# Reduction/Carbonylation flowsheet for the extraction of Critical Metals from Mixed Hydroxide Precipitate (MHP)

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# Expended abstract

# Introduction

Mixed Hydroxide Precipitate (MHP) is an intermediary product of nickel refining from laterite ores. It is produced by high-pressure acid leaching (HPAL), heap leaching and other acid leach processes. As produced, MHP is a very fine and wet material containing approximately 50% of moisture. Wet MHP contains approximately 20% of nickel, 1-2% of cobalt, up to 5 % of manganese, close to 1% of zinc and 1-2% of sulphur (Tables 1 and 2). Four samples of MHP were investigated, including samples from New Caledonia, Indonesia and Turkey.

Currently, the extraction and refining of metals from MHP are done via complex hydrometallurgical processes, which are sensitive to feed material composition and require elaborate waste stream treatment (M. Mackenzie, M.Virnig, A.Feather, (2006) The recovery of nickel from high-pressure acid leach solutions using mixed hydroxide product – LIX® 84-INS technology. Minerals Engineering, 19 (12), 1220-1233; G.M. Dunn, Method for the treatment of mixed hydroxide product produced in a metal extraction process. WO 2010/118455 (2010); J. Vaughan, W. Hawker, D. White, Chemical aspects of mixed nickel-cobalt hydroxide precipitation and refining. In Proceedings ALTA Nickel Cobalt Conference (2011). [1,2,3]

The reduction/carbonylation method was considered before; however, no current commercial operations exist. Westwin is building a demonstration plant in Lawton, Oklahoma, USA, to refine MHP using the carbonyl process and produce battery-grade nickel, cobalt metal powders, and other products.

*Table 1 Composition of MHP samples*

| Prep Sheet # | Project Sample ID | Al | Ca | Co | Cu | Fe | Mg | Mn | Na | Ni | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | NC1-MHP-F01 | 0.094 | 0.026 | 1.86 | 0.110 | 0.044 | 0.342 | 2.72 | 0.136 | 20.9 | 0.395 |
| **2** | IND-MHP-F01 | 0.182 | 0.022 | 1.31 | 0.109 | 0.034 | 0.615 | 2.90 | 0.143 | 18.8 | 0.368 |
| **3** | NC2-MHP-F01 | 0.087 | 0.008 | 1.88 | 0.108 | 0.034 | 0.339 | 2.65 | 0.134 | 19.9 | 0.330 |
| **4** | TRK-MHP-F01 | 0.563 | 0.213 | 0.757 | 0.030 | 0.049 | 1.58 | 2.18 | 0.131 | 17.2 | 0.111 |

Sulphur and carbon were analyzed using the LECO method and presented in Table 2.

*Table 2 Total Carbon and Sulfur analyses*

| Sample ID | Sample Mass (g) | % Carbon | % Sulphur |
|---|---|---|---|
| **NC1-MHP-F01** | 0.1887 | 0.0749 | 1.73 |
| **IND-MHP-F01** | 0.1497 | 0.106 | 1.82 |
| **NC2-MHP-F01** | 0.1278 | 0.0674 | 2.08 |
| **TRK-MHP-F01** | 0.1367 | 0.157 | 2.96 |

# Refining of MHP using the carbonyl process

## PFD description

For several projects, MHP and similar materials were considered as feed materials for the carbonyl process. Reduced MHP is extremely reactive toward the carbonylation extraction process; however, several challenges must be overcome, mostly in handling fine dry MHP feed material.

At the beginning of the 2000s, Falconbridge initiated a project to refine nickel carbonate/nickel chloride mixture to high-purity nickel powder using a reduction/carbonylation process. The produced metallized nickel feed material was extremely reactive, and nickel was extracted at atmospheric pressure. The challenge of the process was that the nickel feed that was produced had a very low bulk density and was very difficult to handle ( M. Collins, S. Kuula, (2007) Production of active nickel powder and transformation thereof into nickel carbonyl. US Patent App. 10/537,069, ) [4].

Westwin developed a flow sheet that overcomes these difficulties and makes the MHP carbonylation process commercially valuable. The basic flowsheet ( Figure 1) comprises feed preparation steps, including MHP drying, briquetting, and reduction.

