this process [7].

However, some impurities such as Pb, Al and Sn in these wastes can also be leached by alkaline medium. It was proposed in our previous work that lead can be cemented quantitatively without concomitant loss of zinc by sulfide precipitation using sodium sulfide as precipitant [4]. In this optimized process, the utilization of Pb, Al and Sn is explored during electrowinning section.

On the other hand, in the production of zinc powder by hydrometallurgy route, the reduction of grain size is a great concern, because ultrafine powder exhibits high reactivity on treating harmful pollutants NOx and displacing the metal impurities in the solution [8, 9]. Hence, a great majority of industries employ the milling process, which has increased energy cost. Another possibility consists of addition of various organic to the electrolyte in order to improve the particle structure [10-12], but these organic additives cause adverse effects on the controlling of the process.

This work proposes an optimized hydrometallurgy route, as shown in Fig.1, for producing ultrafine zinc powder from industry wastes containing zinc. The major character of this process is that using metal impurity removed as additive to promote zinc electrowinning and treat the raw wastes. In this work, the procedures of alkaline leaching, impurity removal, and zinc powder electrowinning were mainly studied.

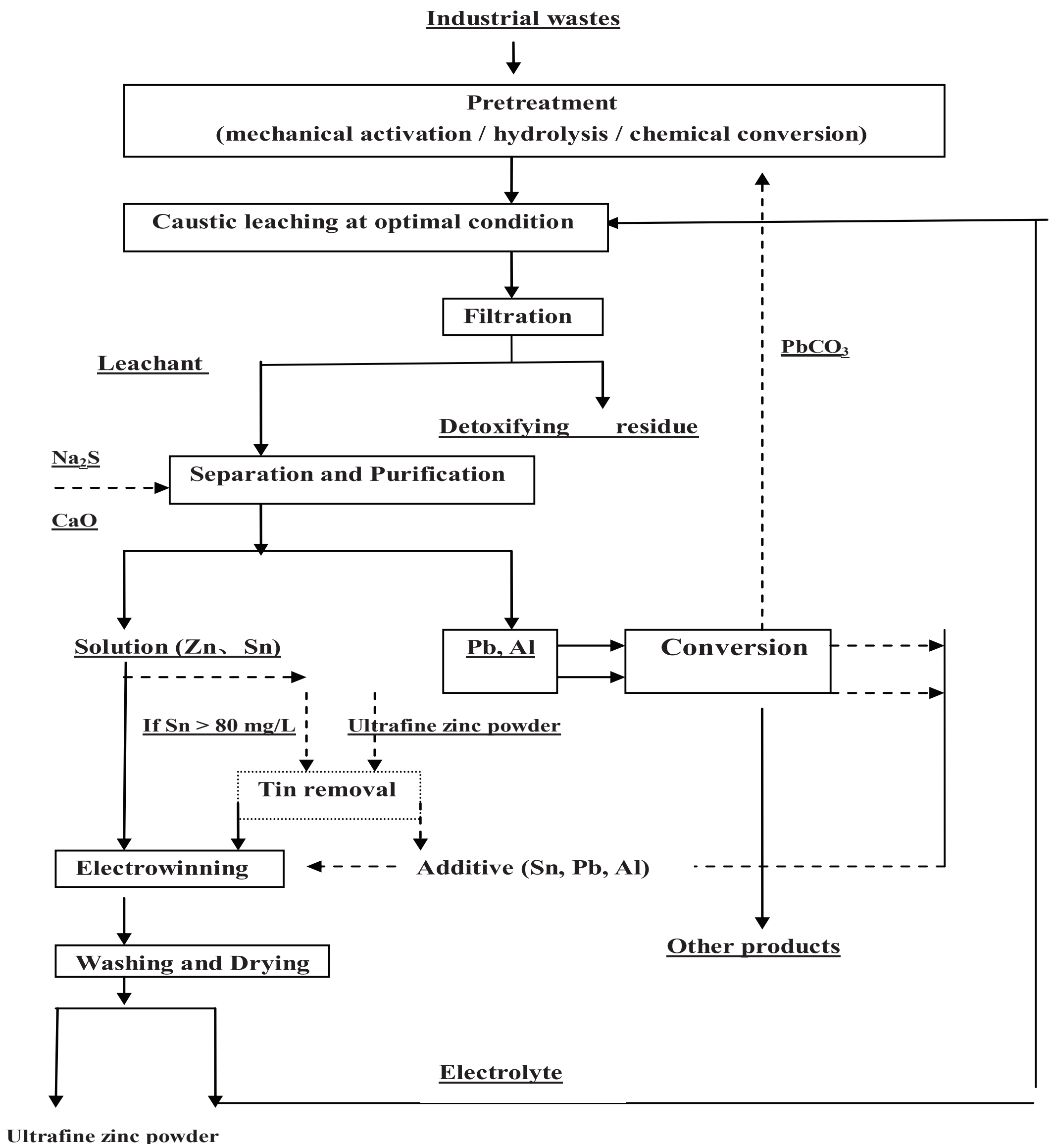

Fig.1. Schematic flow sheet of hydrometallurgical route for ultrafine zinc production from industrial wastes

2. Experimental

2.1. Materials

The fresh sample was a mixture of some industrial wastes such as electric arc furnace (EAF) dust, basic oxygen furnace (BOF) sludge, and jarosite residue. The waste composition used throughout this study is shown in Table 1. All the other chemicals used were of analytic grade, unless indicated otherwise.

