NICKEL EXTRACTION FROM MIXED HYDROXIDE PRECIPITATES VIA CARBONYLATION PROCESS

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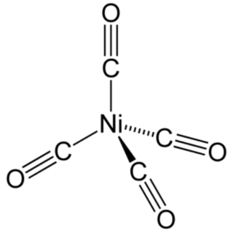

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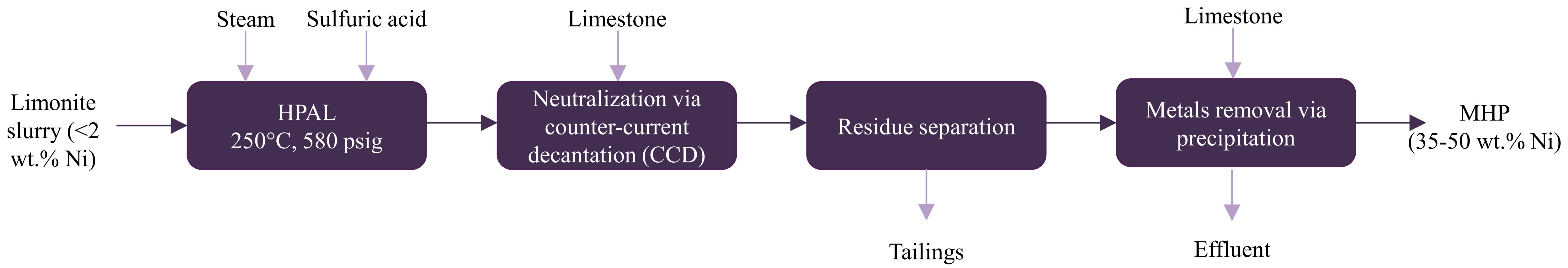
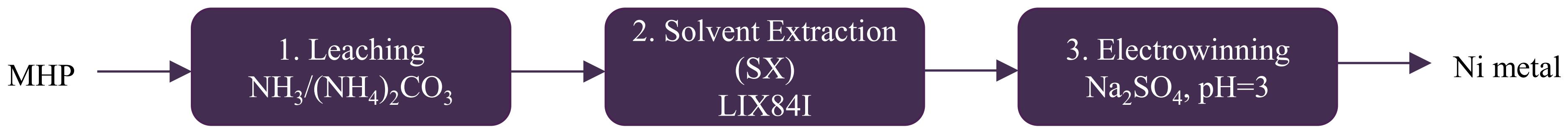
Introduction and Motivation

Mixed-hydroxide precipitate (MHP) production via high-pressure acid leach process (HPAL):



Ni refining from MHP process:



Literature Review

The closed-loop nature of carbonyl refining of MHPs

1. **Dehydration of nickel hydroxide.**

$$Ni(OH)_{2\,(s)} \xrightarrow{210°C,\ 1\ atm} NiO_{(s)} + H_2O_{(g)}$$

2. **Selective reduction of NiO from an impure mining concentrate (containing Fe, Co and other metals).**

$$NiO_{(s)} + H_{2\,(g)} \xrightarrow{450°C,\ 1\ atm} Ni_{(s)} + H_2O_{(g)}$$

3. **Carbonylation of impure metallic Ni.**

$$Ni_{(s)} + 4CO_{(g)} \xrightarrow{50-170°C,\ 1-200\ atm} Ni(CO)_{4\,(g)}$$

Recycled CO

4. **Decomposition of nickel carbonyl at unique conditions into various value-added products.**

$$Ni_{(s)} + 4CO_{(g)} \xleftarrow{\sim 200°C,\ Low\ Pressure} Ni(CO)_{4\,(g)}$$

Bulk class I Ni

Ni Powders

Value-added products (e.g. foams, coatings, etc.)

Nickel tetracarbonyl – $Ni(CO)_4$

- Discovered in 1889 by Mond and Langer (right top and right bottom)
- A colorless, volatile liquid at room temperature
- Normal boiling point at 43°C
- Highly toxic (Threshold Limit Value of 50 ppb in Canada)
- Commercially produced since 1902 for the metallurgical separation of nickel and iron from mining concentrates

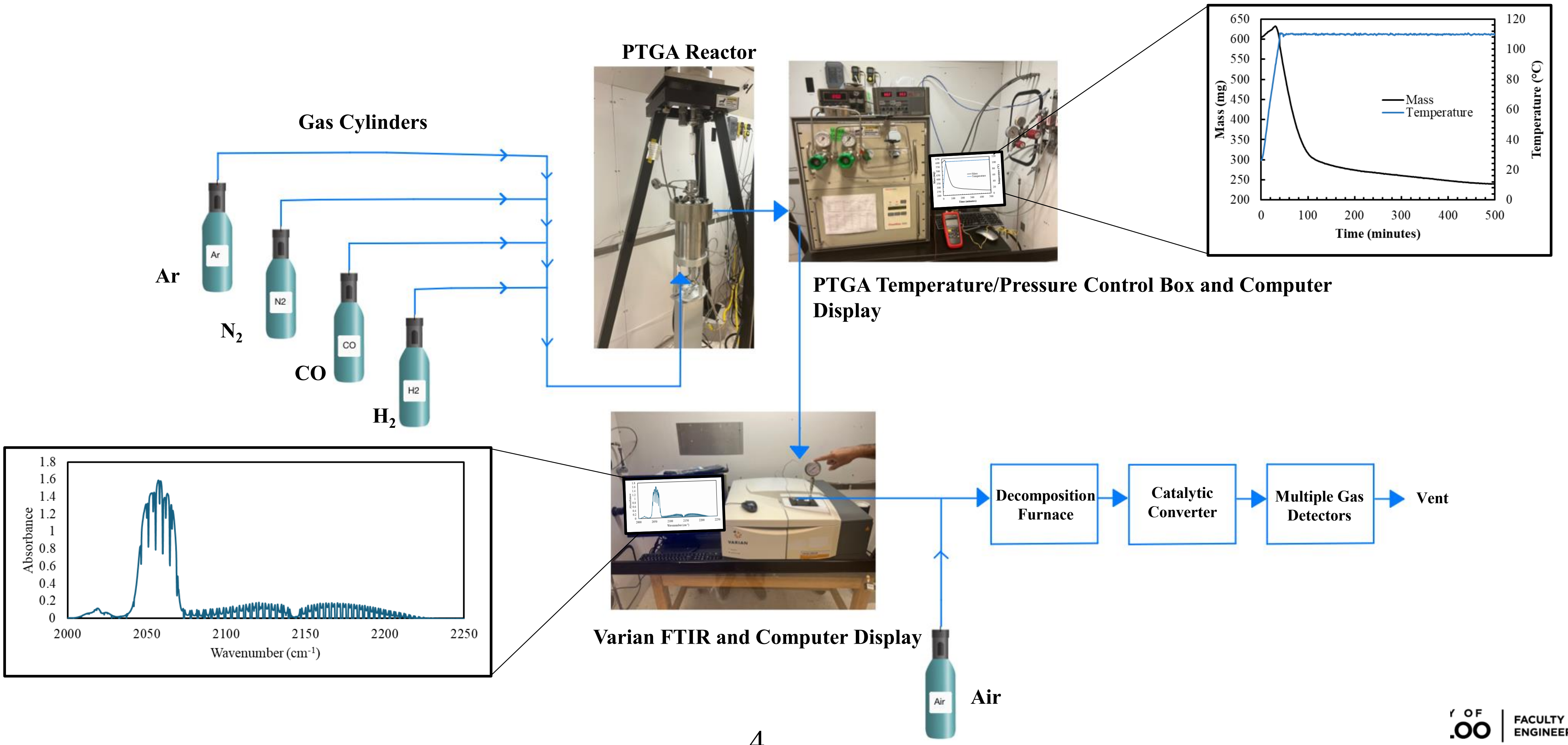
Ludwig Mond
(1839-1909)

Carl Langer
(†1935)

Ludwig Mond and Carl Langer.

Experimental and Methodology

Pressurized thermogravimetric analyzer (PTGA) flow system setup for reduction and carbonylation experiments



Results

Feed sample compositions (prefix "L" stands for laterite-based MHP, prefix "B" stands for black mass-based MHP)

Sample	Al %	B %	Ca %	Co %	Cr %	Cu %	Fe %	K %	Li %	Mg %	Mn %	Na %	Ni %	Balance %
L1-MHP	0.33 ±0.01	0.05 ±0.01	0.22 ±0.01	2.30 ±0.06	0.11 ±0.01	0.00 ±0.01	0.06 ±0.01	0.00 ±0.01	0.00 ±0.01	1.22 ±0.01	3.94 ±0.08	0.00 ±0.01	44.82 ±2.12	~ 45
L2-MHP	0.32 ±0.09	0.08 ±0.01	0.15 ±0.02	3.48 ±1.51	0.07 ±0.05	0.00 ±0.01	0.05 ±0.04	0.04 ±0.03	0.44 ±0. 10	0.60 ±0.31	1.70 ±0.66	0.03 ±0.02	40.40 ±2.18	~ 50
B1-MHP	1.07 ±0.12	0.01 ±0.01	0.01 ±0.01	3.76 ±0.04	0.01 ±0.01	0.06 ±0.01	0.00 ±0.01	0.04 ±0.02	0.00 ±0.01	0.01 ±0.01	3.20 ±0.02	0.00 ±0.01	49.42 ±1.31	~ 40
B2-MHP	0.14 ±0.01	0.00 ±0.01	0.02 ±0.01	11.39 ±0.31	0.00 ±0.01	0.00 ±0.01	0.00 ±0.01	0.03 ±0.01	0.26 ±0.01	0.01 ±0.01	10.57 ±0.05	4.40 ±0.01	32.14 ±0.31	~ 40

Before processing (feed)

Carbonylation residue

Results

MHP Reduction: Effect of Reduction Temperature

✓ **Laterite MHP:**

L1-MHP shows a strong temperature effect

- Higher temperature gives faster reduction and more mass loss
- Suggests multiple reducible oxygen species

L2-MHP reduces very quickly

- Shows little temperature dependence
- All temperatures reach a similar final mass, indicating an easily reducible phase

