KnE Materials Science

Technogen Conference Proceedings
International Conference with Elements of School for Young Scientists
on Recycling and Utilization of Technogenic Formations (2017)

Knowledge E
Engaging minds

Conference Paper

Autoclave Precipitation of Iron from Zinc Sulfate Solutions

K. A. Karimov, A. V. Kritskii, S. S. Naboichenko, O. B. Kolmachikhina, and D. A. Rogozhnikov

Ural Federal University named after the first Russian President B.N. Yeltsin, Russia, 620002, Ekaterinburg, street Mira, 19

Abstract

Zinc concentrates processing technology that includes high-temperature roasting – leaching of cinder – purification of leached liquor – electrowinning is the most widely used technology. Purified solution, which is fed to the electrowinning stage, has a high sensitivity to such an impurity as iron. The presence of iron in the zinc electrolyte has a negative influence both on the current efficiency and the quality of the cathode zinc. The application of autoclave equipment for iron removal from zinc sulfate solutions, obtained after the leaching stage of zinc cinder, is described in this article. All experiments were carried out with a model solution of following composition, g/L: 10-33 H_2SO_4, 1.5 Cu, 5 Mn, 110 Zn, 2.5 Fe. Neutralization and purification of the solution was implemented during low-temperature pressure leaching of the zinc cinder. The optimum conditions for iron precipitation from zinc solution are following: molar flow rate Zn(cinder) / H_2SO_4 = 1.3, t = 80°C, τ = 1 hour, P_{O_2} = 0.2 MPa. It was found, that the concentration of iron can be reduced up to 1-2 mg/L, whereas 83.5% of Zn and 52.1% of Cu being recovered into the solution from zinc cinder.

Corresponding Author: K. A. Karimov; email: kirill_karimov07@mail.ru

🔓 **OPEN ACCESS**

1. Introduction

Metallurgy of non-ferrous metals as one of the most important Ural region industries plays an important role in the structure of exports of the Russian Federation. The global output of zinc is more than 10 million tons, whereas the significant part of which is used for galvanizing [1].

The Ural deposits of polymetallic zinc ores are one of the largest deposits in the world, the proven reserves of which are about 30 million tons of metal. The main hydrometallurgical method of industrial production of zinc includes atmospheric acid leaching as the head process, the product of which is a zinc-rich solution of a complex composition. The content of certain impurities, such as iron, are undesirable due to the negative influence on target product. Therefore, the purification process is needed, which in some cases doesn't provide the appropriate rate of purification or increases the cost of the product.

Thereby, improving the technology of zinc production at the stages of solution purification and electrowinning of zinc is relevant.

At the stage of zinc cinder acid leaching, iron is leached up to a value about 80 % [2]. The negative influence of impurities can be reflected both in the decline of the current efficiency - it leads to an increase of the electricity consumption, and in the decrease of the cathode zinc quality due to the increased content of impurities [3].

The article shows the results of autoclave purification of zinc-containing solutions from iron.

2. Experimental

Zinc cinder leached liquor contains Fe^{2+} ions along with Fe^{3+} ions. This fact makes the method of direct hydrolytic purification not suitable, since under these conditions Fe^{2+} ions are precipitated together with zinc ions. Consequently, preliminary increases in the redox of the system with the following neutralization are required for iron removing.

All experiments were conducted using a model solution of the following content, g/L: 10-33 H_2SO_4, 1.5 Cu, 5 Mn, 110 Zn, 2.5 Fe. It was prepared from chemically pure reagents. Prepared solution fully simulated the real solutions, obtained after the zinc cinder leaching process on metallurgical plants [4].

A mixture of zinc cinder and cyclone dust in a mass ratio of 40/60 was used as a neutralizer (Table 1) and it has the following chemical composition, %: 52 Zn; 1.5 Cu; 1.1 Pb; 9.4 Fe; 0.6 S_S; 3.7 S_{SO_4}. Phase composition of mixture consists zinc in the form of ZnO, $ZnSO_4$, $ZnO \cdot Fe_2O_3$, $2ZnO \cdot SiO_2$ and ZnS, copper in the form of CuO, $CuSO_4$, $CuO \cdot Fe_2O_3$ and $CuO \cdot SiO_2$ and the iron presents as Fe_2O_3 [5–7].

The influence of temperature, oxygen pressure and molar ratio (neutralizer/sulfuric acid) on iron precipitation and extraction of copper and zinc was investigated in the following ranges: t = 46-115°C, Po_2 = 0.0-0.4 MPa, Zn_{cynder} / H_2SO_4 = 0.9 - 1.4. Other parameters kept constant: τ = 1 hour, $[H_2SO_4]_0$ = 30 - 33 g/L. The aim of the experiments was to maximize the precipitation of iron.

