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An efficient approach to chlorine removal in the zinc hydrometallurgical process

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ABSTRACT

Nowadays, most of the metallic zinc is produced through hydrometallurgical processes. To attain high-purity zinc through electrowinning, the concentration of chlorine ions in the electrolyte should not exceed 0.5 g/L due to its negative consequences. One in particular is the corrosion of non-consumable lead anodes, which is responsible for the dissolution of Pb that causes impurities in the produced zinc metal. Moreover, chlorine emission in the work environment could be a danger to the health of staff, which stems from the oxidation of chlorine ions on the non-consumable Pb anodes. In this research, a potential alternative procedure is employed to significantly reduce chlorine in zinc concentrate. The results showed that under the appropriate conditions of T=60 °C and 1 h of experiment, two-step dichlorination using water along with 20 g/L Na_2CO_3 had a salient efficiency of 98% and the lowest amount of 0.48 g/L chlorine remaining in the leaching solution. Compared to traditional dichlorination methods of zinc, the employed procedure had satisfying dichlorination efficiency, considering the economic aspects of the produced zinc, particularly on an industrial scale.

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1 .Introduction

Recently, the importance of zinc continues to increase in the metallurgical industry and particularly, in the galvanization industry. Zinc is produced from both sulphide and oxide-based ores, but the zinc hydrometallurgical process is of paramount importance due to its numerous advantages compared to pyrometallurgy, such as low energy consumption and air pollution [1, 2]. Concerning its invaluable advantages, in recent years, most of the metallic zinc has been produced through the hydrometallurgical process. The zinc hydrometallurgical production process usually involves grinding, acidic leaching, neutralizing, purification, and electrowinning. In the leaching process, sulphuric acid (H_2SO_4) is employed in a solid/liquid = 250 g/L. In the neutralizing step, in order to remove some impurities such as arsenic, germanium, and iron in its hydroxide form, calcium hydroxide is used to increase the pH and adjust it to around 4 [3, 4]. As the next step, the solution undergoes the Hot Purification process after filtration. According to its name, this process takes place at T=70-80 °C, where $KMnO_4$ and [$Ca(OH)_2$] are used to oxidize Co, Mn and remaining Fe and remove them in their oxide and hydroxide forms [5-8]. After removing the mentioned impurities, the final pH of the solution will be 3-3.5. To remove the other remaining impurities, such as Cu, Cd, and Ni, the solution is subjected to the next step, which is the Cold Purification process [8-10]. To remove Cadmium, the best temperature is 50 °C, but Ni requires higher purification temperatures. In this stage, the pH of the solution is 4 – 4.5, and zinc powder is used for purification due to its higher oxidative potential [2, 11]. After these steps, the pregnant leach solution is ready to be electrowin and produce metallic zinc.

Hydrometallurgical zinc production industries deal with the chloride ion, which enters the pregnant leaching solution before moving on to the electrowinning section. Before the electrowinning process, the concentration of chlorine ions in the electrolyte should not exceed 0.5 g/L due to its negative consequences. Chlorine emissions in the work environment could pose a health risk to staff, stemming from the oxidation of chlorine ions on non-consumable lead anodes. Moreover, $HClO_4$, which is formed as a result of the oxidation of chlorine ions, could cause corrosion in non-consumable lead anodes and, consequently, since it is more active compared to zinc and easily deposits on the aluminum cathode, the negligible amount of the dissolved Pb could be responsible for possible impurity in produced zinc through electrowinning process [12].