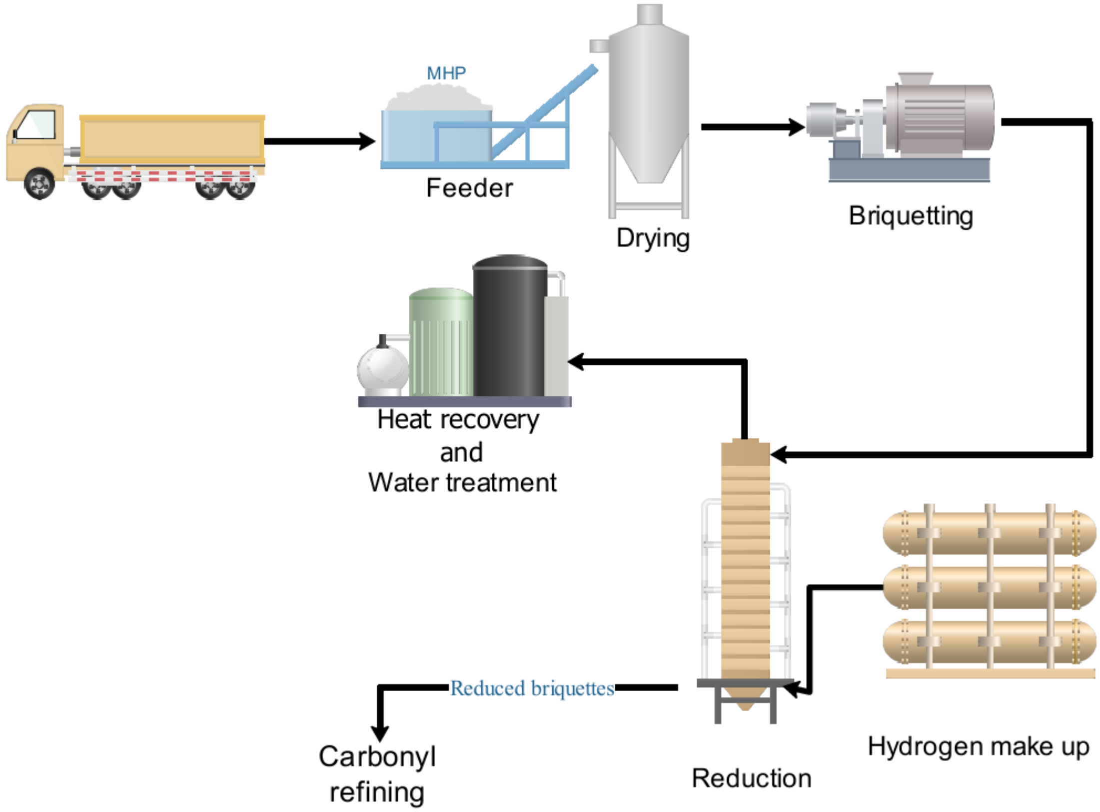


*Figure 1 PFD of the feed preparation process*

Wet MHP is dried and briquetted using sodium silicate as binding material. The selection of sodium silicate is based on the needs of the carbonyl process extraction. Introducing carbon or iron into the feed material might create problems in the next steps of the refining process.

Carbonyl refining PFD is shown in Figure 2. Reduced MHP briquettes are introduced to the carbonylation reactor. Nickel and trace amounts of iron and cobalt react with carbon monoxide at elevated pressure to produce volatile metal carbonyls. Metal carbonyl gas mixture is carried out from the reactor with an unreacted CO stream and condensed. High-purity nickel carbonyl is separated by distillation and decomposed into high-purity nickel powder. The iron and cobalt carbonyl residue is concentrated in the still, collected and decomposed to alloy powder. The residue contains manganese (~30%), zinc (~5%) and unreacted cobalt (~10-15%) sent for future refining.

