PRODUCTION OF BATTERY GRADE NICKEL AND COBALT SULFATE FROM NICKEL LATERITE ORE

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*Presenter

1. Introduction

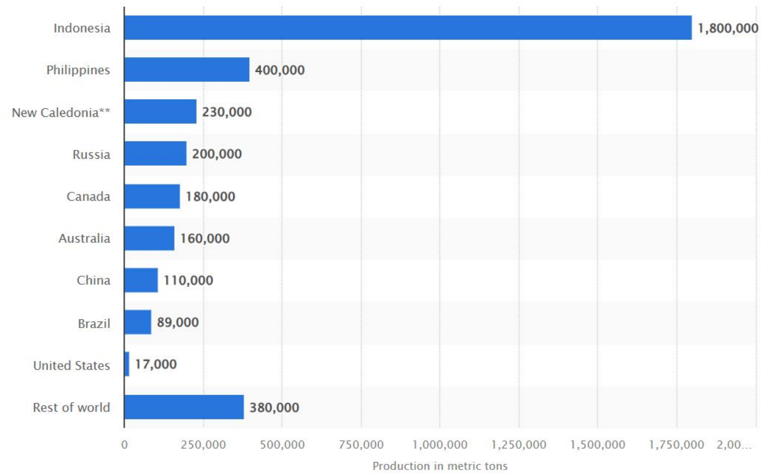
2. Leaching of Nickel Laterite Ores

3. MHP Refining

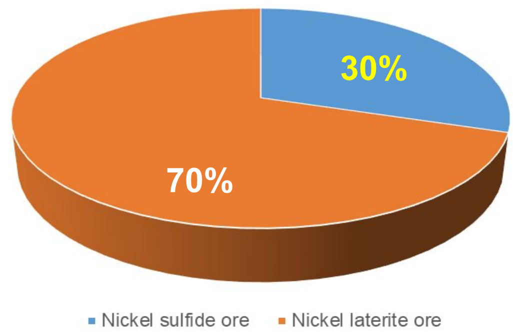
4. Summary

1. Introduction

Nickel mining production in 2023 (metric tons)



Source: USGS



Proportion of ore types in nickel production

- World nickel production: 3.57 Mt in 2023.
- Indonesia nickel production: 1.8 Mt in 2023, accounting for 50.4% of world production.
- Proportion of ore types in nickel production: 30% sulfide ore VS 70% laterite ore.

1. Introduction

◆ Main processes | Nickel laterite ores

Pyrometallurgy

RKEF → ferronickel (Ni>25%)

Blast furnace → pig iron (Ni>5%)

Matte smelting → nickel matte (Ni~70%)

Rotary kiln reduction -- magnetic separation → metallic Ni/Fe powder

Characteristics

- mature and widely used
- high Ni recovery
- high energy consumption
- poor adaptability, suitable for processing high-grade laterite ore
- Co in ferronickel / pig iron devaluated

◆ Main processes — Nickel laterite ores

Hydrometallurgy

High pressure acid leaching (HPAL): a standard technology for limonite laterite ores.

- High nickel extraction (E_{Ni} >95%) ;
- Low acid consumption (iron precipitated as hematite);
- High pressure up to 5.5MPa, high temp. up to 270°C.

Alternative

Atmosphere tank leaching (ATL): LOGIC: Recovery exchanges costs.

Primary leaching: high acid concentration, high Ni and Fe extraction;

Secondary leaching: feed - high magnesium laterite (saprolite), neutralization and iron precipitation with saprolite leaching.

- Low CAPEX and OPEX;
- Lower nickel extraction (E_{Ni} 85~93%) ;
- Higher acid consumption (up to 90% iron precipitated as jarosite or goethite, maybe with lime addition).

