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Minimizing Leaching of Al, Co, Cu, Fe, Li, and Ni During Discharge of Lithium-Ion Batteries

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ABSTRACT

The existing methods for recycling lithium-ion batteries present initial hurdles related to the safe handling and preparation of the batteries to avert potential explosions. Submerging batteries in sodium chloride (NaCl) solution has become an acceptable industrial practice. However, the use of NaCl to discharge lithium-ion batteries rusts the batteries' cases and releases metals which impacts the downstream processes that involve selective recovery of Li. This study aimed to determine the optimal concentrations and pH range of NaCl for the discharge of lithium-ion batteries for the purpose of minimizing the leach of Al, Co, Cu, Fe, Li, and Ni.

INTRODUCTION

Lithium-ion batteries contain valuable metals like cobalt, copper, lithium, and nickel making its recycling economically very attractive (Ojanen et al., 2018). Recycling these metals also helps mitigate social and environmental impacts associated with mining practices of cobalt and lithium (Banza et al., 2009; Liu & Agusdinata, 2020). There are two main practices currently adopted by industry to recycle lithium-ion batteries. The first is the pyrometallurgy approach which consumes high energy and requires a high initial investment (Zhou et al., 2021). The second is the hydrometallurgical processing which requires discharging prior to leaching to avoid potential explosions (Liang et al., 2021). The discharge reaction is shown in Equation 1 (Bartholome et al., n.d.):

$$LiC_6 + CoO_2 \rightarrow C_6 + LiCoO_2 \quad (1)$$

Lithium oxide is still reactive with water, but the reaction occurs at a slower rate than lithium metal with water.

There are primarily two methods for discharging a Li battery. The first involves connecting the battery to an electric circuit, which preserves the battery's shape and other conditions but is not practical for industrial- scale operations. The second method entails immersing the battery in an aqueous solution containing an electrolyte, typically NaCl. In the latter scenario, the NaCl solution serves as a conductive medium by facilitating the flow of electrons. The primary concern with the discharge processes with NaCl, or other media, is the corrosion of the battery casing and the release of metals. (Bae & Kim, 2021). The release of metals is undesirable as they can react with water, generating heat in the process. Moreover, the loss of valuable metals during the discharge process is economically unfavorable. Ultimately, it results in increased costs associated with treating the waste solutions to minimize environmental impacts. (Li et al., 2010).

To control the release of metals (i.e., Al, Co, Cu, Fe, Li, and Ni), this study proposed a 2-step procedure. The first step involved varying the concentration of NaCl in the submerging solution and studying its impact on battery case's corrosion rate at neutral pH. This aimed to select the optimal concentration at which the corrosion is minimal. In the second step, adjustments were made to the other key parameter, namely, pH. The pH is a critical factor as indicated by the Pourbaix diagram shown in Figure 1 (Barnes, 2014). The real challenge associated with this approach was to attain the maximum time limit of 16 hours, designed to ensure practicality in an industrial setting,

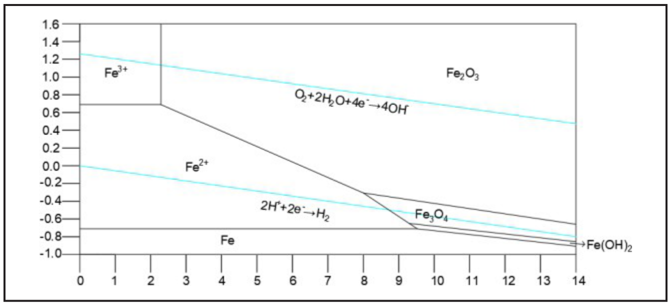

Figure 1. Pourbaix Diagram for iron. At pH 7, a form of Fe^{2+} is more prevalent. Fe^{2+} is highly soluble in water, therefore, other forms of iron are likely to a lesser extent (Earnshaw, 1997)

MATERIALS

Batteries

Batteries were obtained from Catalytic Innovations, a local battery recycling company in Rolla, Missouri, USA. The batteries utilized were of the 18650 types, featuring lithium-ion chemistry.

Reagents

Sodium chloride solution was used as an electrolyte. To use the same raw material intended for industrial use, plain salt Great Value brand was purchased from a local supermarket. Distilled water was used as a medium. Analytical grade potassium hydroxide (KOH) was used to regulate solution's pH. It was purchased from Emplura, USA.

RESEARCH METHOLOGIES

Voltage Measurements

Voltage measurements were made with a Hyper Tough Digital Multimeter TD35235J. The initial voltage of the batteries was set at 4.2 Volts. Complete battery discharge was reported to be at 3.5 Volts or less, as seen in Figure 2. The maximum discharge time was set at 16 hours to ensure the process practicability in industrial settings.

