MECHANICAL ACTIVATION OF WASTE COPPER SLAG IN THE PRESENCE OF REDUCTANTS

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ABSTRACT

This empirical work looks into the technological raw material for the synthesis of zinc, mechanical activation of waste copper slag in the presence of reductants. On the phase makeup of the charge, the effect of mechanically activating slag with coal has been identified. Under the following circumstances, partial breakdown of zinc ferrite and fayalite has been observed: ratios of 1:2 for slag to coal, 4:1 for balls to powder, and 40 minutes for mechanical activation. It has been discovered, that zinc extraction from treated slag has been affected by hydrochloric acid leaching conditions. The largest amount of zinc that could be extracted into solution from activated slag was 33%, compared to only 9% from the original slag. The results demonstrated that the suggested technique for removing zinc from used copper slag is ineffective and should not be used in actual applications.

Keywords: copper slag, mechanical activation, coal, hydrochloric acid leaching.

INTRODUCTION

General description of the work. The Article investigates the mechanical activation of waste copper slag in the presence of reductants as a technogenic raw material for the synthesis of zinc and copper. Hydrometallurgical processing is difficult due to the slag's peculiar mineralogical makeup. Dry mechanical activation of the original slag in a planetary mill was used for the first time to improve the reactivity of copper and zinc minerals present in the slag.

The depletion of nonferrous metals' ore bases, especially zinc and copper, necessitates the hunt for new sources of these raw materials. One such source is copper smelter slag, which is produced in vast quantities during the pyrometallurgical manufacturing of copper. Copper and zinc content in waste slag reaches 2 and 5 wt% or higher, respectively, which is comparable to, if not exceeding, the levels of the specified metals in the ore. Copper slag has a zinc content of around 5%. The most popular process for extracting copper from waste copper slag is flotation enrichment, which yields a concentrate with an average copper content of 8-10%. Because of the low copper concentration in the concentrate and the almost complete loss of zinc with the tailings, we cannot consider flotation enrichment as a viable approach for treating these slags. Another alternative with practical application is slag depletion in electric furnaces; however, this technology is not economically viable due to its high energy consumption.

The goal of the work. Development of conditions of recovering zinc from discarded copper slag by mechanical activation of slag with coal and subsequent hydrochloric acid leaching.

The scientific novelty of the research. Zinc recovery from copper smelter slag was achieved for the first time by using mechanical activation in the presence of coal, followed by charge mechanical activation and hydrochloric acid leaching.

Theoretical importance. The findings of the dissertation research contributed to the body of knowledge in the disciplines of mechanical activation of copper smelter slag and copper, zinc, and iron hydrometallurgical processes.

Practical application. The established technical solutions for mechanical activation of copper smelter slag have industrial potential and will increase the supply of copper and zinc raw materials.

General information of copper slag

Pyrometallurgical processes create around three–quarters of copper. As a byproduct of pyrometallurgical manufacturing, these procedures result in the creation of so-called copper smelter slag [1]. Each ton of copper produced is followed by the formation of 2.2-3.0 tons of slag [1, 2]. During pyrometallurgical or hydrometallurgical copper production, a large amount of slag (2.2 tons per ton of copper) is produced, which typically includes considerable amounts of precious metals such as copper, nickel, cobalt, and iron [3].

Copper slags have a complex chemical and mineralogical composition that changes depending on the composition of concentrates, fluxes, and the manufacturing process [4-9]. The chemical composition of copper smelter slag is affected by the following factors: (i) copper concentrate composition, (ii) charge composition, (iii) melting unit (furnace) characteristics, and (iv) smelting process technical approach [10-16].

MATERIALS AND METHODS

2.1 Raw material characteristics

Different samples of copper smelter slag from Kazakhmys Smelting were used in the experiment (Balkhash, Central Kazakhstan). The slag sample was treated and sieved to a particle size of less than 100 microns. Finally, over 95% of the particles were less than or equal to 100 m in size.

2.2 Chemical reagents

The research work experiments included the use of hydrochloric acid (37%), as well as coal. All washing and cleaning operations were carried out using distilled water.

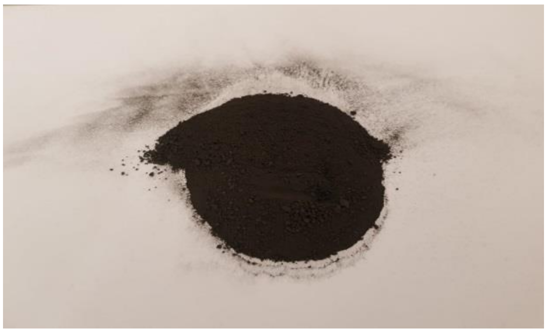

Figure 2.1- copper slag used in the experiment

2.3 Mechanical activation in the presence of coal

Mechanical activation. For mechanical activation of slag samples, a 2-cup planetary ball mill (Fritsch Pulverisette, Germany) was employed. The planetary's steel milling chamber had a capacity of 0.5 L. Steel balls with a diameter of 10 mm weighed 200 g in the milling chamber.