Numerous investigations have been conducted concerning the issue of chlorine ions in zinc hydrometallurgical production [4, 13-15]. Wu et al. [16] have selected copper plates and Ag/AgCl as working and opposite electrodes, respectively, to remove Cl ions in the zinc sulphate solution. They have reported that, under optimum conditions such as t=3 h, potential of 0.6 V, and ultrasonic stirring intensity of 50 W, 54.5% of chloride ions were removed successfully. Ahmadi et al. [17] have investigated the effect of temperature, stirring speed, and potential on Cl ion removal efficiency using copper as an anode and cathode with 99.99% purity. They found the optimum experimental conditions at pH=5, t= 4 h, optimal potential 0.8 V, stirring speed of 200 rpm, and T= 25 °C, which led to the 42.6% Cl removal from the initial concentration of 295 mg/L in the electrolysis solution. Dong et al. [18] investigated the chlorine-deep removal in zinc sulfate solution using highly active copper from copper slag. They obtained a dichlorination rate of 90.41% under the optimum conditions, such as 30 g/L solution acidity, t= 30 min, T = 20 °C, and the ratio of copper slag to zinc powder = 7:6. Furthermore, they found that increasing the amount of zinc powder eight times resulted in a dichlorination of 95.43%.

Şahin et al. [19] investigate methods to remove chlorides from zinc ash, a by-product of galvanizing steel and iron, to enable its reuse in zinc oxide or metal production. Zinc ash generated during galvanizing contains metallic zinc, oxides, chlorides, and contaminant metals, requiring treatment for recycling. Chloride exists in zinc ash mainly as $ZnCl_2$, $PbCl_2$, and associated compounds, which are volatile at high temperatures. Both pyrometallurgical (roasting) and hydrometallurgical (alkali washing) processes, including combined approaches, are examined for their effectiveness in reducing chloride content while minimizing zinc losses and environmental impact. Pyrometallurgical roasting can effectively reduce chloride content, but it causes zinc vapor loss and environmental concerns. Hydrometallurgical treatment

with Na_2CO_3 selectively precipitates zinc and lead carbonates, effectively reducing chloride levels. The research demonstrates that a combined hydrometallurgical and pyrometallurgical treatment yields higher zinc recovery and lower chloride levels, making zinc ash a viable secondary resource for zinc production. Zinc in final products mainly exists as zinc oxide, with metallic zinc content remaining very low.

In this study, we investigated a new method to reduce chlorine in zinc concentrate using several different approaches and dichlorination steps. This research was initiated due to the economic aspects of zinc production and also a potential alternative method for dichlorination using copper or silver, which have significant chlorine ion removal efficiency, albeit they are not cost-effective in the zinc production industry.

2. Materials and Methods

2.1. Material

Sodium carbonate (Na_2CO_3) (98%) and sulfuric acid (H_2SO_4) (98%) were purchased from Mojallali Co. and used as received without any additional purification. The primary material used in the experiments was chlorine-bearing zinc concentrate, which contains approximately 17.5% zinc. This concentrate was supplied by Zanjan Zinc Khales Sazan Industries Company (ZZKICo), located in Zanjan, Iran.

2.2. Experimental Procedure

The dichlorination step was conducted using a beaker, with each approach performed at a pulp density of 350 g/L, a temperature of 60 °C, and a reaction time of 1 h. A mechanical stirrer and a heater were applied to stir the pulp and adjust the desired experimental temperature. Noteworthy is the fact that for those approaches that required heating the concentrate, the chlorine-bearing zinc concentrate was subjected to direct heating, which facilitated the dichlorination process by allowing the desired reactions. Soon after the concentrate heated up, it was added to the beaker due to the dichlorination process. Consequently, upon the expiration of the mentioned dichlorination time, the contents of the beaker were filtered immediately, and the filtrate was subjected to analysis of chlorine and zinc concentration in the solution. Subsequently, the filtercake that remains undergoes a second dichlorination step. After a two-step dichlorination process, the filter cake that remained from the second dichlorination was subjected to acidic leaching using sulfuric acid at a pH around 1. The leaching process's other parameter conditions were conducted under the same conditions as the dichlorination, such as T=60 °C, t=1 h, using a mechanical stirrer and a heater to obtain the desired experimental temperature. As soon as the expiration of the leaching time, the solution was filtered briskly, and the filtrate was subjected to analysis to determine the concentration of Zn and chlorine that was entered into the solution during the leaching process. All dichlorination steps and their conditions are provided in Fig. 1.