Discharge solution and characterization

The concentrations of the NaCl solutions used in the discharging experiments were 0.12 %, 1.2% and 6% m/v. The optimal NaCl concentration, that was used in the consequent experiments wherein pH was varied, was selected based on the slowest complete discharge as it means less corrosion. The optimal concentration was tested as three pH values: pH 8, 10 and 12. The pH was regulated by adding KOH. A pH meter (Fisher Scientific, USA) was used to measure the pH. At the end of the discharge process, all the 6 solutions were collected and analyzed with an Inductively coupled plasma – Mass spectrometry (ICP-MS).

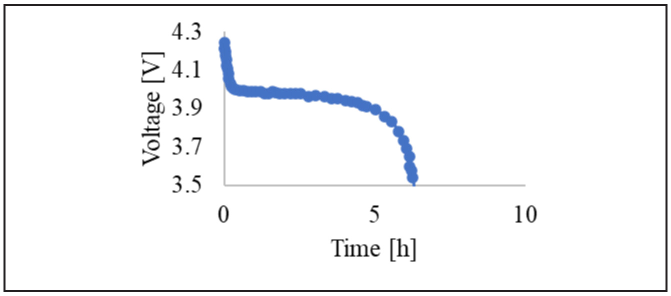

Figure 2. Discharge curve for an 18650 battery (Lozito et al., 2020)

RESULTS AND DISCUSSIONS

Battery Discharge at Different Concentrations and Neutral pH

Figure 3 shows the discharge voltage versus time at three different concentrations of NaCl.

As shown the 12% NaCl solution resulted in the fastest discharge process in about 2 hours. The 6% NaCl solution showed a complete discharge in less than 3 hours. The 0.12% and 1.2% did not provide satisfactory results because the discharging process took more than 16 hours (industry setting limit) Therefore, the 6% NaCl was selected as an optimal concentration that was used in the consequent discharging experiments at varying pH value.

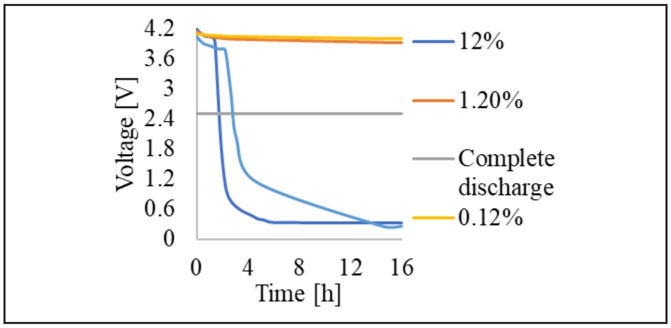

Figure 3. Discharging process at 0.12%, 1.2%, 6% and 12% NaCl concentrations

Battery Discharge with a 6% NaCl at Different pH's

The 6% NaCl solution was selected because it was the only one of the 3 (0.12%, 1.2% and 6%) that complied with the maximum discharge time of 16 hours. This solution was set at pH 8, 10, and 12 because the Pourbaix diagram of iron predicts that the steel battery case will not form soluble species of iron at high pH's. Complete discharge was obtained with the three pH's mentioned above. The results are shown in Figure 4.

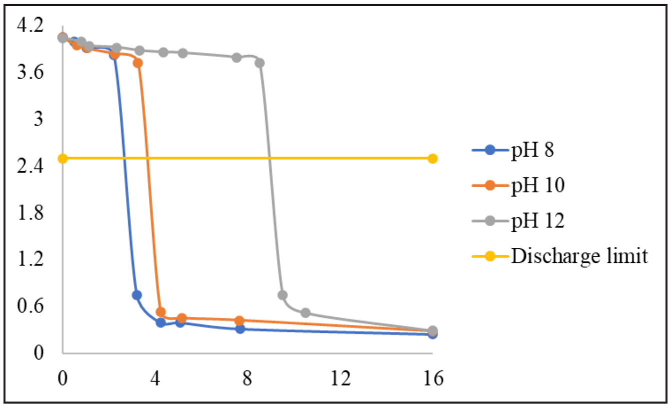

Figure 4. Battery discharge with 6% NaCl solution for different pH's

From Figure 4, a full discharge can be achieved at any of the three pH values tested. However, it was interesting to see the time difference for a complete discharge. For instance, the pH 8 solution needed 3 hours to fully discharge the battery, whereas at pH 12 the discharge time was 9 hours. Nonetheless, the discharge time met the minimum industrial guideline requirements in the 3 cases.

Solution Characterization After Battery Discharge

ICP-MS was used to characterize the solutions after the batteries were discharged. To have comparable data, all batteries were left for 16 hours during the discharge process. Table 1 shows the concentrations of various metals in solution at the three concentrations of NaCl tested in this study.

As seen in Table 1, the NaCl concentration of 0.12% provided the best results because it leached almost a tenth of Fe than concentrations 1.2% and 6%. It also leaches a third of Al, a third of Co, half of Cu, and the fifth of Ni. It would be good to let the battery discharge for a longer period with this concentration to see if it reaches a complete discharge without leaching valuable metals.