All of the tests were carried out in a dry environment. The slag sample was put in a milling chamber and activated under predetermined circumstances in the air environment (ball-to-powder ratio, duration of treatment, rotation speed).

Figure 2.2- planetary ball mill used for mechanical activation of copper slag

The ball to powder ratio was 4:1, the coal to slag ratio was 1:1 and 1:2, and the treatment time ranged from 10 to 40 minutes at a 380 rpm rotation speed.

2.4 Preliminary hydrochloric acid leaching of mechanical activated with coal samples

Copper slag that had been mechanochemically activated with coal was introduced to HCl solution in a glass beaker for leaching studies (250mL). A mechanical stirrer was used to agitate the mixture (IKART5). The rotation speed was set at 600 rpm, and the following leaching conditions were set: The concentrations of hydrochloric acid were 0.5 M, 0.8 M, and 1.0 M, respectively. The density of the pulp was 5g/100 mL, 10g/100 mL, and 15g/100 mL, respectively. Temperatures for leaching were 25°C, 50°C, and 75°C. Duration of leaching varied from 1 hour to 3 hours.

Figure 2.3- Hydrochloric acid leaching of MA copper slag with coal

Figure 2.4- Filtration of solutions after hydrochloric acid leaching

The solution was filtered once it had been leached, and the filtering was done with filter paper. Following filtration, the liquid portion of the solution was placed in a plastic bottle for UV-vis spectroscopic analysis, while the solid portion was heated at 150 °C for 1 h in a laboratory drying oven to remove the HCl-aqueous solution, and 1 g of the residue was placed in a plastic capsule for further XRD analysis.

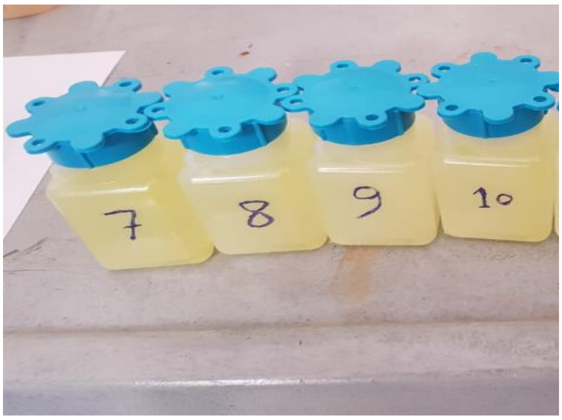

Figure 2.5- Liquid solution samples prepared for absorption spectroscopy

Thermomechanical analysis

The thermodynamics of reduction processes in a certain temperature range is a key signal for determining whether or not a reaction is possible. Carbon gasification and iron compound reduction were the major processes in the reduction roasting process. The following are the reaction and thermodynamic equations [17-18]:

$CO_2 + C \rightarrow 2CO$ (1.8)

$\Delta G\theta 11 = -166550 - 171T\ J\cdot mol^{-1}$

$Fe_3O_4 + C \rightarrow 3FeO + CO$

(1.9)

$\Delta G\theta 12 = 196720 - 199.38T\ J\cdot mol^{-1}$

$FeO+C \rightarrow Fe+CO$ (1.10)

$\Delta G\theta 13 = 149600-150.36T\ J\cdot mol^{-1}$

$Fe_2SiO_4+2C \rightarrow 2Fe+SiO_2+2CO$ (1.11)

$\Delta G\theta 14 = 353924-338.91T\ J\cdot mol^{-1}$

$Fe_3O_4+CO \rightarrow 3FeO+CO_2$ (1.12)

$\Delta G\theta 15 = 30170-29.38T\ J\cdot mol^{-1}$

$FeO+CO \rightarrow Fe+CO_2$ (1.13)

$\Delta G\theta 16 = -16950+20.64T\ J\cdot mol^{-1}$

$Fe_2SiO_4+2CO \rightarrow 2Fe+SiO_2+2CO_2$ (1.14)

$\Delta G\theta 17 = 12510+10.54T\ J\cdot mol^{-1}$

$Fe_2SiO_4+CaO \rightarrow 2FeO+CaSiO_3$ (1.15)

$\Delta G\theta 18 = -82600-32.39T\ J\cdot mol^{-1}$

As the reduction temperature increased, the stage controlling copper slag reduction changed to gas diffusion. The results of the integrated kinetic model show that Fe_3O_4 is first reduced in copper slag, which requires a low reaction activation energy. Meanwhile, Fe_2SiO_4 can react with CaO, decomposing to FeO.