3. Results and Discussion

The temperature of the process has a significant effect on the results of iron precipitation (Figure 1). Precipitation experiments at a molar ratio of Zn_{cynder} / H_2SO_4 = 1 showed that with temperature increase from 45 to 100°C, the final concentration of iron decreases from 2,2 to 0,5 g/L. Further increasing of temperature has not such a strong effect (Figure 1a). The content of free acid at the purified solution decreased
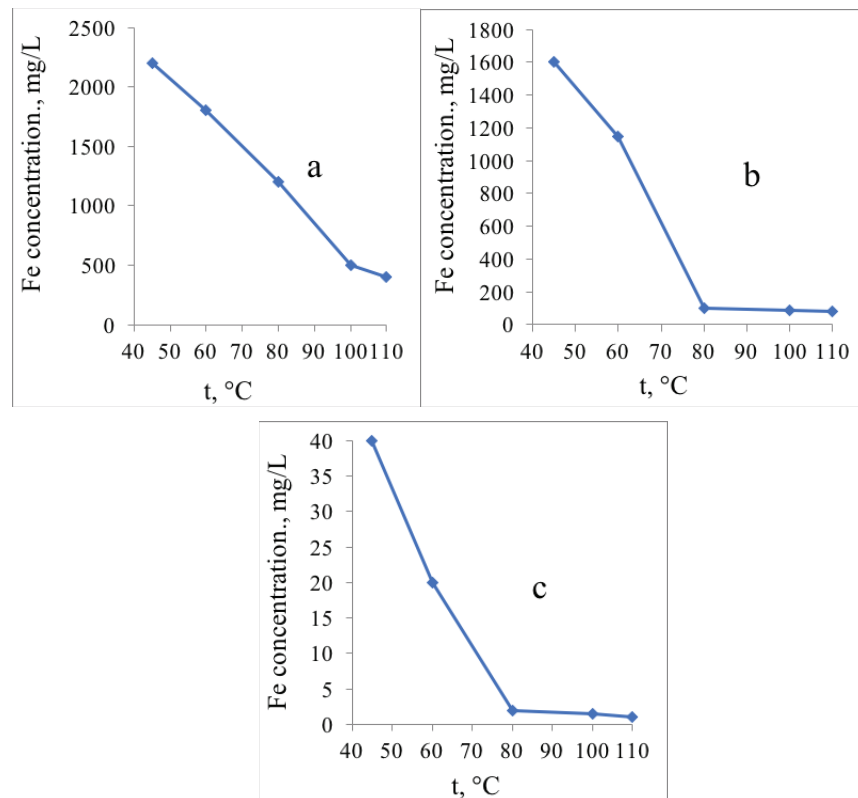
Figure 1: Effect of temperature on the final concentration of iron in solution (τ = 1 hour, Po2 = 0.2 MPa), mole ratio of zinc cinder to sulfuric acid Zn_{cynder} / H_2SO_4: a - 1; b - 1.15; c - 1,3.

down to 0.1 - 0,3 g/L. This indicates an insufficient amount of zinc cinder for complete neutralization of sulfuric acid and explains the high content of iron in final solution.

An increase in the molar ratio Zn_{cynder}/H_2SO_4 from 1 to 1.15 had a positive effect on the precipitation of iron. With an increase in temperature from 45 to 80°C, the final concentration of iron decreases from 1600 to 100 mg/L. Further increase in temperature from 80 to 110°C has less significant impact on precipitation - the final concentration of iron declined from 100 to 80 mg/L (Figure 1a). At the end of the tests pH = 3 - 3.5.

The best precipitation results were obtained with a molar ratio of Zn_{cynder} / H_2SO_4 = 1.3. Due to the increase in temperature from 45 to 80°C - the final concentration of iron decreased from 40 to 2 mg/L. Further increase to 110°C has less significant impact on precipitation which was 1 mg/L (Figure 1c). At the end of the experiment, the solution had a pH range 4.5-4.8. At t $\geq$ 80°C, copper hydroxide precipitation from the solution was observed.

The effect of oxygen pressure on iron precipitation is shown in Figure 2 (t = 80°C, τ = 1 hour, Zn_{cynder} / H_2SO_4 = 1.3).