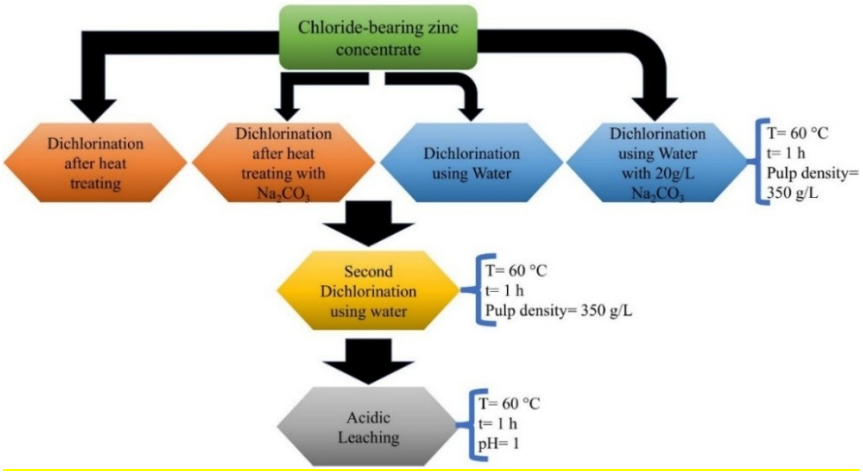

Fig. 1. Dichlorination steps and their conditions.

3. Results and Discussion

The conditions and results of the experiments conducted were presented in Tables 1 to 4. A glance at the Tables supplied reveals some striking information concerning the dichlorination in the zinc hydrometallurgical process. According to Table 1, the first approach involved a two-step dichlorination process using water alone. This method resulted in the dissolution of 15 g/L of chlorine in the first step and 2 g/L in the second step. However, 1.1 g/L of chlorine remained in the leaching solution after this process, indicating limited effectiveness in chlorine removal by water washing.

Table 1. The results of dichlorination using water at T=60 °C and t=1 h, and leaching in H_2SO_4.

Steps	Concentrate weight (g)	Volume of water (mL)	Volume of filtrate (mL)	Zinc concentration (mg/L)	Chlorine concentration (g/L)
First dichlorination	350	1000	985	55	15.4
Second dichlorination	Filtercake of the first step	1000	1024	26	2
Leaching	383.24	1000	865	57000	1.1

In the second dichlorination approach, which is illustrated in Table 2, the chlorine-bearing zinc concentrate was heat-treated for 1 h before undergoing the two-step dichlorination with water. This approach yielded slightly better results, with 17.4 g/L of chlorine dissolved in the first step and 3.5 g/L in the second step. Despite this improvement, the remaining chlorine in the leaching solution was still 1.1 g/L, suggesting that heating did not significantly enhance the dichlorination efficiency.

Table 2. The results of dichlorination after heat treating the concentrate and leaching in H_2SO_4.

Steps	Concentrate weight (g)	Volume of water (mL)	Volume of filtrate (mL)	Zinc concentration (mg/L)	Chlorine concentration (g/L)
First dichlorination	350	1000	795	73	17.4
Second dichlorination	Filtercake of the first step	1000	840	32	3.5
Leaching	438	1000	805	59000	1.1

The introduction of sodium carbonate (Na_2CO_3), as given in Table 3, marked a turning point in the results. When 350 g of the chlorine-bearing zinc concentrate was mixed with 20 g of Na_2CO_3 and heated, the two-step dichlorination process resulted in a dissolution of 20.3 g/L in the first step and 2.6 g/L in the second step. Notably, only 0.625 g/L of chlorine remained in the leaching solution, indicating a substantial improvement in chlorine removal efficiency compared to the water washing method.

Table 3. The results of dichlorination after heat treating the mixture of concentrate and Na_2CO_3, and leaching in H_2SO_4.