◆ Main processes — MHP refining

Pyrometallurgy

Precious nickel matte → refining products

Reduction anode → cathode

Hydrometallurgy

- **Dissolving**
  - **Chemical precipitation process**
    - **Sulfates**
    - **Cathodes**
  - **Solvent extraction process**
    - **Sulfates**
    - **Cathodes**

2. Leaching of Nickel Laterite Ores

◆ Inverse Leaching* Process

(*ALTA 2013 keynote)

2 types of laterite ores

Limonite (high Fe, low Mg)

Saprolite (low Fe, high Mg)

General process

- Limonite ore → HPAL
- Saprolite ore → AL (Neutralization + Leaching)

Inverse leaching process

- Limonite ore → AL (High acid, ~95 °C)
- Saprolite ore → PAL (150~160°C)

2. Leaching of Nickel Laterite Ores

◆ Inverse Leaching Process

BGRIMM's special flowsheet — an inverse leaching process (patented)

Primary leaching: atmosphere tank leaching

- Feed: limonite portion of laterite ores;
- ~95 °C, input: 100% acid, 97~99% E_{Ni} & E_{Fe};

Secondary leaching: autoclave leaching

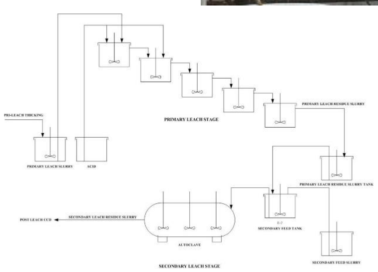
- Feed: saprolite portion of laterite ores;
- Around 150~160°C, no acid input, 500~600kPa;
- Total E_{Ni} 93~96%;
- No acid consumption for 90~95% Fe.

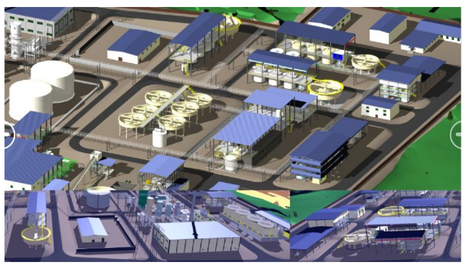
The leaching combination changes the BIG DIFFICULTY of HPAL to "a common routine process"!

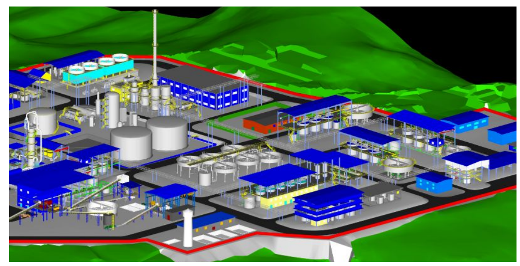
2. Leaching of Nickel Laterite Ores

◆ Inverse Leaching Process

Pilot plant photos







2. Leaching of Nickel Laterite Ores

◆ Inverse Leaching Process

Leaching performance of IL process

	Primary Leach Results			Secondary Leach Results		
	Ni	Fe	Mg	Ni	Fe	Mg
Residue Solids Grade (%)	0.05	8.38	1.32	0.15	21.11	1.57
PLS Concentration (g/L)	5.08	56.70	40.11	5.29	3.40	49.41
Solids-based Metal Extraction (%)	98.40	80.63	94.56	93.44	19.94	92.65
Residue Free Acid (g/L)	18.85	(H_2SO_4)		15.39	(H_2SO_4)	
% Mass Remaining (%)	48.10			64.37		

◆ Two-stage Pressure Leaching Process

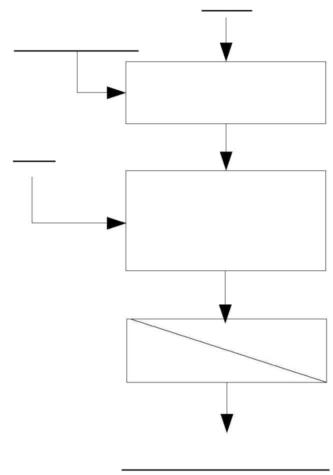
HPAL — AL process used in Indonesia

◆ **Limonite ore → HPAL**

- Ni and Co extraction > 95%
- Fe precipitation → acid release

◆ **Saprolite ore → AL**

- HPAL leached slurry is neutralized by SAP to reduce acid consumption
- Ni extraction : 40~60% (low)