Table. 1. Composition of the wastes studied

Elements	Zn	Pb	Fe	Cu	Al	Mn	Ni	Sn	Cd
Wt.%	57.60	13.80	21.03	0.08	1.06	2.17	0.18	0.26	0.07

2.2. Experimental approach

2.2.1. Leaching stage

The leaching stage was performed in a flask placed on a heated magnetic stirrer-unit under the following condition: L:S ratio (V/W), 8-20:1; NaOH concentration, 220-280 g/L; temperature, 80-100℃; leaching time, 80-120 min.

2.2.2. Purifying stages

The reactor used in the purifying stages was the same utilized in the leaching stage. CaO and Na2S were the agents to remove Al and Pb from the solution. In addition, the ultrafine zinc powder was used as cementation agent when Sn in the electrolyte was above 80 mg/L.

2.2.3. Electrowinning stage

The electrowinning cell was a 1000 mL plexiglass cylinder shown in Fig. 2. Cathode was made from magnesium sheet 8 cm height by 10 cm wide. Two anodes were stainless steel plates of the same dimension. The inter-electrode distance was 3 cm. The temperature, current density, Zn2+ concentration, and NaOH concentrations were set to vary 30 to 70 °C, 500 to 1500 A/m2, 10 to 40 g/L, and 150 to 300 g/L, respectively. Metal impurities were tested as grain refiners when used in the range of concentrations from 10 to 100 mg/L.

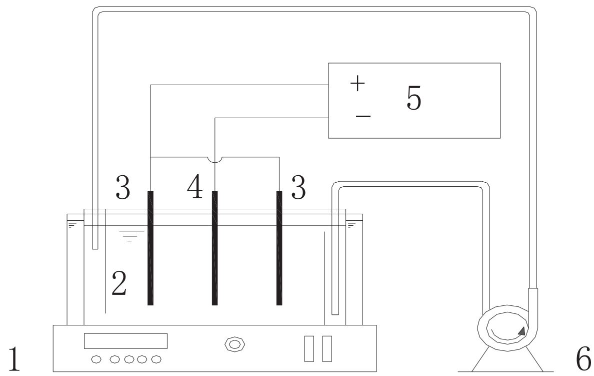

Fig. 2. Schematics of the apparatus for the alkaline zinc electrowinning experiments. 1. Thermostatic bath, 2. Electrolysis cell, 3. Anode, 4. Cathode, 5. DC power supply, 6. Pump

2.3. Analysis methods

The zinc powders obtained were digested in concentrated nitric acid at 90 °C, and the leaching liquor was diluted for chemical analysis. The sample composition was determined by ICP-OES. Sections of the zinc powders were examined by scanning electron microscopy to exam the surface morphology and by laser particle size analyzer to identify the size distribution. .