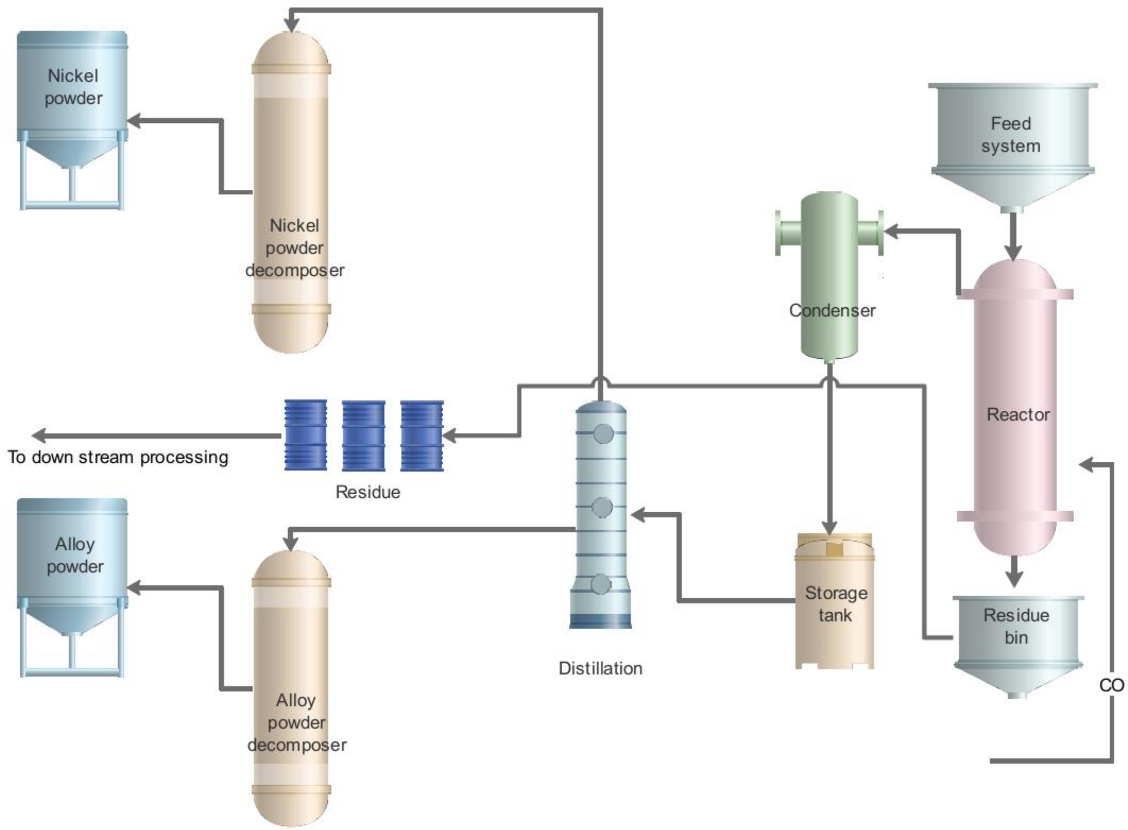


*Figure 2 The carbonylation step of MHP refining*

## Process development and experimental

The metallized MHP briquettes produced are extremely porous and suitable for the carbonyl process. The bulk density of the material is above 2 g/cc compared to 0.4 g/cc of reduced MHP powder.

Reduced MHP briquettes are directly used in the carbonylation process. Table 3 presents the ICP analysis of several MHP samples after drying and reduction. The nickel concentration increases to about 40% after drying and above 60% after reduction.

*Table 3 Samples analysis after roasting and reduction*

| | Al | Ca | Co | Cu | Fe | Mg | Mn | Na | Ni | Weight lost |
|---|---|---|---|---|---|---|---|---|---|---|
| **NC1-MHP roasted** | 0.188 | 0.015 | 3.88 | 0.216 | 0.073 | 0.662 | 5.33 | 0.256 | 38.7 | 52.02% |
| **NC1-MHP reduced** | 0.280 | 0.016 | 6.17 | 0.333 | 0.099 | 0.977 | 8.50 | 0.375 | 60.5 | 39.79% |
| **IND-MHP roasted** | 0.373 | 0.048 | 2.87 | 0.220 | 0.073 | 1.22 | 6.01 | 0.281 | 37.7 | 52.91% |
| **IND-MHP reduced** | 0.534 | 0.054 | 4.31 | 0.350 | 0.093 | 1.75 | 9.25 | 0.405 | 55.7 | 36.76% |
| **NC2-MHP roasted** | 0.049 | 0.135 | 3.16 | 0.030 | 0.072 | 0.909 | 5.57 | 0.288 | 41.9 | 53.23% |
| **NC2-MHP reduced** | 0.063 | 0.194 | 4.81 | 0.047 | 0.106 | 1.36 | 8.58 | 0.433 | 62.9 | 40.96% |

TGA was used to investigate the roasting and reduction parameters of MHP materials. Based on previously published work, a roasting temperature of 140ºC and a reduction temperature of 450ºC were selected (D. A. Huggins and W. Curlook. Separation of nickel from cobalt. US Patent 3,672,873 (1972)) [5].

Roasting and reduction kinetics were studied using TGA Netzsch STA 449, presented in Figures 3 and 4. Typical roasting time was 45-50 minutes, and the reduction time was close to one hour.

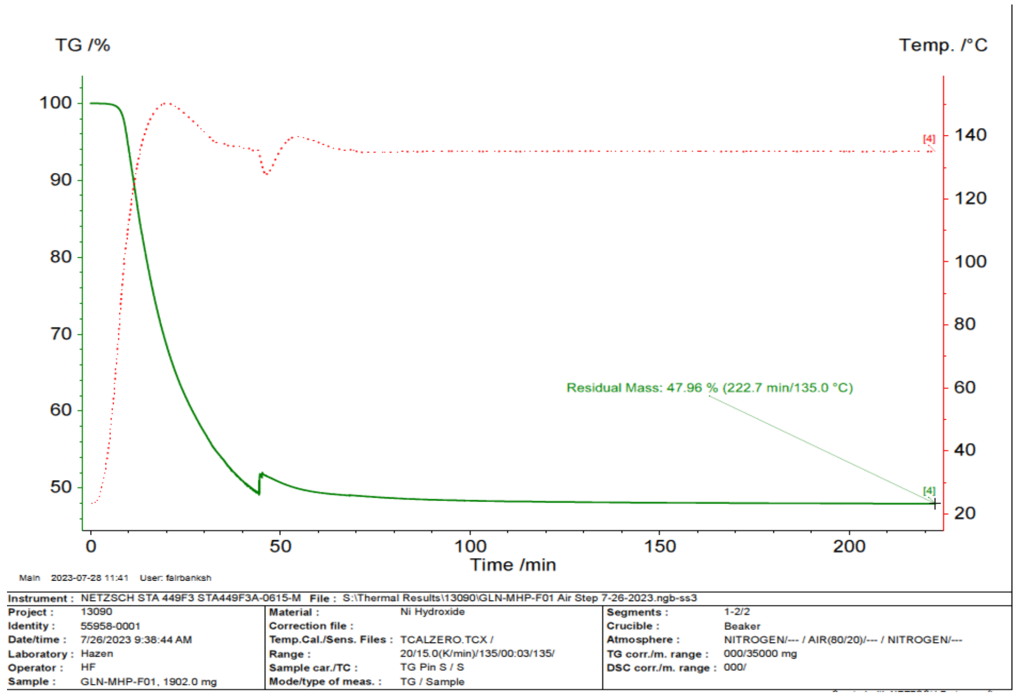


*Figure 3 TGA results of drying and roasting of NC1 MHP sample*

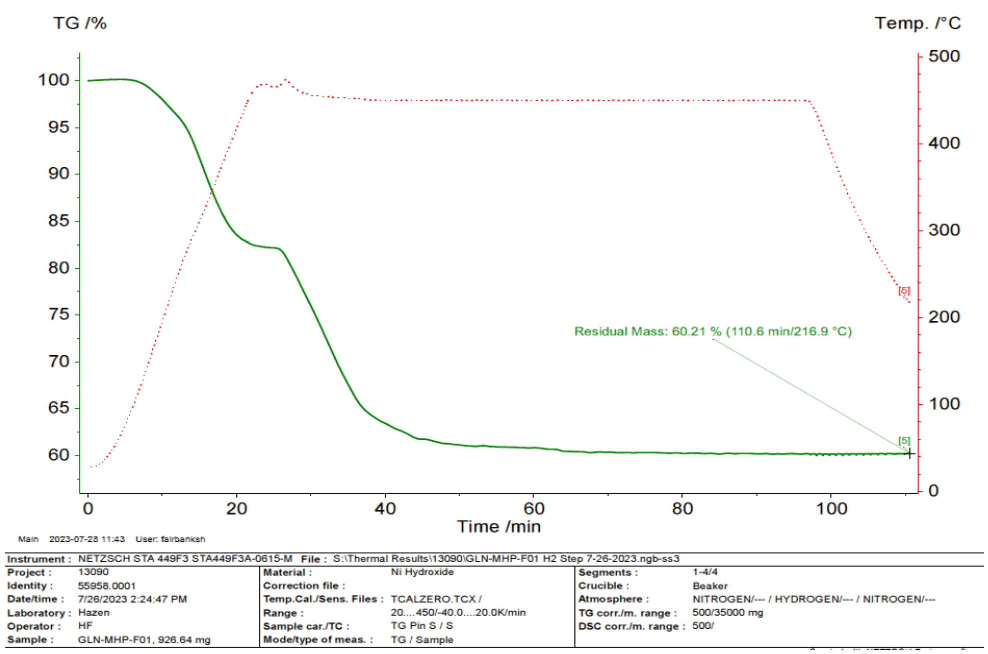


*Figure 4 TGA results of reduction of NC1 MHP sample*

Initial tests on nickel and cobalt extraction confirmed the high reactivity of material toward the carbonyl process. A high-pressure TGA unit (Thermomax 500) was used to perform reduction and carbonylation. The TGA results of the reduction and carbonylation process are presented in Figures 5 and 6.

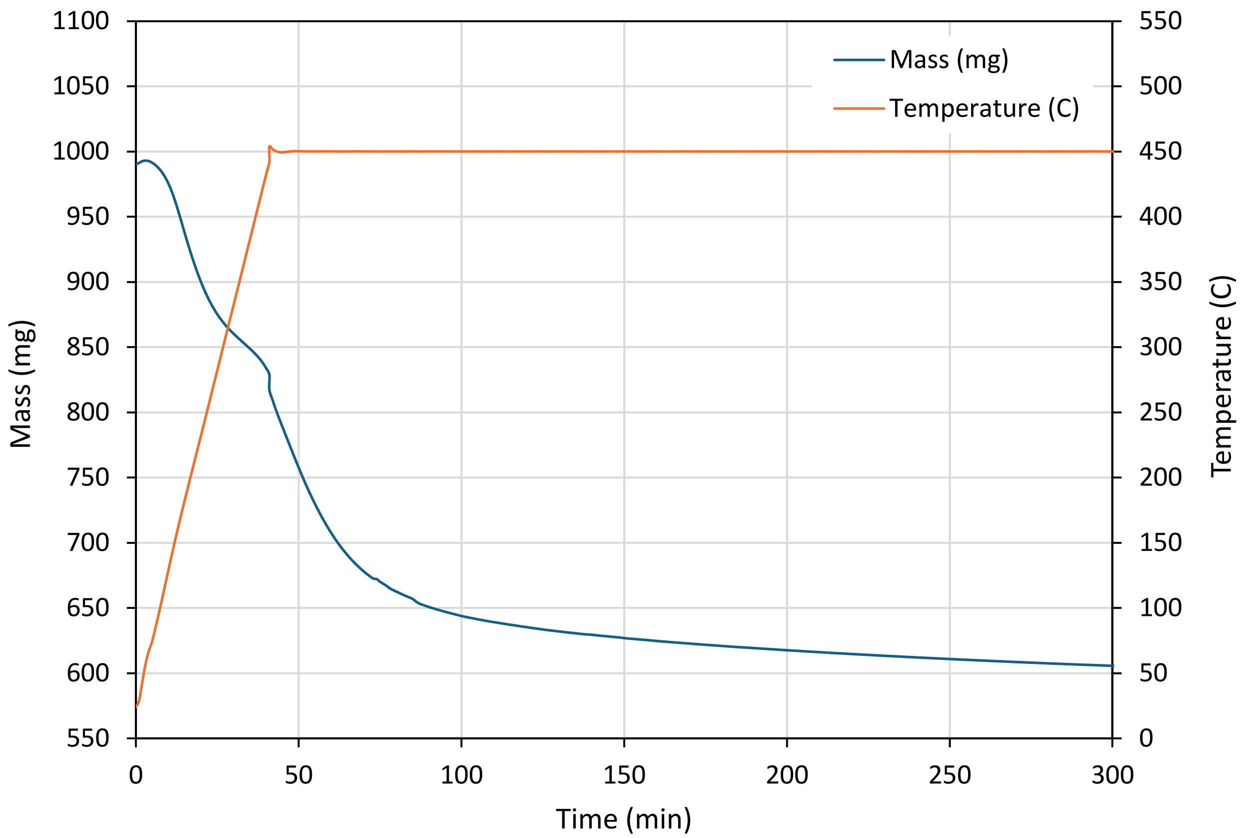


*Figure 5 Roasting and reduction kinetics*

At pressure as low as 90 psi (6 bar), more than 85% of nickel was extracted during 6-hour extraction (Table 5). However, little cobalt was extracted at this pressure. The cobalt extraction process requires high pressure. The extraction kinetics slowed with increased pressure after 300 psi, indicating that the formation of cobalt carbonyl solid started to block the surface of the reduced nickel. Most of the extraction occurred during the first hour and didn't depend on pressure, indicating that the extraction rate depended on the feed material's surface area. Reduced feed material probably contains reduced nickel and reduced nickel/cobalt alloy surface. Initially, pure metallized nickel reacts to form volatile nickel carbonyl. The alloy particles react much slower, and if solid cobalt carbonyl forms, it blocks access to the nickel surface. More work will be done to investigate the mechanism of the reaction and optimize extraction yields.

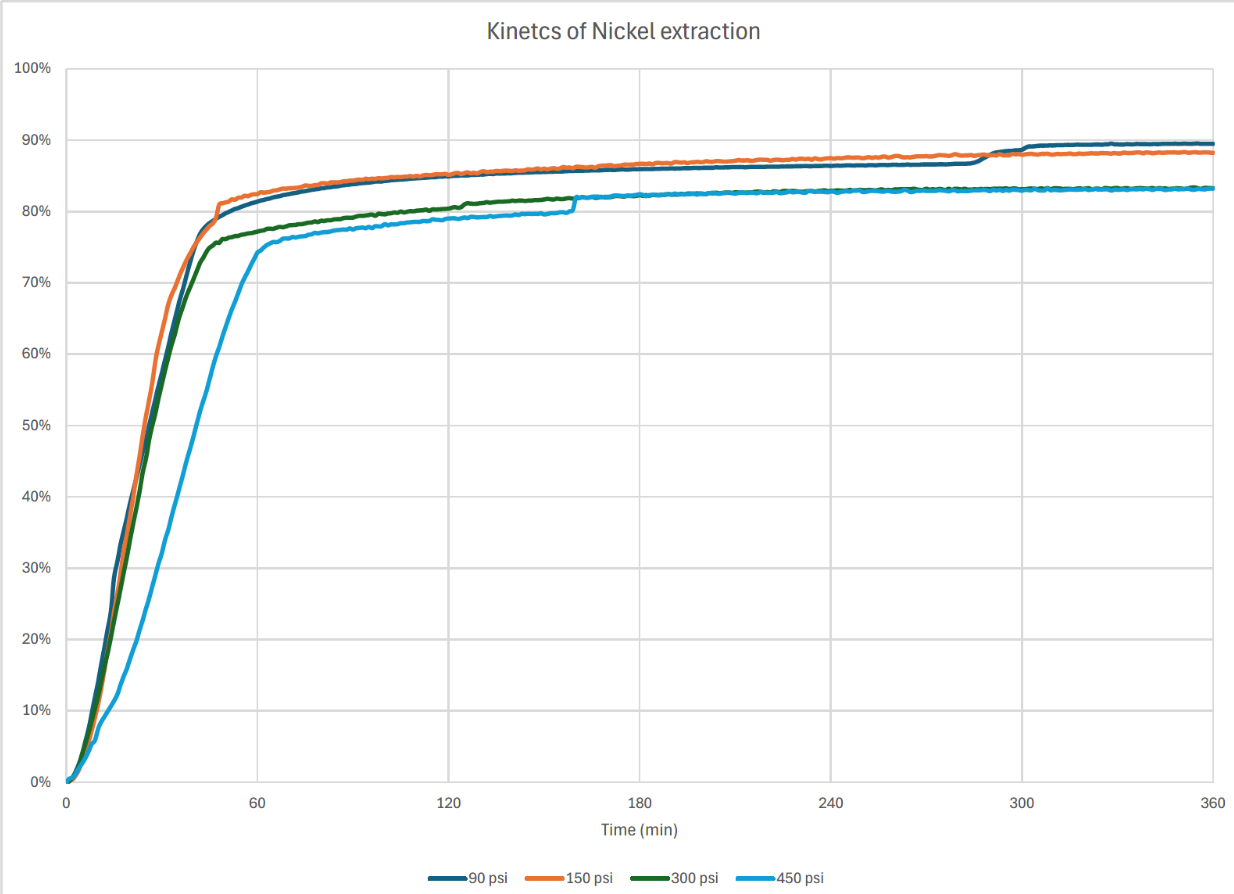


*Figure 6 Extraction kinetics of Ni from reduced MHP*

Extraction yields were calculated based on weight change and ICP analysis of the feed and residue and presented in Table 4.

*Table 4  Extraction yields calculations*

| Pressure (psi) | Co | Fe | Ni |
|---|---|---|---|
| 90 | 8.0% | 0.0% | 85.1% |
| 150 | 7.5% | 0.0% | 84.2% |
| 300 | 0.7% | 0.0% | 81.9% |
| 450 | 17.6% | 0.0% | 84.4% |

In addition to investigating the extraction of nickel and cobalt from commercially available MHP, Westwin and TCM research also developed an alternative process of extracting valuable metals from floatation concentrates. Floatation concentrate is treated by dry chlorination to extract sulphur, iron, and copper. The mixture