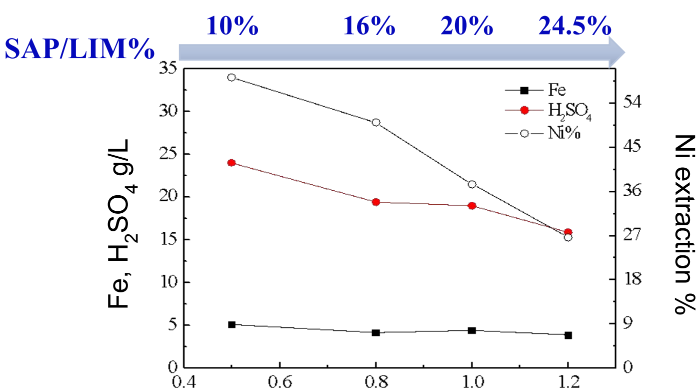
HPAL — AL process

◆ Two-stage Pressure Leaching Process

HPAL — AL process used in Indonesia

◆ **Disadvantages**

- Ni extraction in AL : 50%.
- More Fe is leached when Ni extraction reaches 65~70% with acid introduction.



C_{Fe} comparison of HAPL and AL PLS with different SAP additions (AL remaining acid 10g/L)

SAP/LIM%	Fe, g/L	
	HPAL solution	AL solution
8	2.8	4.2
20	1.6	6.2

2. Leaching of Nickel Laterite Ores

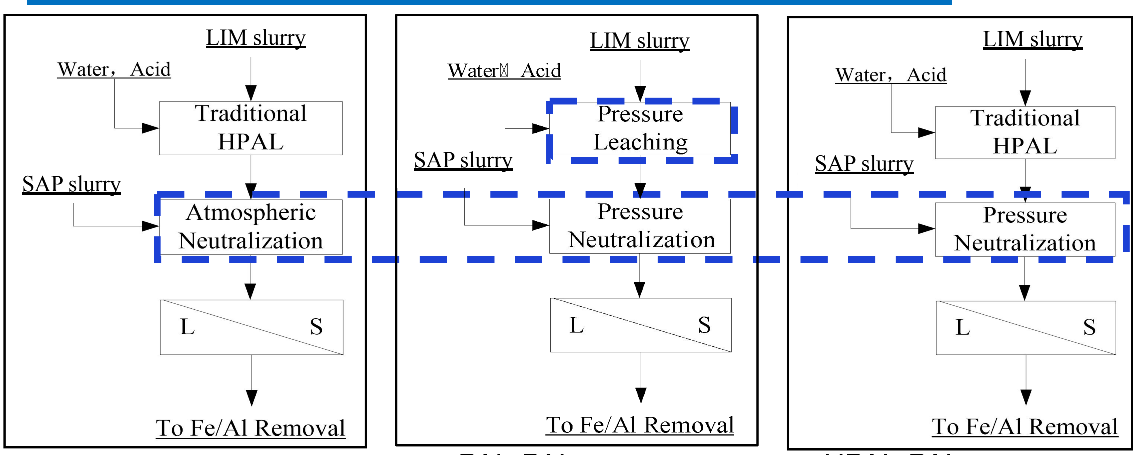
◆ Two-stage Pressure Leaching Process

In order to improve the inverse leaching process and HPAL – AL process, BGRIMM proposed the combinations of two-stage leaching:

- AL – PAL (95 ℃ / 150~225 ℃, 0.5~2.5 MPa)
- PAL – PAL (150~225 ℃, 0.5~2.5 MPa)
- HPAL – PAL (240~270 ℃, 3.3~5.5 MPa / 150~225 ℃, 0.5~2.5 MPa)

2. Leaching of Nickel Laterite Ores

◆ Two-stage Pressure Leaching Process



HPAL-AL process　PAL-PAL process　HPAL-PAL process

Patented

Two-stage pressure leaching process (PAL-PAL, HPAL-PAL)

- LIM → HPAL
- SAP → PAL: HPAL slurry flows to 2nd autoclave without flashing. SAP slurry is leached by using the heat and remaining acid of HPAL slurry.

2. Leaching of Nickel Laterite Ores

◆ Comparison of 3 leaching combinations

Leaching conditions:

- HPAL(250℃) –AL(95℃)
- HPAL(250℃) – PAL (230℃)
- PAL(225℃) -PAL(200℃)

2. Leaching of Nickel Laterite Ores

◆ Comparison 1:

HPAL(250℃) — AL(95℃)

- HPAL: Ni extraction >97%. AL: Ni extraction 47-56%
- Total Ni extraction ~85%.

LIM/SAP		100:25		100:30		100:35	
Leaching stage		HPAL	AL	HPAL	AL	HPAL	AL
Total extraction /%	Ni	96.91	86.80	97.58	85.93	97.58	82.63
Extraction in this stage/%	Ni	96.91	56.06	97.58	55.55	97.58	47.01

2. Leaching of Nickel Laterite Ores

◆ Comparison 2:

HPAL(250℃) — PAL (230℃)

- HPAL: Ni extraction >97%. PAL: Ni extraction 80-87.3%.
- Total Ni extraction 92-94%.

LIM/SAP		100:25		100:30		100:35	
Leaching stage		HPAL	PAL	HPAL	PAL	HPAL	PAL
Total extraction /%	Ni	97.73	94.10	97.91	93.45	96.74	92.15
Extraction in this stage/%	Ni	97.73	87.34	97.91	83.84	96.74	80.18

ZiJin

2. Leaching of Nickel Laterite Ores

◆ Comparison 3:

PAL(225℃) — PAL(200℃)

- PAL: Ni extraction >97%. PAL: Ni extraction 73-78.6%.
- Total Ni extraction 87.6-90.6%.

LIM/SAP		100:25		100:30		100:35	
Leaching stage		1	2	1	2	1	2
Total extraction /%	Ni	96.11	90.57	96.91	89.47	93.25	87.64
Extraction in this stage/%	Ni	96.11	78.63	96.91	75.64	93.25	73.00

2. Leaching of Nickel Laterite Ores

◆ Comparison of 3 leaching combinations

- Use heat and remaining acid of HPAL slurry, Ni extraction greatly improved.

  SAP E_{Ni} 56% (AL)→87% (PAL); Total E_{Ni} 86% (AL)→94% (PAL)
- Under pressure condition and longer retention, more Fe/Al precipitate:

  C_{Fe} 1~2g/L (AL) → 0.75g/L (PAL); C_{Al} 6.5g/L (AL)→0.6g/L (PAL)

  Less limestone consumption and less Ni/Co losses in Fe/Al removal

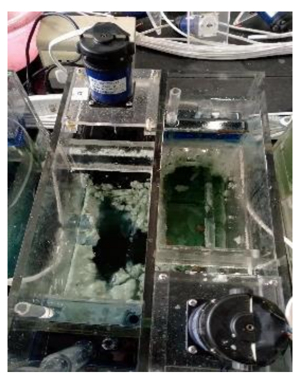
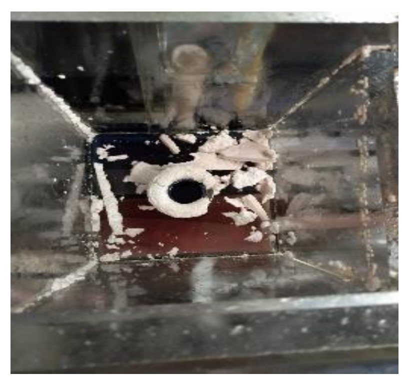
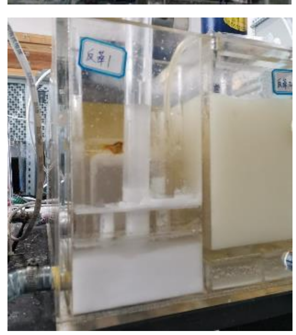
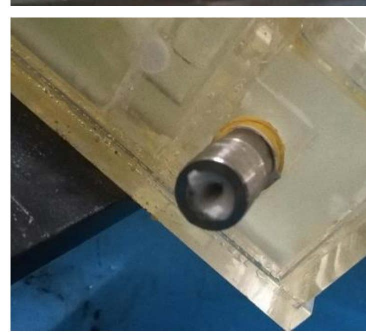
Leaching stage		HPAL-AL	HPAL-PAL	PAL-PAL
Solution/(g/L)	Fe	1.18	0.68	0.75
	Al	6.53	0.63	1.44
Total extraction /%	Ni	**86.80**	**94.10**	**90.57**
SAP — Extraction/%	Ni	**56.06**	**87.34**	**78.63**

*LIM / SAP = 100 : 25

3. MHP Refining

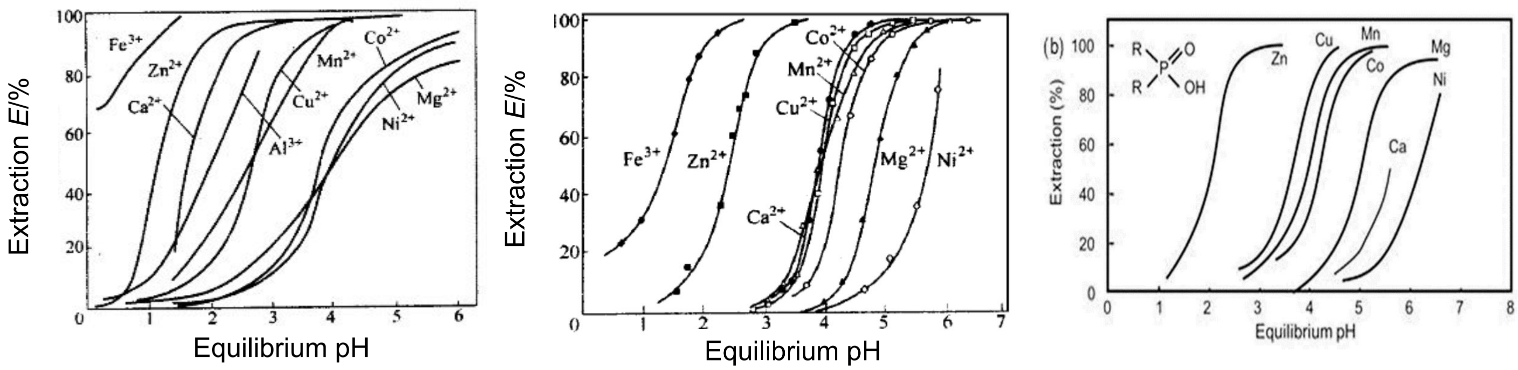
Disadvantages of current MHP Refining Process

- **Large amount Fe/Al residue results in large Ni/Co losses**
- **$CaSO_4$ crystals scaling**
  - CaO to remove Fe/Al.
  - Ca^{2+} saturated.
  - $CaSO_4$ crystals during P204 scrubbing and stripping.
  - $CaSO_4$ scaling on the wall of tank, pipes, impellers, etc..
- **Complex SX combination to separate Ni, Co and Mg**
  - Ni, Co and Mg separation with C272 and P507, respectively

3. MHP Refining

SX isotherm



P204 (D2EPHA)

- $Fe^{3+} > Zn^{2+} > Ca^{2+} > Cu^{2+} > Mn^{2+} > Co^{2+} > Mg^{2+} > Ni^{2+}$
- P204: Cu, Zn, Ca, Mn removal

P507 (PC88A)

- $Fe^{3+} > Zn^{2+} > Ca^{2+} \sim Cu^{2+} \sim Mn^{2+} > Co^{2+} > Mg^{2+} > Ni^{2+}$
- P507: Ni, Co, Mg separation

C272

- $Fe^{3+} > Zn^{2+} > Cu^{2+} > Co^{2+} > Mg^{2+} > Ca^{2+} > Ni^{2+}$
- C272: Ni / Co separation (high efficiency)

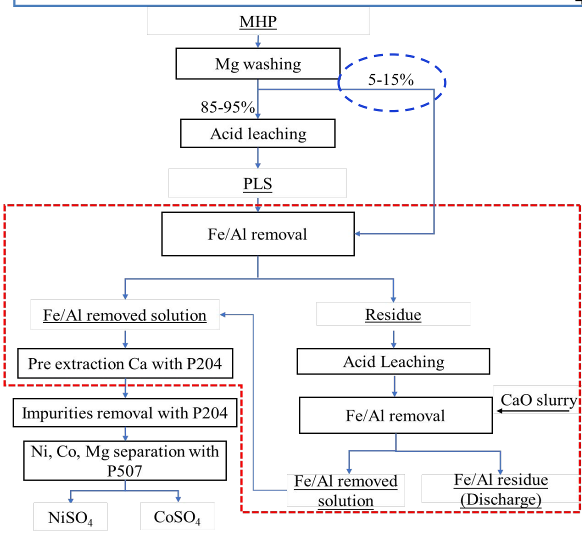
3. MHP Refining

MHP Composition (Ramu)