3. Results and discussion

3.1 Alkaline leaching

3.1.1. Initial studies

Some initial studies were carried out to explore the behavior of metal impurities in the leaching agent. As illustrated in the introduction, Cu and Fe can not be leached from the wastes by NaOH. According to the following calculation, the concentration of metal impurities with respect to the PH was determined (Fig.3-4).

$$CuO_{(s)} + H_2O = Cu(OH)_{2(aq)}, \quad \Delta_r G^{\theta}_{298.15} = 118.963 \text{ kJ/mol}$$

$$CuO_{(s)} + H_2O = Cu^{2+} + 2OH^- , \quad \Delta_r G^{\theta}_{298.15} = 117.520 \text{ kJ/mol}$$

$$[Cu(OH)_{2(aq)}] = EXP(-0.048) , \; [Cu^{2+}] = EXP(17.063 - 4.606\,pH)$$

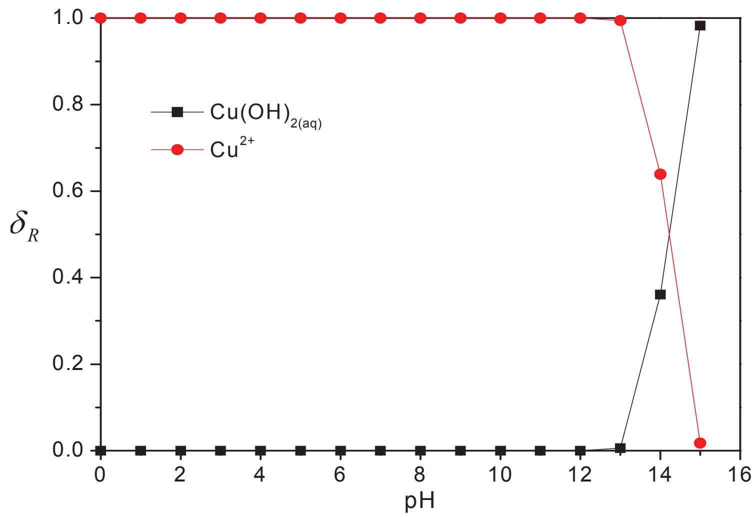

Fig. 3 Relationship between pH value and δ_R of different Cu-containing species (25 ℃).

On the basis of same theory, the other metal impurities such as Fe, Pb, Sn, AL, Ni and Cd were also analyzed in terms of leaching in alkaline solution. These results indicated that the behaviors of metal impurities are strongly dependent on the PH value. The total leached zinc amount increased when high pH values were used. At elevate pH, higher than 14, the OH^- concentration would be high enough to remove the Cu and Fe from the wastes, improving the zinc lixiviation. Thus, in this optimized process, the Cu and Fe remained in the residue whereas Pb, Sn and Al were dissolved together with Zn.

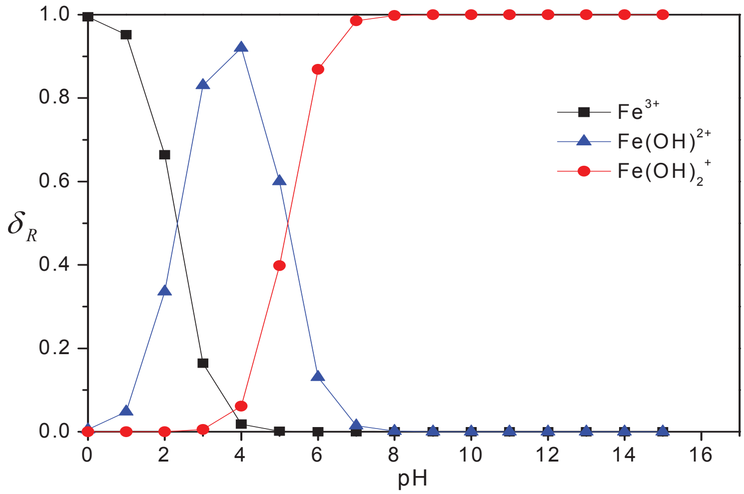

Fig. 4 Relationship between pH value and δ_R of different Fe-containing species (25 ℃).

3.1.2. Optimum leaching conditions for various waste samples

As shown in table 2, five different waste samples were selected taking into account the complexity of the industrial wastes. In case of each sample, the effects of four leaching variables, i.e. NaOH concentration (220-280 g/L), leaching time (80-120 min), temperature (80-100 °C) and the ratio of liquid to solid (L/S 8:1-20:1) on zinc recovery were investigated. The optimum leaching conditions were determined at which maximum impurities precipitation occurred with minimum zinc losses.