of nonvolatile metal chlorides could be reduced with hydrogen, and the carbonyl method could extract nickel, cobalt, and residual iron. Alternatively, metal chloride can be leached by water to produce an MHP product that can be used as feed material for the carbonyl process.

Figures 7 and 8 present the proposed flow diagrams of the process. The process can also be used to maximize the extraction of PM. In the dry chlorination, PGM chlorides report to the nonvolatile metal chlorides fraction. After reduction and carbonylation, the concentration of PGM in the residue increases more than tenfold without losses.

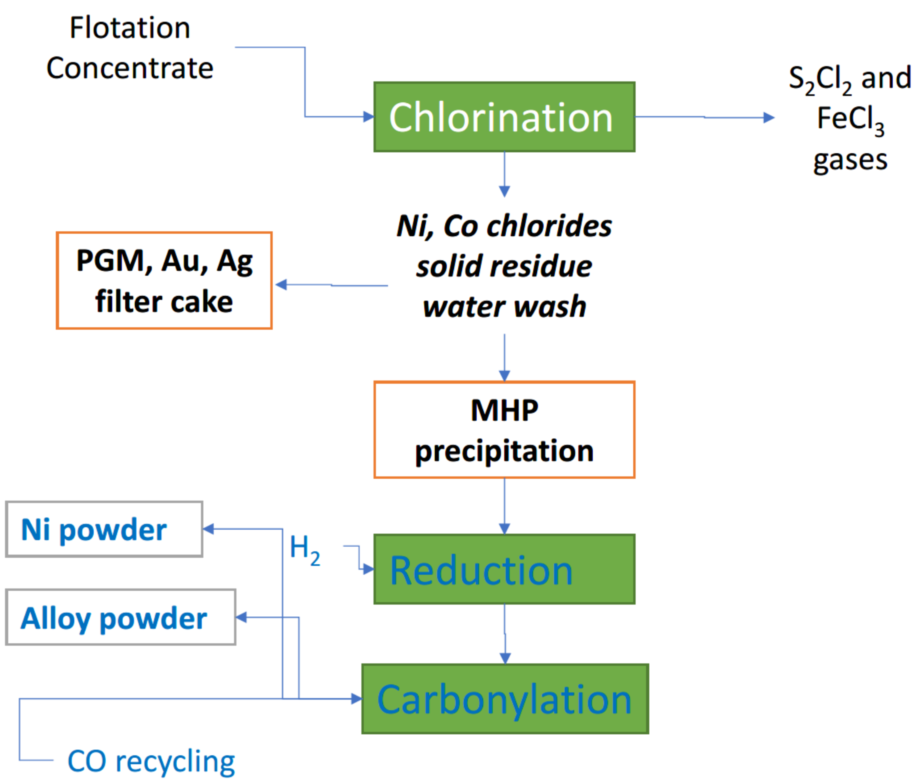


*Figure 7 PFD of chlorination and carbonylation of a flotation concentrate with MHP precipitation.*