Element	Ca	Co	Ni	Cr	Cu	Cd	Fe
Content/%	0.15	3.92	40.85	0.0193	0.10	<0.001	0.076
Element	Li	Mg	Mn	Si	Pb	P	Al
Content/%	<0.001	1.46	5.25	0.14	0.18	0.063	0.24
Element	Ag	Hg	Na	Ti	Zn		
Content/%	<0.001	0.12	0.34	0.014	0.73		

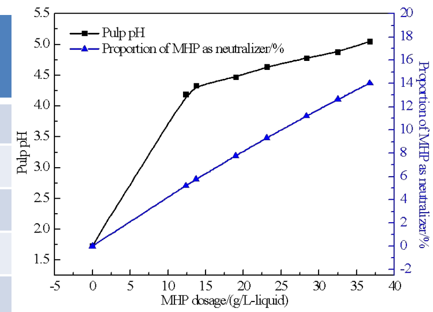
MHP used to remove Fe/Al/Si

- 5~15% MHP is used in neutralization to remove Fe/Al/Si.
- Consume remaining acid.
- 90% CaO consumption is reduced. Thus, the $CaSO_4$ crystallization on scaling is reduced. Meanwhile, Fe/Al residue amount is reduced (less $CaSO_4$), and Ni&Co losses are reduced.



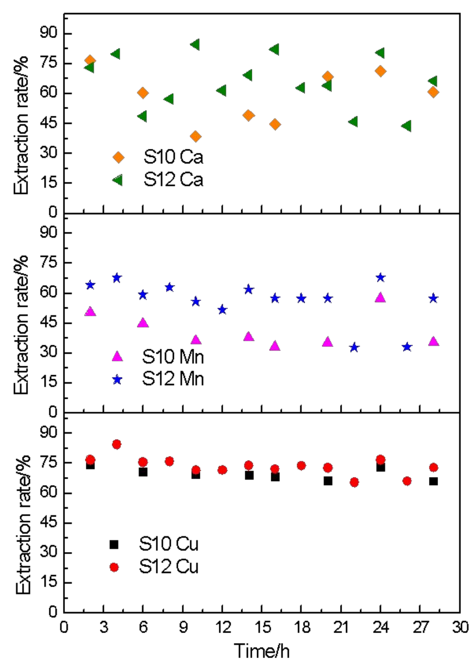
Results

% MHP addition		5.0	11.4	14.7
Final pH		4.19	4.98	5.05
Fe/Al removed solution (g/L)	Fe	<0.001	<0.001	<0.001
	Al	0.099	0.058	0.073
	Cr	0.009	<0.001	0.003
	Si	/	/	0.043



Pre extraction Ca and purification (Cu/Mn/Zn removal) with P204

- Pre extraction Ca with P204.
- 50% Ca is removed.



Ni/Co/Mg separation in one SX train

- 6 stages Na and Ni saponification – 8 stages Ni extraction – 10 stages Mg scrubbing – 4 stages Co stripping – 2 stages acid scrubbing.
- Ni in raffinate. Separate Mg by scrubbing. Co by stripping.

Battery grade products

Product	NiSO4.6H2O	CoSO4.7H2O
Ca	5.00	5.00
Co	5.00	
Ni		5.00
Cl	50.00	50.00
Cr	5.00	5.00
Cr6+	5.00	5.00
Cu	2.00	3.00
Cd	2.00	3.00
Fe	4.00	10.00
K	50.00	50.00
Mg	25.00	25.00
Mn	2.00	3.00
Si	50.00	50.00
Sn	5.00	5.00
Pb	2.00	2.00
Al	30.00	30.00
Mo	10.00	10.00
As	2.00	2.00
Hg	2.00	2.00
Na	50.00	50.00
Zn	2.00	3.00
Minimum Content [w%]		
Ni	22	
Co		20.5

3. MHP Refining

◆ Reduction smelting — crude nickel anode electrolysis

Hydro-process problems:

- SX process: large acid and alkali consumption, large $MgSO_4$ open circuit, large amount of waste water, large amount of hazardous wastes
- Mg removal by fluoride: superfluous F^-; F^- has negative impact on Ni electrolysis

Impurities removal by pyrometallurgy process

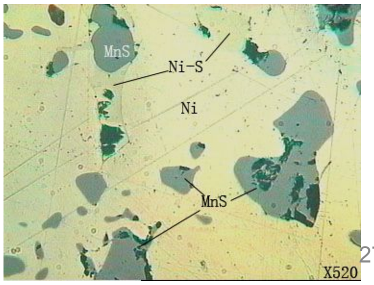
Reduction smelting — crude nickel anode electrolysis — anode liquid purification process

◆ Reduction smelting — crude nickel anode electrolysis

Test No.	Metal					
	Ni	Co	Mn	Fe	Cu	Zn
1	85.5	4.03	4.2	1.08	0.10	0.31
2	83.4	3.87	4.50	2.13	0.012	0.006
3	84.2	3.92	4.35	2.29	0.012	0.15
4	77.0	3.20	6.10	1.97	0.012	0.006
5	82.8	4.05	4.54	1.77	0.011	0.001
6	85.6	4.08	4.38	1.84	0.011	0.010
7	84.4	4.05	4.22	1.92	0.012	0.025

Crude nickel buttons

- Ni/Co/Cu mainly enter to metal. Crude nickel contains 80-85% nickel and 4% cobalt.
- Almost all CaO, MgO, Al_2O_3, and SiO_2 enter into slag.
- 85~97% zinc enters into dust. Zn is removed.
- 20% Mn enters into metal and 80% enters into slag.



◆ Reduction smelting — crude nickel anode electrolysis

Electrolysis test results

Test No.	Anode current efficiency/%	Cathode current efficiency/%
1	95.8	98.2
2	94.7	99.3
3	94.4	98.9
4	94.7	98.7
5	95.0	98.6
6	95.6	98.9

Nickel cathode composition

Element	Ni+Co	C	S	P	Cu	Pb
Standard*	99.96	0.005	0.001	0.001	0.01	0.001
Test	＞99.96	0.0018	0.0004	＜0.0001	0.0015	＜0.0003
Element	Sn	Sb	Bi	Si	Mn	Mg
Standard*	0.0003	0.0003	0.0003	0.002	-	0.001
Test	＜0.0002	0.0002	＜0.0005	＜0.001	0.0001	＜0.001
Element	Zn	Cd	Fe	Al	As	
Standard*	0.0015	0.0003	0.01	-	0.0008	
Test	0.0008	0.0001	0.0021	＜0.001	＜0.0008	

Standard*: GB/T 6516-2010

- GB/T 6516-2010 electrolytic nickel standard
- Grade: Ni9996

4. Summary

- **Inverse leaching (IL) process is very flexible to treat LIM and SAP (Or transitional laterite ore)**
  - Ni extraction ~ 95%, at least 10% higher than ATL.

- **Two-stage pressure leaching (HPAL — PAL) process is very efficient to treat LIM and SAP**
  - Ni extraction increases greatly. SAP E_{Ni} 50% (AL) → 95% (PAL);
  - PLS: C_{Fe} 1~2g/L (AL) → 0.75g/L (PAL); C_{Al} 6.5g/L (AL) → 0.6g/L (PAL);
  - Less limestone consumption and less Ni/Co losses in Fe/Al removal.

4. Summary

- **MHP refining process -- Dissolving and SX-purification -- High pure Ni/Co - sulfates with battery grade**
  - MHP is used in neutralization, to reduce CaO consumption, thus residues and Ni &Co losses could be reduced;
  - Reduction of $CaSO_4$ crystals during impurities removal with P204 -SX;
  - Ni/Co/Mg separation with P507 in one SX - train;
  - Continous SX purification and separation flow-sheet.

- **Reduction smelting — crude nickel anode electrolysis process**
  - High recovery: Ni >97%, Co > 90%;
  - Easy removal of Ca, Mg, Al, Si, Mn and Zn (into slag / dust);
  - Suitable for low grade MHP (low cost), due to low acid and alkali consumption;
  - Environment friendly (much less wastes).

Thank you!

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