Table.2. Optimum leaching conditions for various waste samples

	NaOH concentration g/L	Leaching time min	Temperature °C	L/S
Raw sample	280	120	100	15:1
Raw sample + ZnO	263	95	90	9:1
Raw sample + $ZnCO_3$	245	90	85	12:1
Raw sample + Zn_2SiO_4	257	100	85	12:1
Raw sample + ZnS	272	80	100	20:1

Table 2 shows that the sample composition affects greatly the optimal leaching condition. The waste samples added with ZnO, ZnCO3, and Zn2SiO4 are easier to be recovered relative to the other samples. For the wastes mainly containing ZnS and EAF dust, the value extraction are strongly dependent on the L/S ratio and the pretreatment methods (hydrolysis, mechanical activation).

3.2. Removal of metal impurities

A simulated leaching solution with a composition same to the above experiments, was used in this section. The Na_2S, CaO, and Zn were used to remove Pb, Al, and Pb respectively. Fig.5 shows that, when a weight ratio of 2.0 was taken, nearly 100% of lead, 85% of Al and 45% of Sn were removed from the solution.

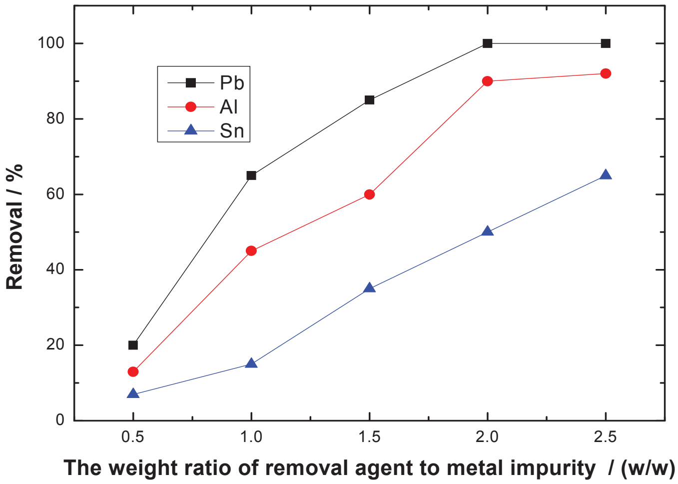

Fig.5 Separation of impurities from wastes by adding removal agents

Furthermore, the experiments also indicates that the small amount of metal impurities (Sn < 80 mg/L, Pb < 50 mg/L, Al < 100 mg/L) have a neglected effect on current efficiency. Additionally, the impurity electrowinning was controlled by mass transport, causing little influence on zinc purity. Moreover, the presence of Al inhibits the electrowinning of Sn from electrolyte duo to the increase in viscosity.

3.3. Electrowinning of ultrafine zinc powder in the presence of metal additive

The electrowinning experiments of zinc in the presence of Sn, Pb, and Al were undertaken using caustic soda solution. Previously, the effects of variable parameters such as current density and reaction temperature were studied. The optimum condition could be current density 800-1000 A/m^2 and temperature 30-40 °C.

The above metal impurities removed are now regarded as potentially useful materials for facilitating the electrowinning of ultrafine zinc powder. The Pb and Al were used to reduce grain size, due to that they could increase nucleation overpotential (Fig.6). However, Sn was also considered as grain refiner, owing to its relation with inhibition intensity. Namely, tin could co-deposit to some degree with zinc.