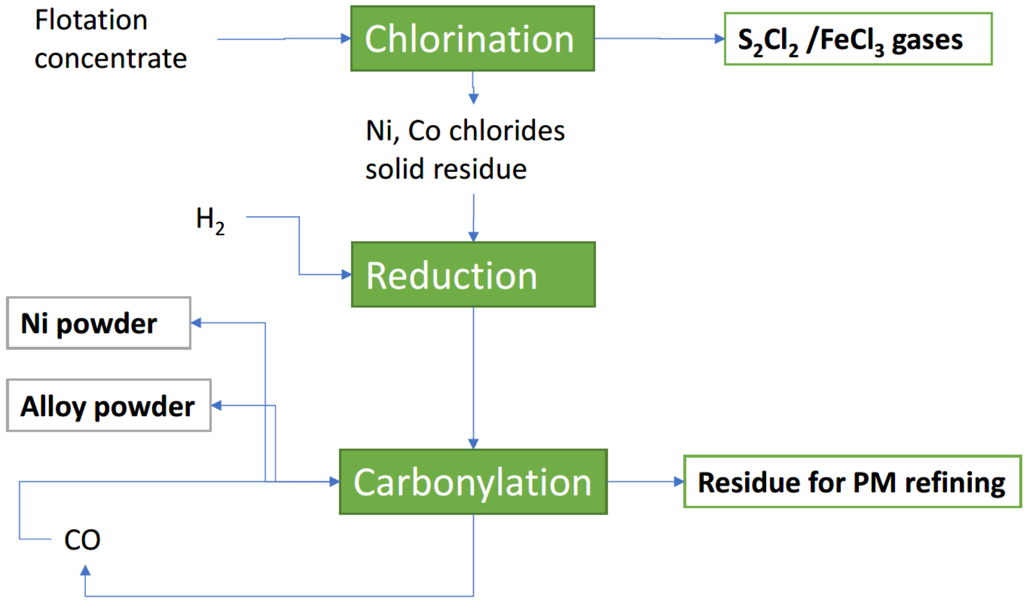


*Figure 8 PFD of chlorination and carbonylation of a flotation concentrate without MHP precipitation*

# Advantages of the process

1. The carbonylation process extracts mainly nickel to produce high-purity nickel powder.
2. The process doesn't include hydrometallurgical steps; therefore, no liquid waste is produced.
3. Carbonylation process kinetics is very fast at low pressure compared to other carbonyl operations.
4. Because of the low iron concentration in the feed and low pressure of the process, no iron is extracted from the reduced MHP, making purification of nickel carbonyl by distillation simple and efficient.

# Conclusions

1. PFD was developed for the extraction of nickel and cobalt using the carbonyl method.
2. Different MHP were tested for reduction and extraction kinetics using TGA.
3. The extraction kinetics of nickel from reduced MHP is fast compared to other carbonyl processes.
4. Iron and cobalt extraction is minimal at these conditions, making the purification of nickel simple and efficient.

# References:

1. M.Mackenzie, M.Virnig, A.Feather, The recovery of nickel from high-pressure acid leach solutions using mixed hydroxide product – LIX® 84-INS technology. Minerals Engineering, 19(12), 1220-1233 (2006).
2. G.M. Dunn, Method for the treatment of mixed hydroxide product produced in a metal extraction process. WO 2010/118455 (2010).
3. J. Vaughan, W.Hawker, D.White, Chemical aspects of mixed nickel-cobalt hydroxide precipitation and refining. In Proceedings ALTA Nickel Cobalt Conference (2011).

4. M Collins, S Kuula., Production of active nickel powder and transformation thereof into nickel carbonyl. US Patent App. 10/537,069, (2007)

5. D. A. Huggins and W. Curlook. Separation of nickel from cobalt. US Patent 3,672,873 (1972)