The optimum oxygen pressure is Po_2 = 0.2 MPa, since the final iron concentration under this conditions was 2 mg/L, and further increase the oxygen pressure up to 0.4 MPa did not effect on the precipitation of iron.
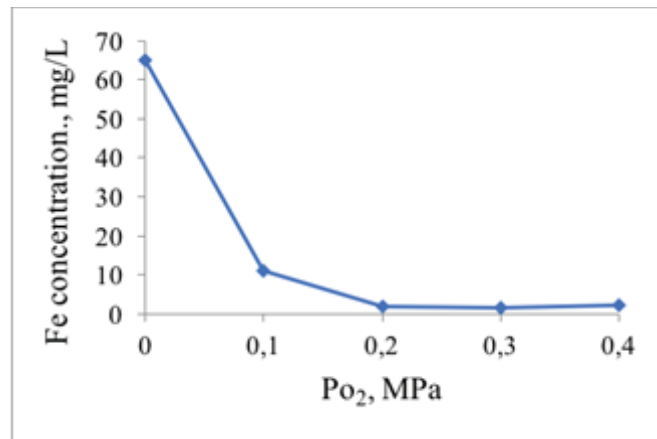
Figure 2: Effect of oxygen pressure on the final concentration of iron in solution (t = 80°C, τ = 1 hour, Zn_{cynder}/H_2SO_4 = 1.3).

The oxidant for ions Fe^{2+} besides partial oxygen could be Cu^{2+} ions [8]:
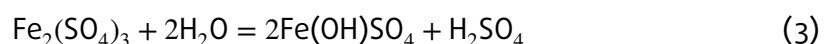
$$Fe^{2+} + Cu^{2+} = Fe^{3+} + Cu^+ \tag{1}$$

The addition of ZnO into the leached liquor, consisted of metals sulfates ($Zn(SO)_4$, $Fe_2(SO_4)_3$), causes a sharp rise in pH as a result of neutralization reaction of the free sulfuric acid. This removes the system from hydrolysis equilibrium and accelerates the hydrolysis reaction. At the end of the experiment, the pH maximum is reached, while the dissolution of ZnO is completed and hydrolysis proceeds to form hydroxo-complexes.

In a medium with a pH of 4.8 - 5.4 and a low concentration of iron in the solution, Fe^{3+} is hydrolyzed by the reaction:

$$Fe_2(SO_4)_3 + 6H_2O = 2Fe(OH)_3 + 3H_2SO_4 \tag{2}$$
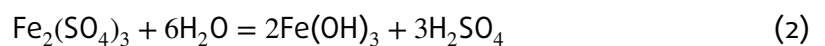
Also, basic ferric sulfates can be formed by the following reaction:

$$Fe_2(SO_4)_3 + 2H_2O = 2Fe(OH)SO_4 + H_2SO_4 \tag{3}$$

During the precipitation of iron from sulfate solutions, depending on solution composition and the process temperature, is possible to obtain the following crystalline phases: $FeOHSO_4$, $FeOOH$, Fe_2O_3, $Fe(OH)_3$ [9].

Thus, the optimum conditions for the precipitation of iron from the zinc solution are: molar ratio Zn_{cynder}/H_2SO_4 = 1.3, t = 80°C, τ = 1 hour, Po_2 = 0.2 MPa. Extraction of Zn is up to 83.5%, of Cu up to 52.1%. The final solution (pH = 4.8) has the following composition, g/L: 142 Zn, 2 Cu, 0.002 Fe.

Phase name	Chemical formula	Content, %
Franklinite	$ZnFe_2O_4$	60,0
Quartz low	SiO_2	16,0
Coesite	SiO_2	5,6
Dizinc Silicate	$ZnSiO_4$	11,5
Delafossite	$CuFeO_2$	2,2
Anglesite	$PbSO_4$	4,4

TABLE 1: Decoding of phases.

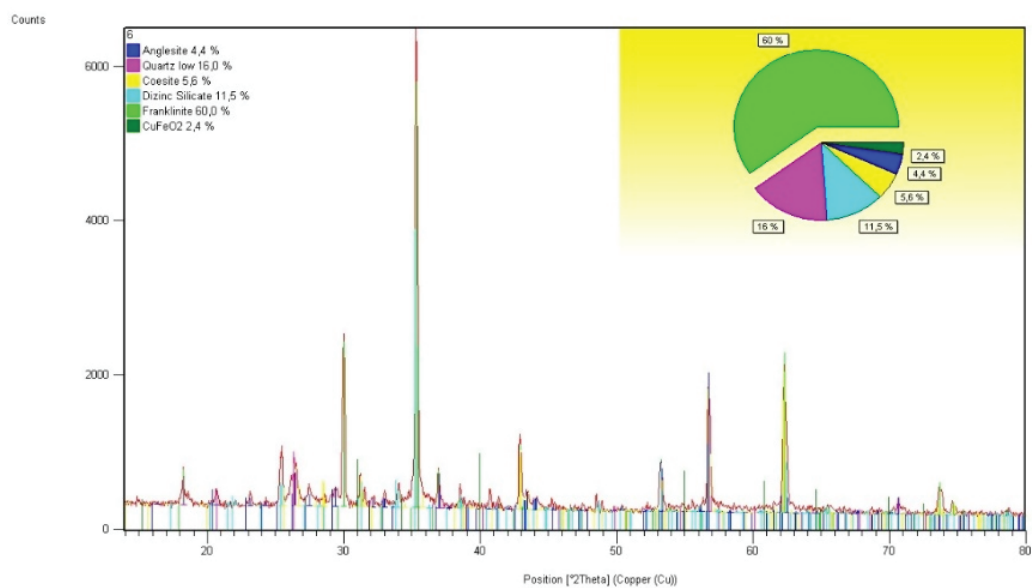**Figure** 3: The roentgenogram of the residue (Zn_{cynder} / H_2SO_4 = 1.3, t = 80°C, τ = 1 hour, Po_2 = 0.2 MPa).

A residue after solution purification contains, %: 21 Zn, 4.2 Cu, 25 Fe, 3 Pb. The roentgenogram of the residue after leaching is presented in Figure 3. The phase interpretation and their percentage, according to X-ray phase analysis data, are presented in Table 1.

According to X-ray phase analysis data (Figure 3), the remaining zinc is in the form of $ZnFe_2O_4$ and $ZnSiO_4$, as well as residues currently produced on the real plants. The residue after drying can be sent to the Waeltz process for the most complete extraction of zinc. It is logical to send the iron-free solution to the cement cleaning by zinc powder from copper and cadmium and the subsequent stage of electrolysis.

4. Conclusion

1. Autoclave purification allows to reduce the concentration of iron in solution from 20-50 to 1-2 mg/L for 1 hour.

2. The optimal conditions for autoclave precipitation of iron from the zinc cinder leached liqour are: molar flow Zn_{cynder} / H_2SO_4 = 1.3, t = 80°C, τ = 1 hour, Po_2 = 0.2 MPa. The concentration of iron can be reduced down to 1-2 mg/L with simultaneous extraction of Zn (83.5 %) and Cu (52.1 %) from zinc cinder and cyclone dust mixture.

3. The autoclave purification operation of zinc sulfate solutions can be included in the current production; after the leaching, can be sent to the waxing and the solution after post-cleaning to electroextraction.

References

[1] M. Sethurajan, D. Huguenot, R. Jain et al., "Leaching and selective zinc recovery from acidic leachates of zinc metallurgical leach residues," Journal of Hazardous Materials, vol. 324, pp. 71–82, 2017.

[2] J. Han, W. Liu, W. Qin, Y. Zheng, and H. Luo, "Optimization Study on the Leaching of High Iron-Bearing Zinc Calcine After Reduction Roasting," Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science, vol. 47, no. 1, pp. 686–693, 2016.

[3] R. Abelha, L. Lanza, C. R. Ara, and T. Matencio, "Effect of iron on zinc electrowinning usng sulfate solutions, Tecnol. Metal. Mater. Miner," São Paulo, vol. 4, pp. 3583–3593, 2010.

[4] Z.-G. Ru, C.-X. Pan, G.-H. Liu, X.-T. Wang, G.-Y. Dou, and K.-S. Zhu, "Leaching and recovery of zinc from leaching residue of zinc calcine based on membrane filter press," Transactions of Nonferrous Metals Society of China (English Edition), vol. 25, no. 2, pp. 622–627, 2015.

[5] J. Han, W. Liu, W. Qin, K. Yang, D. Wang, and H. Luo, "Innovative methodology for comprehensive utilization of high iron bearing zinc calcine," Separation and Purification Technology, vol. 154, pp. 263–270, 2015.

[6] J. Han, W. Liu, W. Qin, B. Peng, K. Yang, and Y. Zheng, "Recovery of zinc and iron from high iron-bearing zinc calcine by selective reduction roasting," Journal of Industrial and Engineering Chemistry, vol. 22, pp. 272–279, 2015.

[7] H. Han, W. Sun, Y. Hu, and H. Tang, "The application of zinc calcine as a neutralizing agent for the goethite process in zinc hydrometallurgy," Hydrometallurgy, vol. 147-148, pp. 120–126, 2014.

[8] C. Akilan and M. J. Nicol, "Kinetics of the oxidation of iron(II) by oxygen and hydrogen peroxide in concentrated chloride solutions – A re-evaluation and comparison with the oxidation of copper(I)," Hydrometallurgy, vol. 166, pp. 123–129, 2016.

[9] E. R. Encina, M. Distaso, R. N. Klupp Taylor, and W. Peukert, "Synthesis of goethite α-FeOOH particles by air oxidation of ferrous hydroxide Fe(OH)$_2$ suspensions: Insight on the formation mechanism," Crystal Growth and Design, vol. 15, no. 1, pp. 194–203, 2015.