Steps	Concentrate weight (g)	Volume of water (mL)	Volume of filtrate (mL)	Zinc concentration (mg/L)	Chlorine concentration (g/L)
First dichlorination	350	1000	735	121	20.3
Second dichlorination	Filtercake of the first step	1000	875	13	2.6
Leaching	408	1000	805	58000	0.675

The most effective approach involved dissolving 20 g of Na_2CO_3 in 1000 mL of water and conducting the dichlorination at 60 °C for 1 h. This method achieved remarkable results, which are illustrated in Table 4, with 18.8 g/L of chlorine removed in the first step and 3.4 g/L in the second step, leaving less than 0.5 g/L of chlorine in the leaching solution. This was the lowest concentration of chlorine remaining across all tested methods, demonstrating the effectiveness of using Na_2CO_3 in the dichlorination process.

Table 4. The results of dichlorination using water along with 20 g/L Na_2CO_3 at T=60 °C and t=1 h, and leaching in H_2SO_4.

Steps	Concentrate weight (g)	Volume of water (mL)	Volume of filtrate (mL)	Zinc concentration (mg/L)	Chlorine concentration (g/L)
First dichlorination	350	1000	875	120	18.8
Second dichlorination	Filtercake of the first step	1000	935	298	3.4
Leaching	387	1000	790	62000	0.48

Fig. 2 illustrates the dichlorination efficiency for each approach. Dichlorination, which was conducted after heating the concentrate in the absence of Na_2CO_3, does not have a salient dichlorination efficiency compared to other approaches and resulted in 94.98% dichlorination. With clarity, using sodium carbonate (Na_2CO_3) has significantly improved the dichlorination efficiency, both along with the thermal effect and adding to water, which resulted in 96.93 and 98.10% dichlorination efficiency, respectively. Dichlorination using water containing Na_2CO_3 had a striking dichlorination, which was the most effective approach. The overall dichlorination efficiency was significantly enhanced when sodium carbonate was used. The efficiency reached 96.93% and 98.10% for the methods involving Na_2CO_3, compared to 94.98% for the method without it. This highlights the critical role of sodium carbonate in improving the dichlorination process according to reaction 1. Şahin et al. [21] investigated the influence of Na_2CO_3 addition on chlorine leaching efficiency under controlled conditions. The findings, based on this study, indicate that a maximum leaching efficiency of 93.75% was observed with the addition of Na_2CO_3. These results underscore the significance of Na_2CO_3 concentration in optimizing dichlorination processes.

$$ZnCl_2 + Na_2CO_3 \rightarrow ZnCO_3 + 2NaCl \quad (1)$$

According to Fig. 3, which demonstrates the concentration of chlorine in the leaching solution, dichlorination using water and also after heating the concentrate had the highest remaining chlorine in the leaching solution, which was 1.1 g/L for both of the mentioned approaches. Dichlorination using Na_2CO_3, which was conducted in two different approaches, had lower chlorine remaining in the leaching solution. This amount was 0.48 g/L in dichlorination using water along with 20 g/L Na_2CO_3, and 0.675 g/L in dichlorination after heating the mixture of concentrate and Na_2CO_3. As discussed above, the most significant approach to removing chlorine from chlorine-bearing zinc concentrate was the one in which 20 g/L Na_2CO_3 was solubilized in water and used in dichlorination.

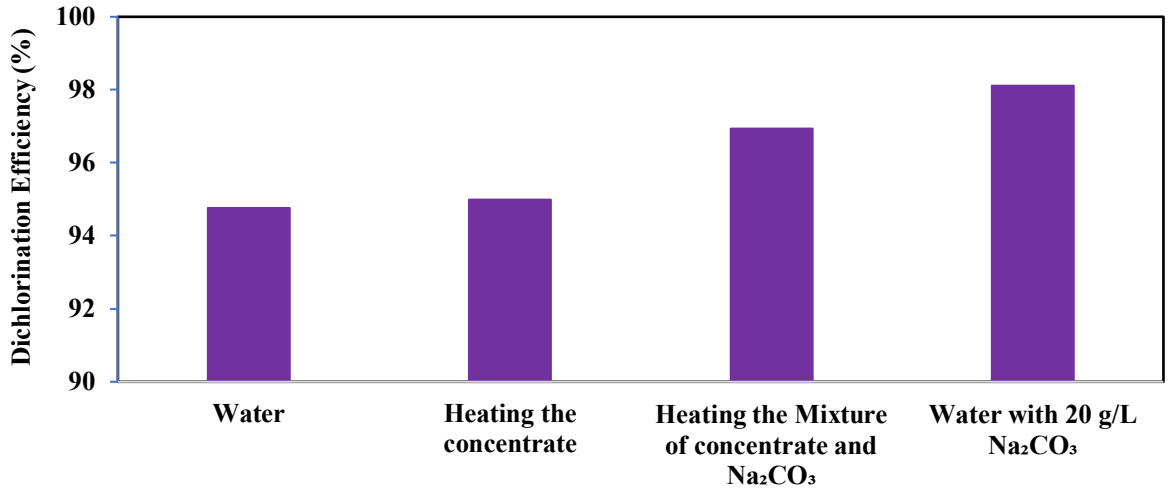

Fig. 2. Dichlorination efficiency for each approach.

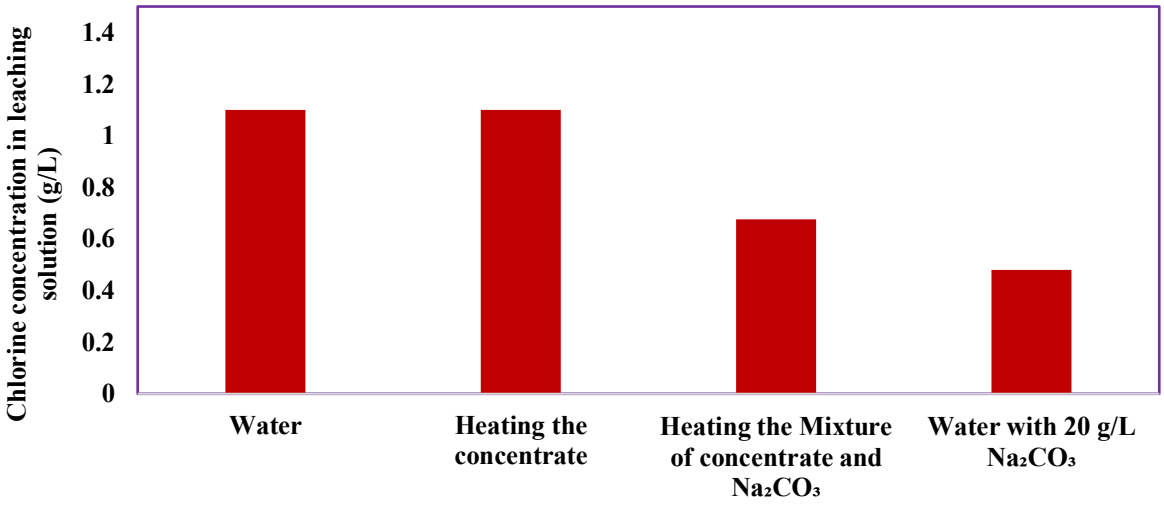

Fig. 3. The amount of chlorine in the leaching solution for each approach.

4. Conclusions

In this research, different approaches were investigated concerning the dichlorination of chlorine-bearing zinc concentrate. The results showed that in almost all the employed approaches, significant dichlorination efficiencies were obtained, and more than 90% of the chlorine was removed. Dichlorination using 20 g/L Na_2CO_3 solved in water at T=60 °C, and 1 h of dichlorination resulted in approximately the highest dichlorination efficiency of 98.10% and the lowest concentration of chlorine in the leaching solution, 0.48 g/L. So, it was selected as the appropriate approach compared to the others. Concerning traditional procedures that used copper and silver in the dichlorination of zinc PLS, this approach had satisfactory efficiency, particularly in the economic aspects of the produced zinc. The obtained results suggest a potential alternative to traditional dichlorination procedures, especially on an industrial scale.

Ethical Considerations

The authors avoided data fabrication, falsification, and plagiarism, and any form of misconduct.

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Conflict of Interest

The authors declare no conflict of interest.

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