Table 1. Concentration of selected metals [ppm] in NaCl solutions of various concentrations after complete discharge

	NaCl Concentration m/v		
Element	0.12%	1.2%	6%
Al	99.02	372.56	683.96
Co	1.71	12.94	10.89
Cu	4.45	19.32	6.55
Fe	398.47	2394.07	2020
Li	61.49	41.06	36.92
Ni	13.91	110.45	56.93

Table 2. Metal concentrations in 6% NaCl solution after discharging at varying pH values.

	pH 8	pH 10	pH 12
Al	895.62	1054.78	915.78
Co	1.09	1.9	1.23
Cu	3.38	3.69	4.33
Fe	2343.62	2271.39	1964.52
Li	49.83	57.49	47.28
Ni	55.98	48.82	41.56

Table 2 shows the metal concentrations in 6% NaCl solution after discharging at varying pH values.

At pH 8, the results resembled those obtained with at neutral pH. The concentration ranges are as follows: 683.96–895.62 ppm Al, 1.23–1.71 ppm Co, 4.33–4.45 ppm Cu, 2,020–2343.62 ppm Fe, 36.92–49.83 ppm Li, and 55.98–56.93 ppm Ni.

The most favorable outcomes were achieved at pH 12. Under these conditions, Fe and Ni concentrations were the lowest among all the experiments, excluding the 0.12% NaCl test that did not produce satisfactory results. Monitoring Fe and Ni is crucial, as a concentration of zero indicates that the battery case is well-preserved, and metals were not liberated.

For all metals, except Cu, the leaching trend increased with increasing pH, reaching its peak at pH 10. However, it is noteworthy that elevating the pH to 12 resulted in lower metal concentrations.

CONCLUSIONS

The discharge of lithium-ion batteries usually required a sodium chloride concentration greater than 12%. However, findings from this research indicated that a complete discharge can be achieved at 6% of NaCl in 3 hours. Using a lower concentration of NaCl (<6%) might not lead to complete discharge within the set time limit of 16 hours.

For the 6% NaCl concentration, set as an optimal concentration due to a slower corrosion rate, the discharge time increased with an increase in pH. The concentration of metals in this solution was consistently high regardless of the pH. However, at pH 12, the concentrations of metals were lower than those obtained with pH 8 and 10. This could be attributed to specific chemical reactions or conditions at pH 12 that result in a more controlled release of metals, potentially mitigating their concentration compared to other pH levels. For instance, at higher pH, some metal hydroxides could form. Hydroxides are generally less soluble and might form a protective layer on the battery case surface, reducing further dissolution.

Finally, even though NaCl was used in this study, it is worthwhile to explore other discharging media. These salts could potentially be less corrosive, helping to avoid metal leaching from the battery (Shaw- Stewart et al., 2019). For instance, saturated Na2SO4 solutions have been employed to discharge lithium-ion batteries (Li et al., 2018). Additionally, solutions such as FeSO4, and ZnSO4 have shown promising results (Ojanen et al., 2018).

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24-062

Navigating Operational Hurdles in SAG Mills: Identifying and Addressing Common Challenges

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ABSTRACT

This paper explores prevalent operational challenges encountered globally in SAG mills, including suboptimal throughput, liner wear, excessive energy consumption, and SAG mill load stability. The paper delves into the root causes behind these issues, such as ore variability, poor operating strategy, or inadequate process control. Drawing on industry experience and case studies, the paper highlights the significance of addressing these challenges to enhance overall mill performance and efficiency. It underscores the necessity of tailored strategies, encompassing improved monitoring, optimized liner designs, and refined control techniques to mitigate these challenges and promote sustainable SAG mill operation.

INTRODUCTION

The semi-autogenous grinding (SAG) mill is the heart of the milling circuit and is often the primary throughput limiting constraint. The SAG mill load must be stable to maximize the SAG mill power draw to achieve maximum throughput [1].

There are challenges to maintaining a stable load in the SAG mill. These challenges are contributed, quite often, by interplaying variables related to the ore conditions (competency, hardness, size distributions, viscosity) performing in set mill-operating conditions. This paper explores the common operational challenges frequently observed through constraints assessments and operational optimization projects, highlights the root causes of SAG mill load instability, and provides a path forward.

Stabilizing the load within the SAG mill is the critical parameter in maximizing SAG mill performance. Yet, several factors influence it, including feed size distribution, the responsiveness of process control systems, and the design and state of wear and design of the mill liners and discharge grates [1]. A poorly tuned control system or suboptimal operator decisions can result in excessive control actions, leading to instability in mill operations. Proactive feed rate and mill speed management is essential in addressing these issues. Neglecting the wear state of mill liners can result in increased mill filling, which negatively impacts milling efficiency and throughput [2].

Objective of the Paper

To maintain a stable SAG mill load for changing ore competency and feed size distribution, the following key variables need to be manipulated, controlled or fixed (Figure 1).

The paper focuses on the following four opportunities and strategies for maintaining a stable SAG mill load, which are some of the key prevalent issues at most SAG-based operations—where immediate opportunities can be achieved: