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A MINI-REVIEW ON OPTIMAL LEACHING PARAMETERS IN THE HYDROMETALLURGY RECYCLING OF Ni-Cd BATTERIES

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Abstract

Despite the decrease in the share of nickel-cadmium (Ni-Cd) batteries in general use caused by the better overall performance of similar nickel-metal hydride (Ni-MH) batteries, and especially lithium-based batteries, Ni-Cd batteries still have their applications for particular purposes. Their mass production has also been reduced due to the cadmium toxicity. So, they are used only in critical areas where their application is allowed, similar to solder alloys containing cadmium (mainly military applications and aviation). The mature technologies for recycling these batteries were developed, including the pyrometallurgical and hydrometallurgical processes or their combination. This mini-review paper deals with the analysis of the results of hydrometallurgical processes, primary sulfuric acid leaching, and the results published in scientific papers. Although the leaching parameters converge to the certain values, there are significant deviations that are far from the approximate mean value. From the above mentioned analysis, conclusions were drawn about the possible causes of such deviations, which are more significant than usual for such well-defined hydrometallurgical processes.

***Keywords**: recycling, Ni-Cd batteries, hydrometallurgy, parameter analyses*

1. INTRODUCTION

The Ni-Cd battery, a product of the late XIX century, underwent a significant design improvement in the 30s of the XX century with the introduction of sintered electrodes. The sealed form of this battery, a major advancement, emerged immediately after the WWII in the US, with the first production of pocket-size batteries in the US in 1946. The 1960s saw the rise of these batteries for electronics and portable devices, thanks to the developments by Sanyo Corporation [1].

The NiMH batteries were developed in the late 1980s and soon after commercialized in Japan in 1990. They have small but numerous (in almost every technical aspect) advantages over NiCd [2]. Recently after this, in the 1990s, the lithium-ion batteries came into existence and have been widely used in portable electronic devices [3,4]. It was expected that the NiCd batteries would be quickly replaced, especially because these newer types of batteries have better characteristics and fewer environmental problems, but the NiCd type is still used today. The NiCd batteries were expected to be quickly replaced, mainly because these newer types of batteries have better characteristics and fewer environmental problems. However, the NiCD type is still used today. However, their use is strictly restricted globally, with the most rigorous legislation in the EU, starting with the 'battery directive' 2006/66/EC, which was replaced recently with the Regulation 2023/1542, which prohibits the NiCd batteries in portable applications, from August 18, 2025 [5]. Nevertheless, with use in special applications and numerous NiCd batteries in use today, their recycling is a very actual and important the environmental issue.

Large-scale recycling of NiCd batteries mainly uses the pyrometallurgical processes (based on Cd distillation). This type of plant was operational in the 1980s and 1990s in the EU and US [6,7] and is still the leading technology for all the above types of batteries; lithium-ion recycling is usually an expansion of the existing plants for Ni-Cd and Ni-MH worldwide. Companies Snam (France) and Accurec (Germany) are known for the purely pyrometallurgy processes, while others, such as Umicore (Belgium), usually combine the pyro- and hydro- followed by electrometallurgy. Recycling facilities, based only on the hydrometallurgical processes, are still scarce (e.g., Recupyl in France) [8]. Besides that, most of the review papers, published in the 2010s, investigated the hydrometallurgical methods [9], which have the lower investment costs, smaller carbon footprint, and are more economical [10,11]. After pretreatment, the acid leaching of Ni-Cd elements usually uses the strong inorganic acids, namely H_2SO_4, HCl, HNO_3, and aqua regia. Over 95% of metal recovery is possible even with the simple sulfuric acid leaching under the optimal conditions [11-13]. However, it can be improved to about 99% when it is electro-assisted or assisted with a suitable oxidizing agent (H_2O_2, Fe^{3+}, or similar) [14-16]. Bioleaching is still in the developing phase, and the use of organic acids or glycine has been promising but was not as efficient as inorganic acid till recent breakthrough research with formic the acid/H_2O_2 leaching reported 98.5% to 100% metal recovery [17]. This article analyzes the results of published research on the leaching of Ni-Cd battery scrap with sulfurous acid over the last two decades. It provides a critical review of the observed differences.

2. SULFURIC ACID LEACHING OF ELECTRODES MATERIALS – THE MAIN LEACHING PARAMETERS

Sulfuric acid is considered as the optimal leachant for the recycling of the Ni-Cd batteries [13,16]. Although, according to some research studies, HNO_3 [13,18] and HCl [19,20] could get similar and even slightly better results, both of these acids are not appropriate for leaching at higher temperatures (over 50 °C) because they cause fumes to create a need for additional gas purification, which rises the costs and worsening the working environment.

Several parameters influenced the recovery rate of the main metal constituent of the electrodes (Ni, Cd and Co). Due to its toxic properties, the recycling of Cd is the most studied. The parameters are stirring rate, liquid-to-solid rate (L/S), acid concentration, temperature, and leaching time. The stirring rate is not investigated in detail, although the research teams agreed that it "had a positive influence on leaching" [15]. Usually, a magnetic stirrer was used with speeds from 200 to 300 rpm, although a mechanical stirrer with 500 rpm was also applied [16]. Nevertheless, this parameter was rarely quantified. However, an in-depth Ni-Cd recycling study has shown that a four-blade impeller with 200, 500 and 1000 rpm produced similar results, confirming the lower significance of mixing, even though the highest speed could slightly improve the recovery rate of Ni at the shorter times of leaching (1-2 h for the anodic material) [21]. The leaching time was also not thoroughly investigated except in the kinetics studies, and even then, with dissimilar and in concrete results. The optimal leaching time was determined between 3 and 5 h, with the recovery rate of Cd (and Co when studied) over 98% and Ni more than 95% [11-15]. However, Ni from the anode plate (Cd) usually had recovery of just 80% [20], but it is considered a minor problem due to its low content. The $Ni(OH)_2$ and Cd require shorter times for nearly complete recovery, 30 to 70 minutes [14,21]. Detailed time dependence investigations reveal that 3 h could be the optimal leaching time [13,21]. However, recovery maximization requires up to 4-5 h, which is finding of the most researches [16,18,22]. This is valid especially for Ni, while for Cd, 1 h is optimal for pH<2 [23].

Sulfuric acid concentration is one of the two most significant parameters for the leaching process. It has been researched in detail, but two different conclusions have been drawn: the optimal concentration is between 2M and 3M [16, 21-23], and 4M or 5M H_2SO_4 is optimal [22,13]; the first is more common but is not prevailing. These differences are not insignificant and need a good explanation. Although not explicitly stated in the articles, they are most affected by the pretreatment, often performed by diluted sulfuric acid, which is poorly explained even when stated, with only a few exceptions [20-23]. Another highly influenced factor is the applied temperature of leaching, where the higher optimal acid concentrations were at lower temperatures, e.g., 70°C [13], while the concentrations of about 2.5M were at 90-100°C [16,22,23]. In both cases, recovery of Cd is nearly 100%, and of Ni is above 90%. Here is convenient to mention that H_2O_2 addition drastically improve the kinetics of leaching, especially at lower temperatures (25-50°C) [14,16].

The second most important factor was the temperature. This parameter is strongly connected to the acid concentration so that they can be observed and analyzed together. However, even a single impact is evident since it is significant. Differences between 50°C and 85°C are substantial; Ni's recovery was increased from 50% to 95% [21], nearly doubled; rising temperature from 50°C and 95°C almost tripled recovery rate of Ni [23]. Considerable better results with the same acid concentration were confirmed in every published research. It is also quantified in kinetics studies. Finally, even double higher acid concentration (5M vs. 2-3M) at 70°C showed slightly worse results (~90% vs. ~95%) [13,22]. Finally, the optimal L/S ratio was also differently set. Although 20:1 was the most common [21], it can deviate from 17:1 [23] to 25:1 [13], and an L/S ratio of 10:1 is also claimed as optimal [22]. The higher L/S ratio is usually connected with the higher acid concentrations, which then explains a lot, but it was not always the case [22].

3. IMPACT OF THE OTHER IMPORTANT FACTORS

Pretreatment, the grain-size distribution of leached parts, and their phase composition were always mentioned but rarely analyzed in detail. Pretreatment includes disassembling, crushing, grinding, and finally washing. The shredder is mostly used with previous manual dissembling or not. Characterization of the shredded metal parts was a theme of several papers. However, generally, it is just characterized by the chemical composition and figure of the ground parts or estimated average size of them, not with granulometric analysis, which is very important for further treatment of the electrode material. A few papers show that the size of the particles ranges from several tens of μm to a couple of mm, e.g., 40 μm-2.0 mm [23]. Interestingly, one study showed a result that did not agree with the general theory that an increase in the specific area gives higher dissolution [21].

Phase composition is another thing that is often given qualitative (XRD) but is not always separated in the chemical analysis. Thus, hydroxides and oxides of metals (Ni, Cd) are present and could be in a high content. Although it should be similar for all Ni-Cd, it can vary widely, reach about a third of the whole metal content, and be a significant factor that strongly influences the sulfuric acid leaching kinetics. Because of that, it is important to state that leaching of NiOOH and especially $Ni(OH)_2$ requires lower acid concentrations and room temperature, where the whole phase can be dissolved at room temperature and just 0.1M H_2SO_4. At the same time, it is sufficient even for the metal phases of Co and Cd (over 90%) [23].

4. CONCLUSIONS

This short review demonstrated the differences in optimal parameters of sulfuric acid leaching of Ni-Cd electrode materials. Through brief analysis, the following conclusions were drawn:

1. Small dissimilarities were caused by the studied parameters that were not identical; mostly, it was a case with temperature/acid concentration.

2. One of the main causes of the observed distinctions was the different grain-size distribution of the shredded parts that were leached.

3. Phase composition caused the moderate differences in results since the ratio between the pure metals and their hydroxide/oxide varied widely, particularly with Ni.

4. The most significant cause of different results was the pretreatment of the material that was leached in the studies. The wash was performed by water followed by the low (under 1M) H_2SO_4 concentrations but with appreciable variations between different research studies.

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