-REPLY TO COMMENT ON PAPER

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Possibility of using waelz kiln technology (reduction roasting) for processing Chehel-Kureh complex sulfide ore

Peiman Khakbaz [a] , Kianoush Barani [b, *] , Shahab Romiani [c] and Mohammad Mahmoudi Maymand [d]

[a] *Ahangaran Mining Complex Manager, Sormak Company, Malayer, Iran.*
[b] *Lorestan University, Khorramabad, Iran.*
[c] *Canymes Engineering Company, Tehran, Iran.*
[d] *Iran National Copper Industries Company, Kerman, Iran.*

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ABSTRACT

The Chehel-Kureh copper deposit in southeastern Iran contains complex sulfide ores rich in copper, lead, and zinc, posing significant challenges for conventional flotation processing. Despite various flotation strategies, the plant has struggled to produce clean copper concentrates and separate lead and zinc products, resulting in low recoveries and environmental concerns due to metal losses in tailings. In this study, the application of Waelz kiln technology—a process commonly used for zinc recovery from metallurgical residues—was investigated as an alternative approach for metal recovery from Chehel-Kureh ore. Reduction roasting experiments were conducted on raw ore, as well as differential and bulk flotation concentrates, using coal as a reductant. The effects of roasting temperature, duration, and coal ratio on metal volatilization were examined. Under optimal conditions, volatilization of lead, copper, and zinc reached 89%, 84%, and 75% for the raw ore; 92%, 62%, and 74% for the differential concentrate; and 68%, 62%, and 43% for the bulk concentrate, respectively. These findings indicate that the Waelz process can achieve high metal volatilization efficiencies, particularly for lead and zinc, offering a promising alternative for pre-treatment and recovery of valuable metals from complex Cu–Pb–Zn ores while potentially minimizing environmental impacts.

Keywords: *Chehel-Kureh , Walez technology, Complex ore, Roasting, Reduction.*

1. Introduction

The Chehell-Kureh mine, located in Sistan and Baluchestan province (in Iran), contains a complex sulfide ore of copper, lead, and zinc. The ore body exhibits a complex structure composed of veins, lenses, and irregular shapes, with mineralization including quartz, dolomite, ankerite, siderite, and calcite, alongside pyrrhotite, arsenopyrite, pyrite, chalcopyrite, marcasite, molybdenite, sphalerite, galena, ilmenite, and rutile. Among these, chalcopyrite, sphalerite, and galena are the economically valuable minerals, occurring in fine to medium grain sizes(Maanijou et al., 2008).

Initial metallurgical studies and processing experiments on drill core samples of Chehell-Kureh ore were conducted in 2012 by the Australian company AMMTEC. The results indicated that chalcopyrite, sphalerite, galena, and pyrite are the main sulfide minerals, with minor amounts of covellite. Sphalerite commonly occurs as inclusions within chalcopyrite, complicating separation. Efforts to float lead and zinc reduce copper recovery, making it difficult to produce a clean zinc concentrate.

Based on the results of the metallurgical tests and mineralogical studies, a plant flowsheet (Fig. 1) was designed, incorporating crushing, grinding, and flotation circuits. Mineralogical studies indicated that valuable minerals are liberated up to 80% at a particle size of 25 µm. Consequently, in the first grinding stage, materials are ground to a D80 of 53 µm, followed by a second grinding stage to achieve a D80 of 25 µm. Figure 1 illustrates the grinding and flotation circuit of the Chehel-Kureh copper processing plant (Wong and Heyes, 2012).

The Chehel-Kureh processing plant, which began operations in March 2017, continues to face challenges after nearly eight years of operation, especially in producing separate copper, lead, and zinc concentrates. Metallurgical performance evaluations indicate that in differential flotation, approximately 9% of copper and over 80% of lead and zinc are lost to tailings, while in bulk flotation, nearly 10% of copper and 60% of lead and zinc are discarded. The concentrates in both flotation conditions exhibit low copper grades and significant lead and zinc content, complicating the smelting process. Additionally, significant amounts of lead and zinc are sent to the tailings dam daily, posing environmental risks, especially due to lead's toxicity.

Several studies have been undertaken to address operational challenges at the Chehel-Kureh copper plant and to explore the recovery of lead and zinc from its copper ore. In one such study, conducted by Zarfaravar Company, various ore types from the Chehel-Kureh deposit as well as the plant's copper concentrate were examined using flotation, with the objective of producing separate copper and zinc concentrates (Zarfaravar Engineering Company, no date). The Research Center of the Sarcheshmeh Copper Complex conducted experiments on the Chehel-Kureh copper concentrate with the aim of increasing the copper grade in the copper concentrate and producing a separate zinc concentrate.The results of these studies showed that, despite the use of

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* Corresponding author. *E-mail address:* barani.k@lu.ac.ir (K. Barani).

various depressant systems for lead and zinc, the successful production of a zinc concentrate was not achieved (Complex, 2021).

Despite significant advancements, flotation still faces challenges when processing complex copper-lead-zinc ores, as evidenced by the issues encountered with the Chehel-Kureh ore. A major difficulty is the similar behavior of copper sulfide, galena, and sphalerite, which complicates their separation (Bayraktar et al., 1992). This problem is common to many complex copper-lead-zinc ores, where flotation often struggles to efficiently separate these metals. Hydrometallurgical methods are increasingly being explored as a viable alternative to flotation for metal recovery. Techniques such as ferric and bioleaching, pressure leaching, roasting, chlorination, nitric-sulfuric acid leaching, glycine leaching, sodium metabisulfate leaching, and hydrogen peroxide leaching have been proposed for copper and zinc recovery (Lorenzo-Tallafigo et al., 2021).

One of the methods or technologies used alongside hydrometallurgy for metal recovery from ores, particularly oxidized ores and especially zinc ores, is Waelz kiln technology. The Waelz process is a well-known method for recovering zinc and other volatile metals from metallurgical wastes, such as electric arc furnace (EAF) dust, leaching residues, and recyclable materials. It uses a rotary kiln to reduce and volatilize metals, which are then recovered from the kiln dust. The process, first patented in 1910 and industrialized in Germany in the 1920s, has been recognized since 2000 as the Best Available Technology for EAF dust treatment (Maczek and Kola, 1980; Antuñano et al., 2019).

The feed for the Waelz kiln can consist of either zinc ore or processed concentrates, and the ZnO grade in the kiln product is directly related to the feed grade. Before feeding, the zinc-bearing material (~74 wt%) is mixed with metallurgical coke or coal (~19 wt%) and lime (~7 wt%), then pelletized. The coal acts primarily as a reductant but also provides heat and promotes fluidization inside the rotating kiln, preventing agglomeration of fine zinc particles (Maczek and Kola, 1980; Antuñano et al., 2019).

The Waelz process is a continuous, high-temperature rotary kiln method (1000–1500°C) used for recovering zinc and other low-boiling-point metals. The key chemical reactions in the kiln include:

$$\mathrm{ZnO} + \mathrm{C} \rightarrow \mathrm{Zn}\ (\text{vapor}) + \mathrm{CO} \tag{1}$$

$$\mathrm{Zn}\ (\text{vapor}) + \mathrm{CO} + \mathrm{O_2} \rightarrow \mathrm{ZnO} + \mathrm{CO_2} \tag{2}$$

$$\mathrm{ZnS} + \mathrm{CaO} + \mathrm{C} \rightarrow \mathrm{Zn}\ (\text{vapor}) + \mathrm{CaS} + \mathrm{CO} \tag{3}$$

Zinc compounds in the feed are reduced, vaporized, and then condensed into zinc oxide powder using filters. The kiln achieves up to 97% recovery efficiency. Along with zinc, the oxide product may contain lead, cadmium, silver, and halogen compounds, which can be recovered by leaching.

In a review of the literature on the use of the Waelz process for the recovery of metals such as lead, zinc, and copper from ores or concentrates, limited research was found. Most of the available articles focused on the recovery of zinc from electric arc furnace dust, rather than from traditional lead-zinc-copper ores or concentrates. However, a study from a lead-zinc mine in South Africa presented an example where one of the plant's products is a silicate zinc concentrate (willemite), containing 45% zinc, produced at a rate of 3000 tons per month using flotation. Due to the fine particle size of this silicate zinc, significant amounts are not recoverable by flotation and are instead discarded as tailings, which still contain 18% zinc. In 1976, German researchers explored the recovery of zinc from both the concentrate and its tailings using the Waelz process on a pilot scale. The results showed that 90% of the zinc vaporized before reaching 1100°C, ultimately producing a zinc oxide product containing 63% zinc and 10% lead (Clay and Schoonraad, 1976).

In Hamadan Province, at the Ahangaran lead-zinc mine near Malayer, a Waelz kiln production line is in operation. The feed for this line consists of low-grade oxide ore from the mine. The process produces a product containing both zinc and lead, which is then subjected to leaching. Zinc is dissolved and separated through cementation, while lead remains in the final solid form. Both products are subsequently sold. According to the plant's data, the Waelz process at Ahangaran achieves an 85-95% zinc recovery and approximately 90% lead recovery from the initial feed.

In this study, the potential of applying Waelz kiln technology for metal recovery from the Chehel-Kureh copper ore was investigated.

2. Material and methods

2.1. Sampling

Sampling was conducted from both the primary ball mill feed (raw ore) and the flotation concentrates. The plant initially operated under a differential flotation circuit (targeting copper flotation while suppressing lead and zinc) until June 15, 2023. After this date, the circuit was modified to implement bulk flotation of copper, lead, and zinc. However, in spring 2024, the plant returned to the differential flotation configuration. Accordingly, grid-based sampling was performed from both the differential and bulk flotation concentrate stockpiles. Sampling of the plant feed was carried out over a 2 hours period, with samples taken every 15 minutes and combined to form a representative sample.

The flotation concentrates had a particle size of $d_{80} = 25$ µm. The plant feed was also ground to $d_{80} = 25$ µm. After homogenization, 30 g subsamples were prepared for reduction roasting experiments to evaluate the applicability of the Waelz kiln process.

2.2. Materials characteristics

The chemical composition of the raw ore, the differential flotation concentrate, and the bulk flotation concentrate was determined. The concentrations of copper, lead, zinc, and iron were measured using wet chemistry methods. The results are presented in Table 1.

Table 1. Chemical analysis of the samples.

Sample	Fe (%)	Cu (%)	Pb (%)	Zn (%)
Raw Ore	7.68	0.74	1.25	2.53
Differential Flotation Conc.	17.21	13.74	5.23	10.66
Bulk Flotation Conc.	18.90	11.65	6.32	11.48

2.3. Reduction roasting experiments

The reduction roasting experiments were carried out on the raw ore sample, bulk flotation concentrate, and differential flotation concentrate. In each experiment, a certain amount of powdered coal was mixed with 30g of the sample and heated in a programmable laboratory furnace capable of reaching temperatures up to 1200°C, for a specified time and temperature. The percentage of coal, roasting temperature, and roasting time were varied and studied to investigate their effects on the reduction roasting process. The weight of the sample was determined after the experiment was completed, and the roasted material was chemically analyzed by wet chemistry methods to measure copper, lead, zinc, and iron content. Based on the weight of the sample before and after roasting, as well as the chemical analysis before and after roasting, the evaporation percentages of copper, lead, zinc, and iron were calculated. All experiments and the chemical analyses were performed at the Ahangaran Lead and Zinc Complex in Malayer.

3. Results and discussions

3.1. Analysis of experiments on the raw ore sample

Fig. 2 shows the effect of increasing the amount of coal on the evaporation of metals for the ore sample at a temperature of 950°C after 1 hour. It can be observed that with an increase in the amount of coal, the amount of metal evaporation increases. Generally, the metals lead, copper, zinc, and iron have the highest evaporation rates in that order. Given that the evaporation percentage of the metals is less than 80%, the reduction roasting temperature was increased in subsequent experiments.

Fig. 3 shows the effect of increasing the amount of coal on the evaporation of metals for the ore sample at a temperature of 1100°C after 1 hour. It can be observed that with an increase in the amount of coal, the amount of metal evaporation did not significantly increase (except for zinc). Under the best conditions (20% by weight of coal, 1100°C, and one hour), 89% of lead, 84% of copper, and 74% of zinc entered the vapor phase. This indicates that, aside from economic considerations, the Waelz furnace technology is feasible for the raw ore sample.

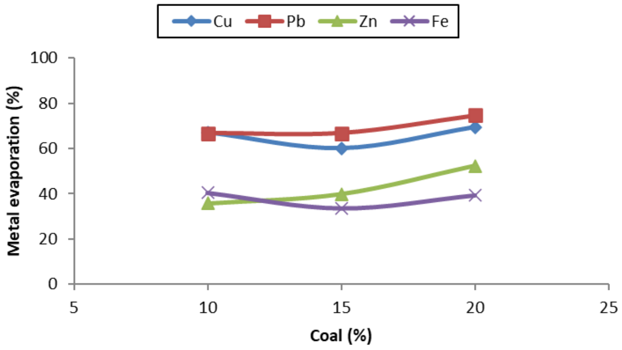

Fig. 2. The effect of increasing the amount of coal on the evaporation of metals for the raw ore sample (temperature of 950°C and time of 1 hour).

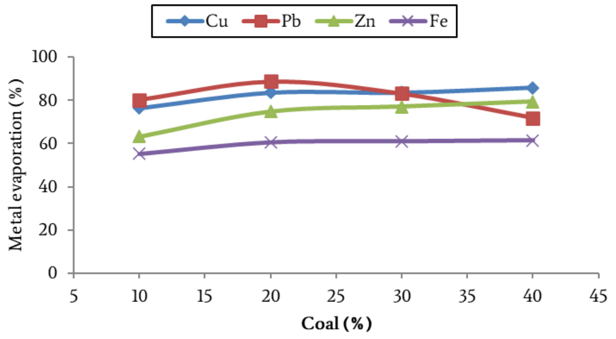

Fig. 3. The effect of increasing the amount of coal on the evaporation of metals for the raw ore sample (temperature of 1100°C and time of 1 hour).

3.2. Analysis of experiments on the bulk flotation concentrate

Fig. 4 illustrates the effect of increasing coal content on the extent of metal evaporation from the bulk flotation concentrate at 950°C and a duration of 1 hour. The results indicate generally low evaporation rates for all metals under these conditions. The highest evaporation occurred at 20 wt.% coal, where 20% of iron, 17% of copper, 12% of zinc, and 7% of lead transitioned into the vapor phase. These modest rates prompted further experiments with increased coal content and higher roasting temperatures.

Fig. 5 presents the effect of coal addition on metal evaporation from the bulk flotation concentrate at an elevated temperature of 1100°C, also for 1 hour. It was observed that even at this higher temperature, the evaporation of copper, lead, and zinc remained below 40% across all conditions tested. The maximum evaporation was achieved at 40 wt.% coal, resulting in 60% of iron, 37% of copper, 37% of lead, and 30% of zinc being evaporated. Due to the still limited volatilization of the target metals, subsequent experiments focused on further increasing the coal content, roasting temperature, and duration.

Fig. 6 demonstrates the impact of temperature on the evaporation of metals from the bulk flotation concentrate using 45 wt.% coal. At a temperature of 1150°C, the evaporation rates significantly improved, with 72% of iron, 68% of lead, 62% of copper, and 43% of zinc entering the vapor phase. These conditions yielded the most favorable results for the bulk concentrate. However, partial melting of the sample was observed at this temperature, leading to adhesion on the refractory brick surface. Additionally, increasing the roasting time to 2 hours at 1100°C did not result in further enhancement of metal evaporation.

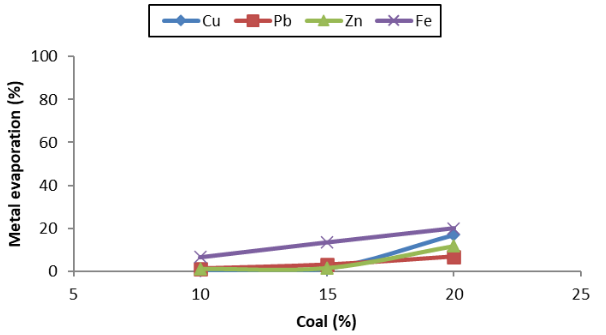

Fig. 4. The effect of increasing the amount of coal on the evaporation of metals for the bulk concentrate sample (temperature of 950°C and time of 1 hour).

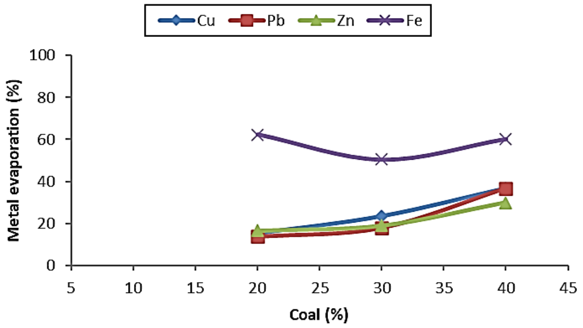

Fig. 5. The effect of increasing the amount of coal on the evaporation of metals for the bulk concentrate sample (temperature of 1100°C and time of 1 hour).

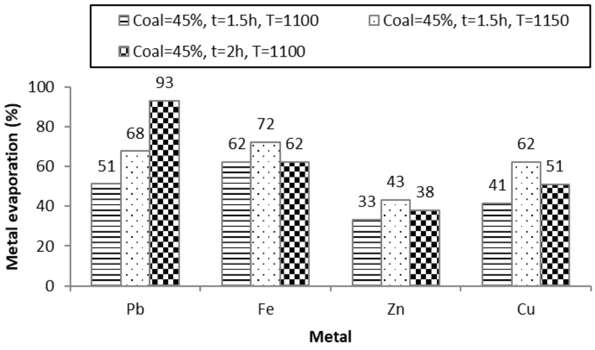

Fig. 6. The effect of increasing the amount of coal on the evaporation of metals for the bulk concentrate sample (different condition)

3.3. Analysis of experiments on the differential flotation concentrate

Fig. 7 illustrates the effect of increasing coal content on the evaporation of metals from the differential flotation concentrate at 950°C for 1 hour. As shown, metal evaporation remains low under all conditions tested. The maximum evaporation occurred at 20 wt.% coal, where 8% of iron, 21% of copper, 39% of zinc, and 19% of lead were volatilized. Based on these results, subsequent experiments were conducted at higher coal percentages and elevated roasting temperatures.

Fig. 8 shows the effect of coal addition on metal evaporation from the differential flotation concentrate at 1100°C for 1h. The results indicate that increasing the coal content leads to enhanced metal evaporation. The highest evaporation values were observed in the order of lead > zinc > copper > iron. At 40 wt.% coal, 92% of lead, 74% of zinc, 62% of copper, and 58% of iron were transferred to the vapor phase. To further improve the volatilization of metals, later experiments involved increasing the coal content, temperature, and roasting time.

Fig. 9 presents the effect of increasing temperature on metal evaporation from the differential flotation concentrate using 45 wt.% coal and a roasting time of 1.5 hours. At 1150°C, 90% of lead, 55% of iron, 67% of zinc, and 66% of copper were evaporated. However, it was observed that at this temperature, the sample partially melted and adhered to the surface of the refractory brick.

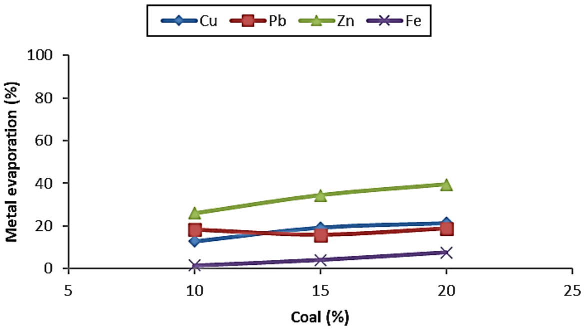

Fig. 7. The effect of increasing the amount of coal on the evaporation of metals for the differential concentrate sample (temperature of 950°C and time of 1 hour).

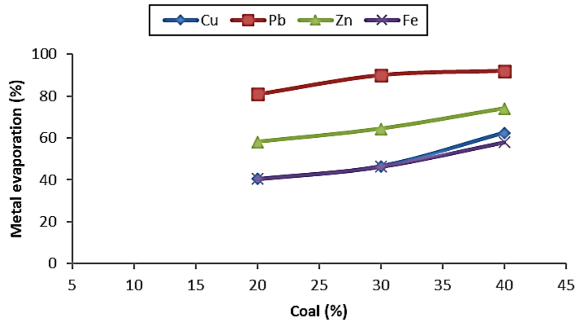

Fig. 8. The effect of increasing the amount of coal on the evaporation of metals for the differential concentrate sample (temperature of 1100°C and time of 1 hour).

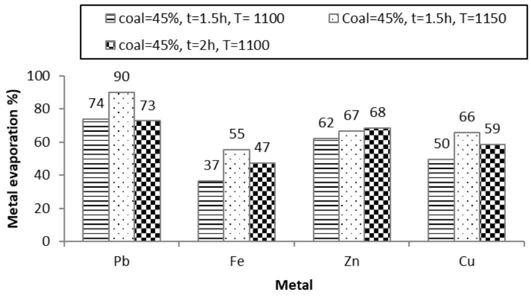

Fig. 9. The effect of increasing the amount of coal on the evaporation of metals for the differential concentrate sample (different condition).

3.4. The optimal conditions

Based on the highest metal vaporization percentages, the optimal conditions for the reduction roasting experiments of all three samples are presented in Table 2.

4. Conclusions

The results of the reduction roasting experiments demonstrated that metal volatilization efficiency is significantly influenced by sample type and roasting conditions, including coal content, temperature, and duration. For the raw ore, the highest metal evaporation was achieved at 20 wt% coal, 1100 °C, and 1 hour of roasting, with lead, copper, and zinc volatilization reaching 89%, 84%, and 75%, respectively. In the case of the bulk flotation concentrate, optimal results were obtained under more intense conditions, 45 wt% coal, 1150 °C, and 1.5 hours, resulting in 68% lead, 62% copper, and 43% zinc vaporization. Meanwhile, the differential flotation concentrate showed the highest volatilization rates at 40 wt% coal, 1100 °C, and 1 hour, with 92% lead, 62% copper, and 74% zinc being evaporated.

These findings suggest that the differential concentrate is more responsive to reduction roasting under moderate conditions compared to the bulk concentrate, which required higher coal content and temperature to achieve acceptable volatilization levels. Furthermore, an inverse correlation was observed between the initial metal grade and its volatilization percentage, indicating that higher metal concentrations in the feed may inhibit efficient vapor-phase transfer during roasting. This trend was particularly evident for copper, where increasing the feed grade from 0.4% to 6% reduced its volatilization from 83% to 62%, with minimal further reduction at grades above 6%.

Table 2. Optimal reduction conditions for maximum metal vaporization.

sample	Coal content (wt. %)	Roasting temp(°C)	Roasting time(h)	Metal evaporation (%)			
				Cu	Zn	Fe	Pb
Raw Ore	20	1100	1	83.55	74.78	60.52	88.74
Differential Flotation Conc	45	1150	1.5	62.44	43.19	72.35	67.66
Bulk Flotation Conc	40	1100	1	62.37	74.06	58.07	91.98

Due to limitations in the laboratory-scale furnace setup, it was not possible to collect and condense the volatilized metals in the form of fume or dust, and therefore leaching experiments on the collected product were not conducted. However, for further research and better process evaluation, it is recommended to perform pilot-scale roasting tests under optimized conditions where dust collection systems are employed. Leaching experiments can then be carried out on the collected dust to assess metal recovery efficiency. Given that such fume products are typically oxide-rich in nature, it is expected that more than 90% of copper and zinc can be dissolved through acid leaching.

Finally, economic considerations must be taken into account to determine whether the combination of a Waelz kiln-based volatilization process followed by leaching of the collected dust is both energy-efficient and economically viable at industrial scale.

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