Then, the FeO began to be reduced to metallic iron with carbon monoxide. The control steps of each step of the copper slag reduction reaction were different. The main reason was that the composition of copper slag is complex, and different iron compounds in copper slag have different reduction characteristics. In general, a high reduction temperature can improve the reduction of iron compounds in copper slag.

2.5 Materials characterization

XRD analysis. The XRD patterns were recorded using a D8 Advance diffractometer and CuK (40 kV, 40 mA) radiation (Bruker, Germany). XRD patterns in the 2 theta range of 5-80° were detected with a step size of 0.03° and a step time of 6 seconds. For phase analysis, the JCPDS-PDF2 database and the Diffracplus EVA software were utilized.

ICP AAS measurements. Using a Shimadzu AA-6200 spectrometer, the concentration of zinc and iron in liquid samples was measured using atomic absorption spectrometry (AAS) (Shimadzu, Japan). The concentration of selected elements in the initial slag was determined by AAS using a SPECTRAA L40/FS spectrometer (Varian, Australia).

RESULTS AND DISCUSSION

3.1 Slag sample characterization

The copper smelter slag sample utilized in this study came from a copper smelting factory in the town of Balkhash, which is located in the central region of Kazakhstan. XRD examination indicated fayalite, zinc ferrite, and quartz as key components of the slag sample (as major components of the slag sample).

Fe-39.7% w%, Si-13.9 w%, Zn-5.1 w%, Al-1.5 w%, Cu-0.1 w%, S-1.2 w%, Ca-0.7 w%, and Mg-0.2 w% made up the chemical composition of copper slag. Because zinc has a concentration of somewhat more than 5%, it was chosen as the subject of research on its behavior under leaching circumstances.

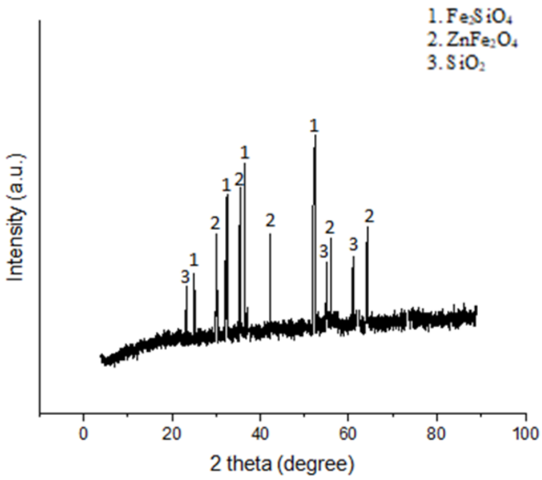

Figure 3.1- XRD pattern of initial slag

Figure 3.1 demonstrates that the copper slag comprises fayalite, zinc ferrite, and quartz, as seen by the XRD pattern.

3.2 Effect of mechanical activation of copper slag with coal

Mechanical activation is a technique of mechanical action on a solid that uses a lot of energy. Grinding during impact, impact-abrasion, or abrasion causes structural flaws in solid particles, phase changes, and even amorphization of crystals, all of which alter chemical activity.

Table 3.1- Mechanical activation of beginning slag under experimental conditions.

Sample number	Ball – to – powder ratio	Time (min)
M1	4:1	10
M2	4:1	20
M3	4:1	30
M4	4:1	40

The ball-to-powder ratio remained constant (4:1), but the treatment time was varied from 10 to 40 minutes to avoid any possible chamber reactions.

The following are the assumptions for adopting MA: 1) enhance specific surface area; 2) achieve amorphous phase; and 3) obtain particles with more reactive capacities during probable mechanochemical reactions.

Mechanical activation of copper smelter slag samples with coal was used in this dissertation study before hydrochloric acid leaching.

3.3 Effect of mechanical activation of copper slag

Aside from the four tests with mechanically activated copper slag that were conducted without the use of coal, eight further tests with mechanically activated copper slag were conducted with the use of coal. The treatment period and ball-to-powder ratio were the same as in the preceding case, as indicated in Table 3.2.

The diffractogram of mechanical activated copper slag in the presence of coal is according the following reactions:

$$Fe_2SiO_4+C = 2Fe+SiO_2+CO_2 \quad (3.1)$$

It is noteworthy that this mechanical activation of copper slag with coal is under moderate conditions.