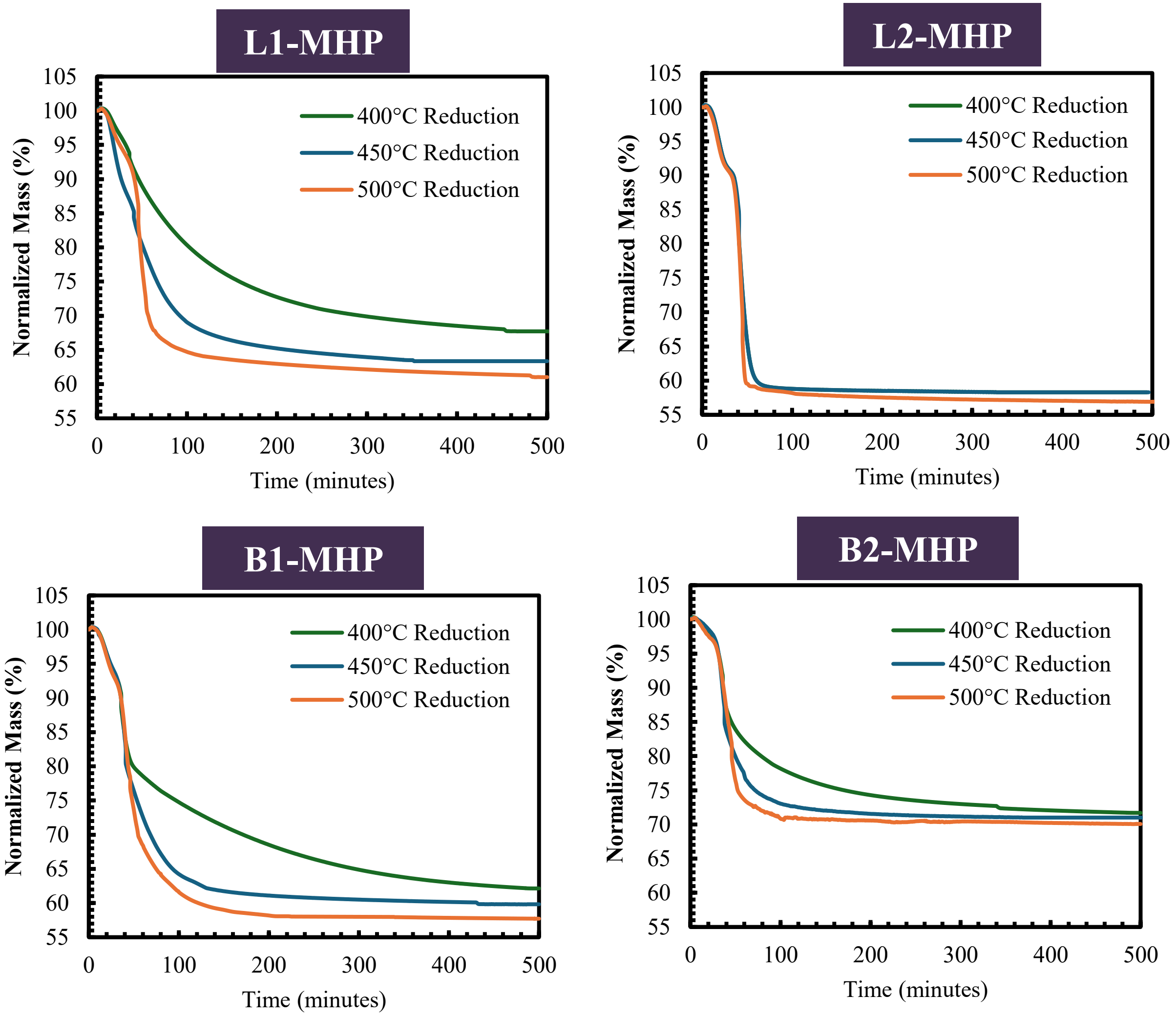
✓ **Black mass MHP:**

B1-MHP shows a strong temperature effect

- Reduction at 400 °C is incomplete, especially at longer times

B2-MHP shows less mass loss during reduction

- It keeps a higher final mass, likely due to its lower nickel content



Mass change during reduction under H_2 atmosphere at 6 psig and temperatures of 400-500 °C

Results

MHP Reduction: Effect of Reduction Temperature on Surface Area

- **Fresh samples:**

✓ Surface area differs between samples.

✓ Laterite MHPs have lower surface area than BM-MHPs.

✓ Differences come from different minerals and particle shapes.

- **After reduction at 400 °C:**

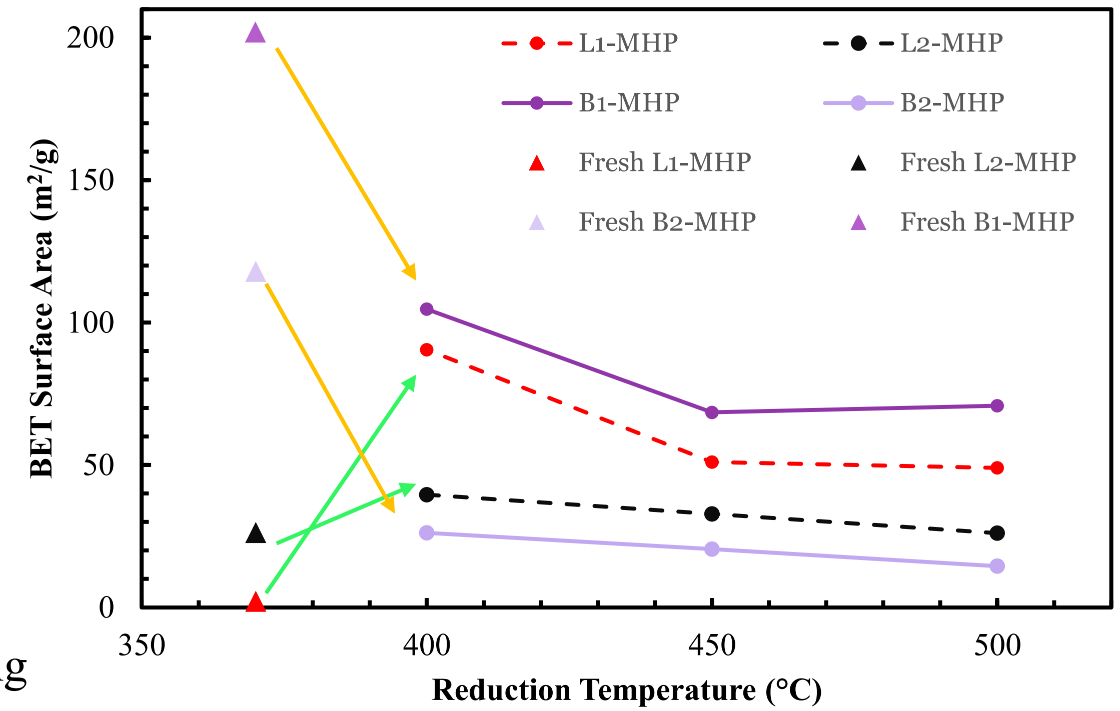
✓ Laterite MHPs show an increase in surface area due to oxygen removal and opening of pores

✓ L1-MHP increases more than L2-MHP.