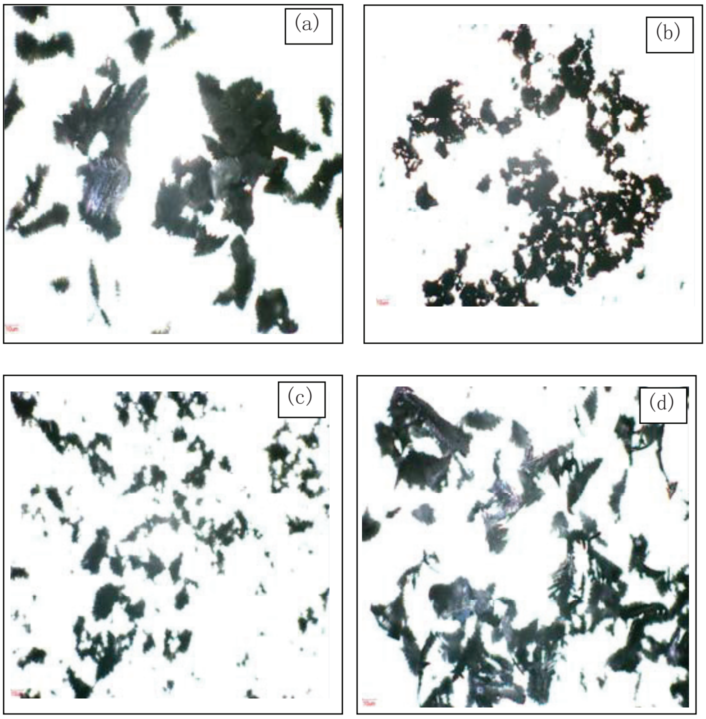

Fig.6 Micrographs of zinc powders electrowon from alkaline solution, with the addition of different metal: (a) addition-free; (b) 80 mg/L Sn; (c) 50 mg/L Pb; (d) 100 mg/L Al.

The surface morphologies were examined by scanning electron microscopy (Fig.6). They consist of packed uniform nodules, comprised of sharply defined hexagonal zinc plate-like crystals. It was found that the grain size of zinc powder was substantially reduced. This result can be confirmed by the size distribution measurements; the mean diameters of ultrafine zinc powders are lower than 10 μ m.

4. Conclusion

On the basis of the data presented in this paper, an optimized hydrometallurgical route for the production of ultrafine zinc powder, by electrowinning, from industrial wastes, is suggested. This process exhibits the following merits: the overall leaching recovery of Zn was above 80 % under optimum case, and it was further improved by adjusting waste sample composition. After purification stage, the total impurities concentration in the liquor could be lower than 100 mg/L. The grain size of zinc powders was substantially reduced to be less than 10 μ m, with addition of metal elements obtained in purification section.

Acknowledgments

This work was financially supported by Science and Technology Commission of Shanghai Municipality (No. 08 DZ 1202802, 09 DZ 1204105 and 09 DZ 2251700).

Reference

[1] Z. Youcai, R.Stanforth, Integrated hydrometallurgical process for production of zinc from electric arc furnace dust in alkaline medium, J. Hazard. Mater. 80 (2000) 223–240.
[2] J. Shaohua, Z. Yifei, Z. Yi, X. Peiyi, W. Yihui, Clean hydrometallurgical route to recover zinc, silver, lead, copper, cadmium and iron from hazoudous jarosite residues produced during zinc hydrometallurgy, J. Hazard. Mater. 192 (2011) 554–558.
[3] D. Herrero, P.L. Arias, B. Güemez, V.L. Barrio, J.F. Cambra, J. Requies, Hydrometallurgical process development for the production of a zinc sulphate liquor suitable for electrowinning, Miner. Eng. 23 (2010) 511–517.
[4] Z. Youcai, R. Stanforth, Selective separation of lead from alkaline zinc solution by sulfide precipitation, Sep. Sci. Technol. 36 (2001) 2561–2570.
[5] S.R. Swarnkar, B.L. Gupta, R.D. Sekharan, Iron Control in Zinc Plant Residue Leach Solution, Hydrometallurgy. 42 (1996) 21–26.
[6] L. Muresan, G. Maurin, L. Oniciu, D. Gaga, Influence of metallic impurities on zinc electrowinning from sulphate electrolyte, Hydrometallurgy. 43(1996)345 –354.
[7] S. Gurmen, M. Emre, A laboratory-scale investigation of alkaline zinc electrowinning, Miner. Eng. 16 (2003) 559–562.
[8] S.C. Tjong, H. Chen, Nanocrystalline materials and coatings, Mater. Sci. Eng. 45 (2004) 1–88.
[9] M. Vaghayenegar, A. Kermanpur , M.H. Abbasi, H. Ghasemi Yazdabadi, Effects of process parameters on synthesis of Zn ultrafine/nanoparticles by electromagnetic levitational gas condensation, Adv. Powder Technol. 21 (2010) 556–563.
[10] M. F. de Carvalho, W. Rubin, I. A. Carlos, Study of the influence of the polyalcohol mannitol on zinc electrodeposition from an alkaline bath, J. Appl. Electrochem. 40 (2010) 1625–1632.
[11] A. Recendiz, I. Gonzalez, J. Nava, Current efficiency studies of the zinc electrowinning process on aluminum rotating cylinder electrode (RCE) in sulfuric acid medium: Influence of different additives, Electrochim. Acta 52 (2007) 6880–6887.
[12] I. Ivanov, Increased current efficiency of zinc electrowinning in the presence of metal impurities by addition of organic inhibitors, Hydrometallurgy 72 (2004) 73–78.