Table 3.2- Mechanical activation of beginning slag in the presence of coal under experimental conditions.

Sample number	Slag – to – coal ratio	Ball – to – powder ratio	Time (min)
M5	1:1	4:1	10
M6	1:1	4:1	20
M7	1:1	4:1	30
M8	1:1	4:1	40
M9	1:2	4:1	10
M10	1:2	4:1	20
M11	1:2	4:1	30
M12	1:2	4:1	40

Figure 3. 2 shows an X-ray diffractogram of mechanical activated copper slag with carbon (coal) in moderate conditions.

It can be easily identified that there is a difference between two diffractograms, namely there is one additional peak is appeared of Fe in Figure 3. 2, which is occurred according 3.1 reaction.

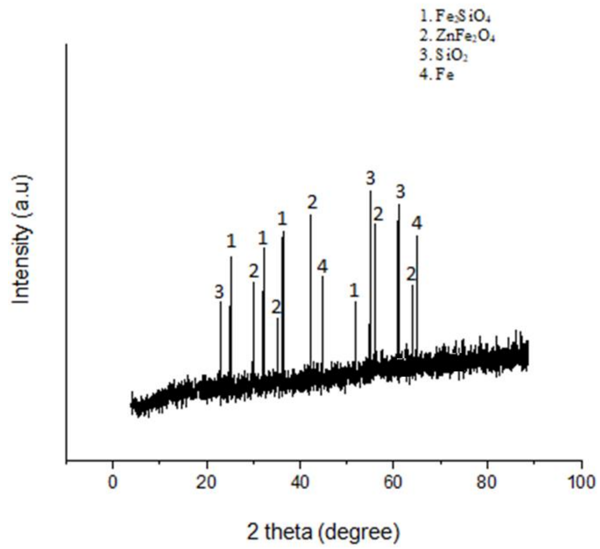

Figure 3.2- XRD pattern of mechanical activated copper slag sample with coal at moderate conditions

Figure 3. 3 shows an XRD diffractogram of mechanical activated copper slag with carbon (coal) in intense conditions. In these conditions ball to powder ratio and duration of treatment was more compare to the previous one.

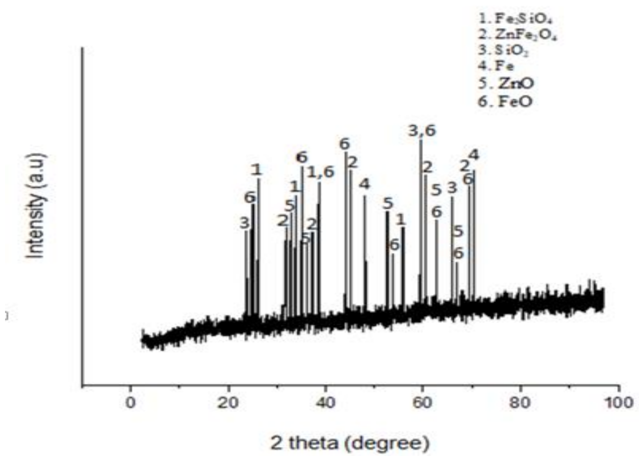

Figure 3.3- XRD pattern of mechanical activated copper slag sample with coal at intense conditions

It can be easily identified that there are some differences between last two diffractograms, namely there are additional peaks is appeared of ZnO and FeO in Figure 3. 3, which are occurred according 3.2 reaction.

$Fe_2SiO_4 + C = 2ZnO + 4 FeO + CO_2$ (3.2)

$ZnFe_2O_4 + 0.5 C = ZnO + 2FeO + 0.5 CO_2$ (3.3)

The decomposition of Fayalite coal results in the formation of ZnO and FeO.

3.4 Hydrochloric acid Leaching of mechanical activated copper smelter slag

Leaching chemistry

Hydrochloric acid, by all accounts, is a popular process for extracting zinc from copper slags. This reagent is a result of non-ferrous metallurgical endeavors, and it is available in large quantities and at a low cost.

The main mineral interactions with hydrochloric acid are shown in these equations:

$ZnFe_2O_4$ (s) + 2HCl (aq) = $ZnCl_2$(aq) + Fe_2O_3(aq) + H_2O(l) (3.3)

$ZnFe_2O_4$ (s) + 8HCl (aq) = $ZnCl_2$(aq) + $FeCl_3$(aq) + $4H_2O$(l) (3.4)

Zinc ferrite is insoluble in water, dilute acid solution, alkali, and ammonia Because of its solid crystalline form, it may be used at room temperature and pressure. As a result, there was no way to deal with it in a general way. However, a large amount of iron oxides were dissolved, complicating future iron precipitation methods and making iron recovery more difficult.