✓ B-MHPs show a decrease in surface area, suggesting early sintering

- **At higher temperatures reduction (450 and 500 °C):**

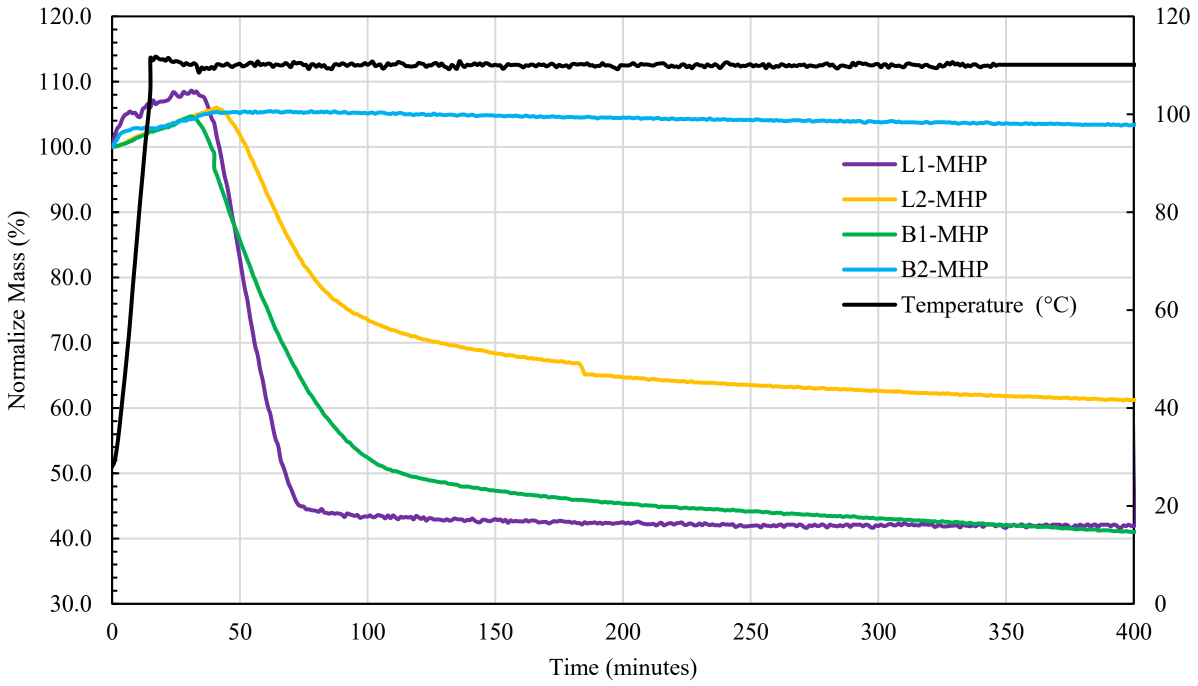
✓ Surface area decreases for all samples caused by sintering.



Results

MHP Carbonylation

- **B1-MHP** and **L1-MHP** show the largest mass loss, indicating high nickel extraction
- **B2-MHP** shows almost no mass loss, meaning very limited carbonylation
- **L2-MHP** shows moderate behavior, with mass loss slowing and stabilizing after about 200 minutes



Mass change of MHPs during carbonylation step. Reduction condition: 450°C and atmospheric pressure. Carbonylation condition: 110°C and 3.1 MPa.

Nickel extraction efficiency of samples.

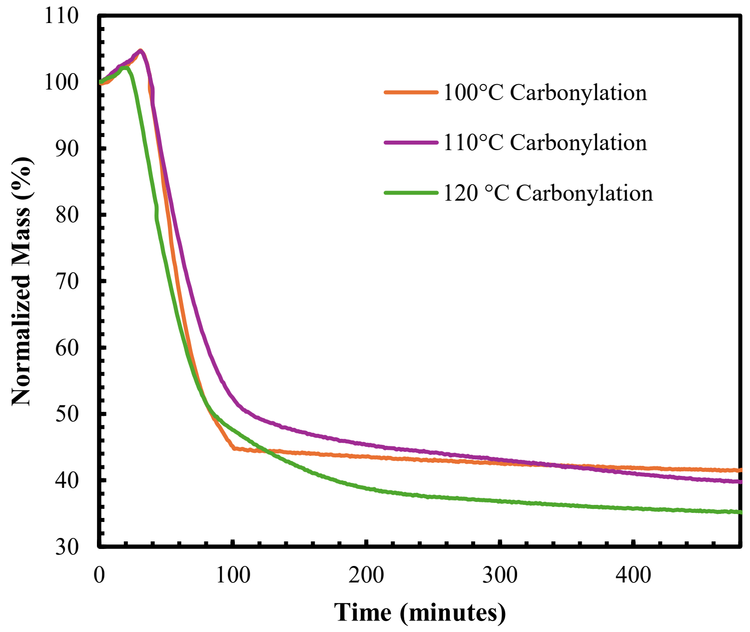
Sample	Ni Extraction efficiency from ICP results (±5%)
L1-MHP	83
L2-MHP	78
B1-MHP	95
B2-MHP	15

Results

MHP Carbonylation: Effect of Carbonylation Temperature on Ni Extraction

Initial Adsorption:

- 100°C & 110°C: Initial CO adsorption phase (mass increase) lasts for 45 min, similar kinetics until 60 min
- 120°C: No initial mass increase; curve shifted earlier, indicating faster CO adsorption and initiation



Normalized mass for carbonylation at conditions of 3.1 MPa and different temperatures for B1-MHP (reduced at 450°C).

B1-MHP Processing Conditions	Ni Extraction from ICP (%)
Reduction at 450°C, Carbonylation at 100°C, 3.1 MPa	96
Reduction at 450°C, Carbonylation at 110°C, 3.1 MPa	95
Reduction at 450°C, Carbonylation at 120°C, 3.1 MPa	93

Results

MHP Carbonylation: Effect of Carbonylation Pressure on Ni Extraction

Large PCO affect on Ni extraction (ICP):

- L2-MHP: 57 → 78%, B1-MHP: 78 → 95%

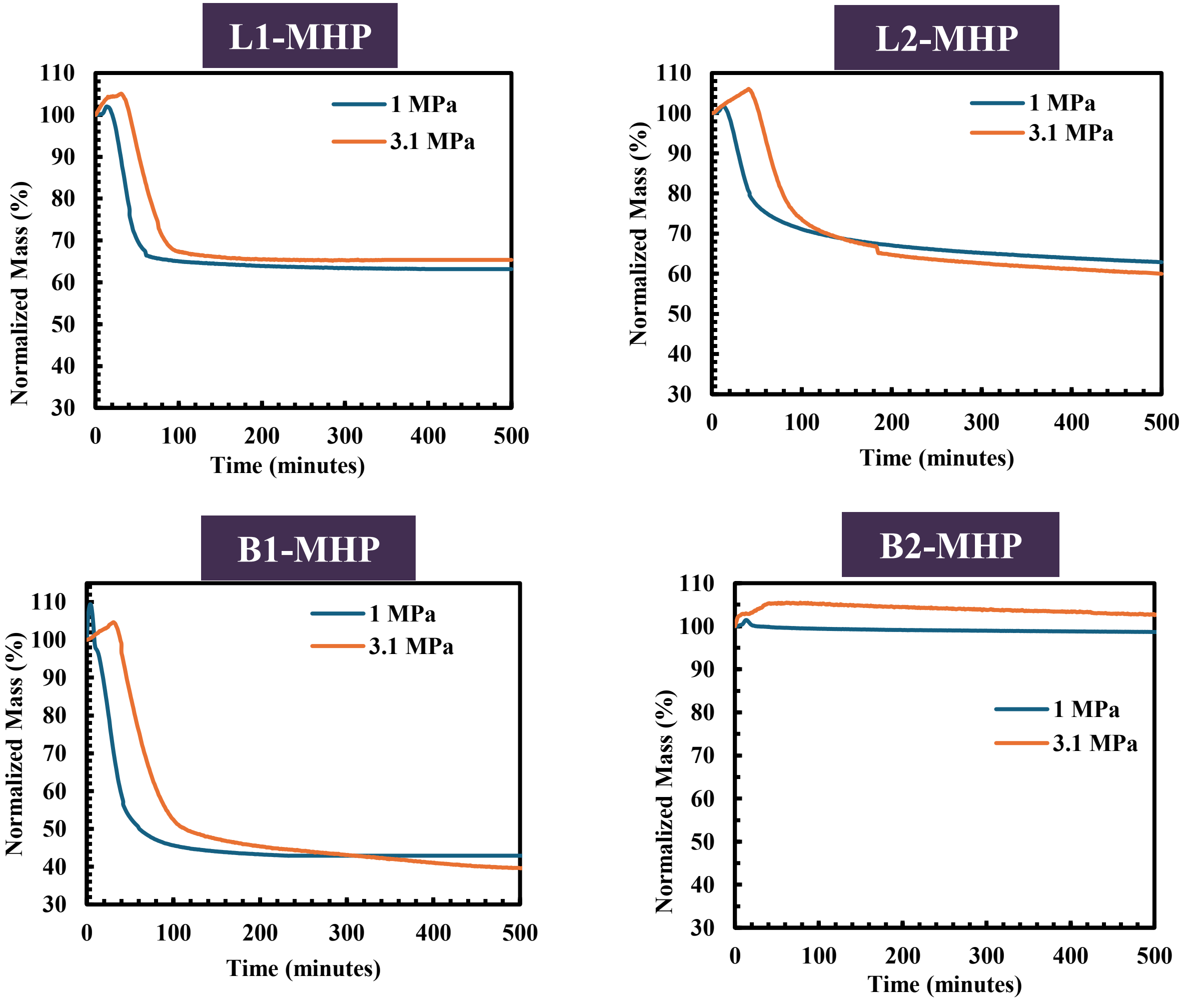
Minimal PCO affect on Ni extraction (ICP):

- L1-MHP and B2-MHP showed negligible improvement.

Structural Influence:

- B1-MHP: Surface area >2× B2-MHP, enhancing CO accessibility.

sample	CO Pressure (MPa)	extraction efficiency from ICP (±5%)	
		Nickel	Cobalt
L1-MHP	1	77	~ 0
	3.1	80	4
L2-MHP	1	57	4
	3.1	78	5
B1-MHP	1	78	~ 0
	3.1	95	9
B2-MHP	1	13	3
	3.1	16	4



Normalized mass for carbonylation at conditions of 1MPa and 3.1 MPa, 110°C (samples reduced at 450°C).

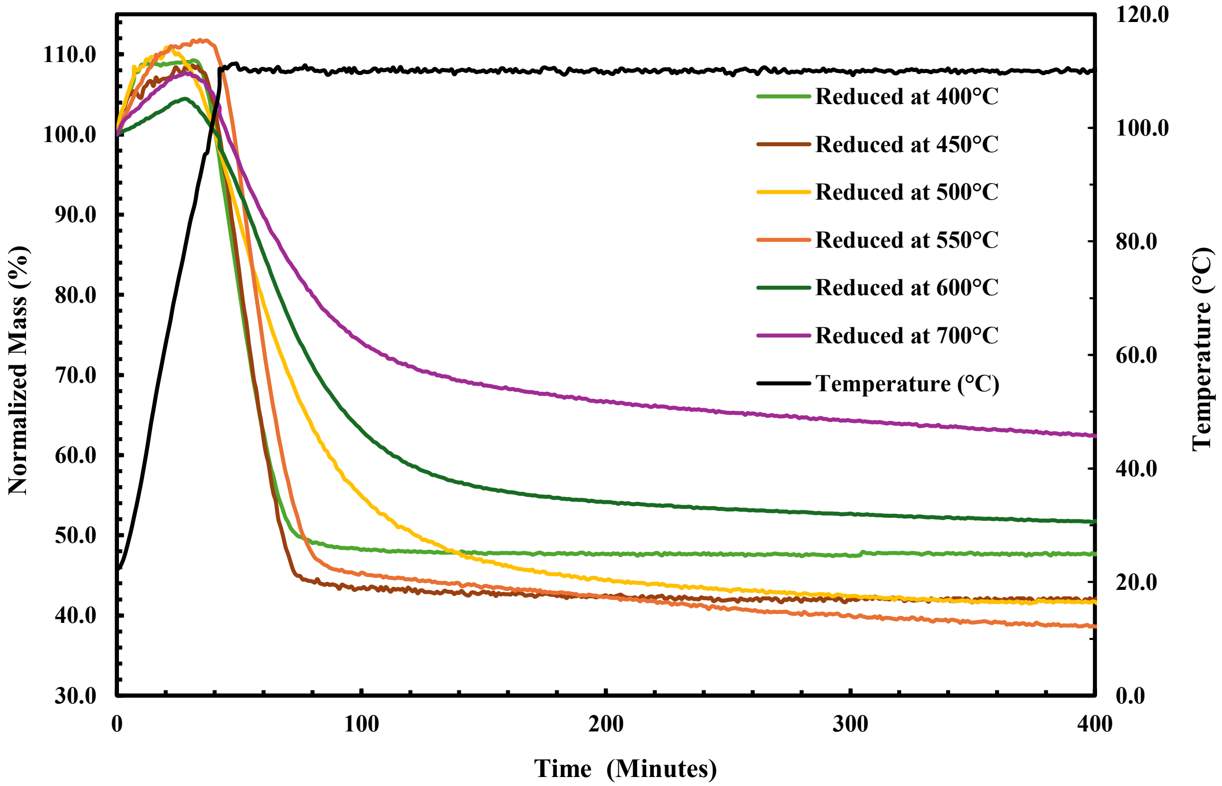
Results

MHP Carbonylation: Effect of Reduction Temperature on Ni Extraction

- ✓ **L1-MHP** shows an optimal reduction temperature
  - Nickel extraction increases up to 550 °C
  - Extraction decreases above 550 °C as samples start to sinter

Sample	Temperature of reduction step (°C)	Ni Extraction efficiency from ICP results (±5%)
L1-MHP	400	78
	450	83
	500	88
	550	94
	600	92
	700	58

L1-MHP

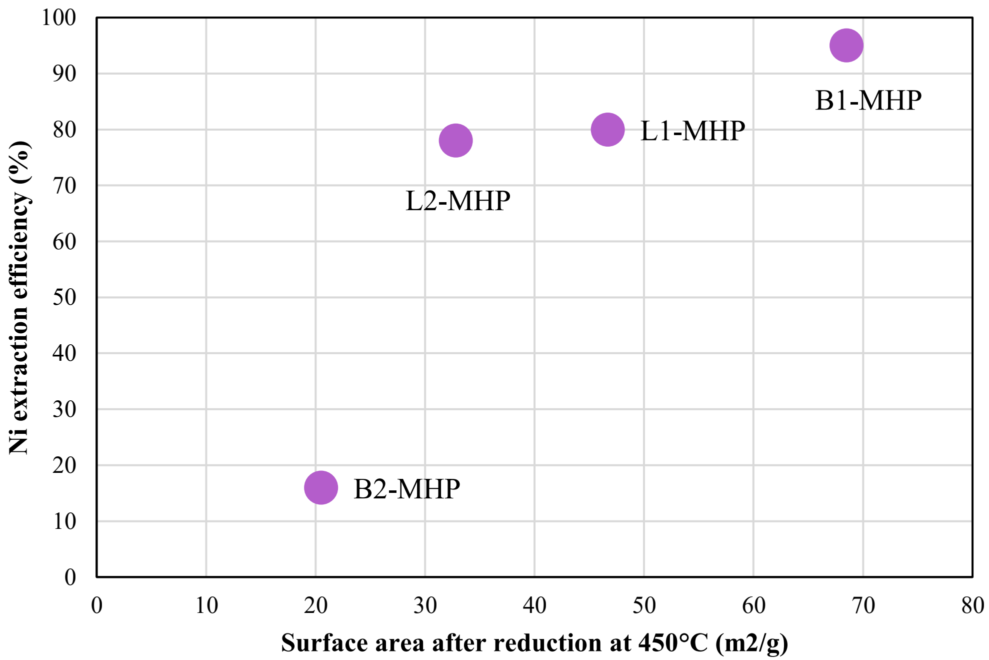


Normalized mass for Effect of MHP reduction temperature on nickel carbonylation at 3.1 MPa

Results

BET surface area after reduction vs. Ni extraction efficiency according to ICP results

- The results indicate that higher post-reduction surface area facilitates nickel carbonylation, leading to improved nickel extraction efficiency



Ni extraction (%) at carbonylation conditions of 3.1 MPa, 110°C (reduced at 450°C) against BET surface area after reduction.

Summary

- **Reduction temperature affects the final mass and reduction level of MHP samples.**
- **Surface area depends on reduction temperature and MHP source. At high reduction temperatures can cause sintering and reduce surface area.**
- **Reduction temperature is important for carbonylation because it changes both reduction level and surface area.**
- **Most of the mass loss during carbonylation occurred in the first 100 minutes.**
- **Nickel extraction reached up to about 95%, showing that carbonylation is an effective method for producing high-purity nickel from MHP.**

Thank you for your attention.