The influence of hydrochloric acid leaching conditions on the extraction of zinc into solution from the original and mechanically activated in the presence of coal is shown in Figures 3.4 and 3.5.

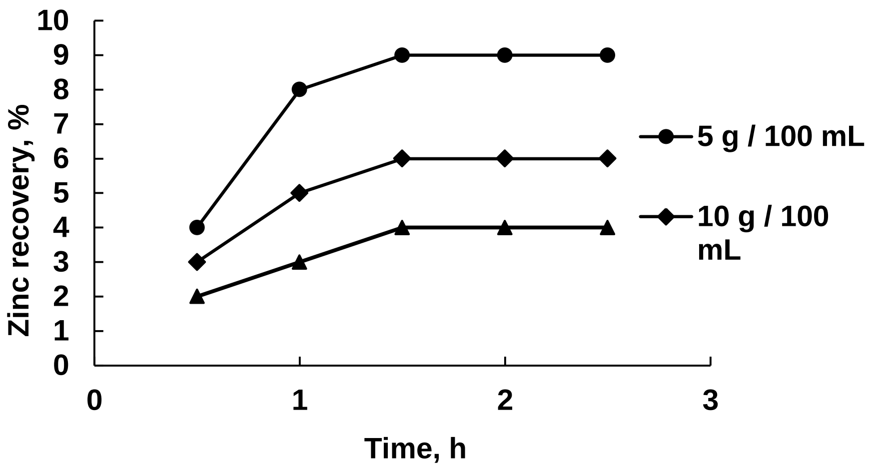

Figure 3.4- Influence of the conditions of hydrochloric acid leaching of the initial slag on the extraction of zinc into solution (1 M HCl)

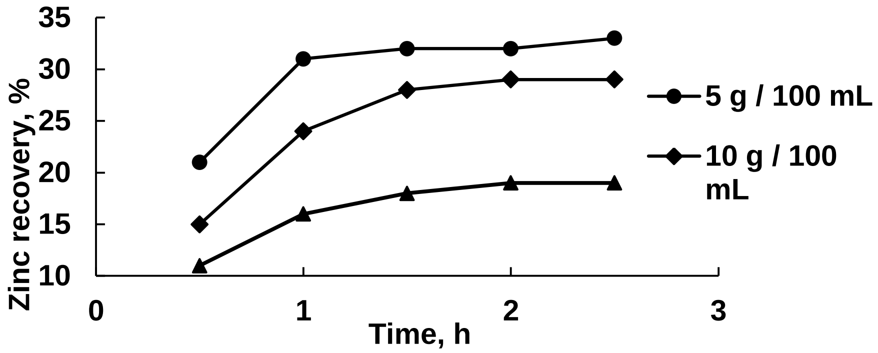

Figure 3.5 - Influence of the conditions of hydrochloric acid leaching of the initial slag mechanically activated in the presence of coal on the extraction of zinc into solution (1 M HCl)

It can be seen that in all cases, an increase in pulp density has a negative effect on the extraction of zinc into solution during leaching (Fig.3.4). When leaching the original slag, the maximum extraction of zinc was 9%. It was reached 1.5 hours after the start of leaching at a pulp density of 5 g/100 ml of solution. When using a denser pulp, the extraction of zinc was lower: 4% at 15 g / 100 ml solution and 6% at 10 g / 100 ml solution.

During the leaching of slag mechanically activated in the presence of coal (40 min), the degree of extraction slightly increased in comparison with the extraction of zinc from the original slag (Fig.3.5). At a pulp density of 5 g/100 ml of solution, the maximum recovery achieved was 33%. This fact confirms the hypothesis put forward earlier about the partial decomposition of zinc ferrite with the formation of zinc oxide, which dissolves relatively easily during hydrochloric acid leaching.

The results obtained showed that the proposed method for extracting zinc from waste copper slag is inefficient and is not recommended for practical use.

CONCLUSIONS

1) The impact of slag mechanical activation with coal on the charge's phase composition has been determined. partial decomposition of zinc ferrite and fayalite has been detected under the following conditions: slag-to-coal ratio of 1:2, ball-to powder ratio of 4:1, mechanical activation duration of 40 min;

2) The impact of slag mechanical activation with coal on zinc and iron extraction into solution during subsequent hydrochloric acid leaching has been found;

3) The impact of hydrochloric acid leaching conditions on zinc extraction from treated slag has been revealed. The maximum achieved extraction of zinc into solution from activated slag was 33%, while this figure was only 9% from the original slag. The results obtained showed that the proposed method for extracting zinc from waste copper slag is

inefficient and is not recommended for practical use.

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