MATTE SMELTING AND PURIFICATION PROCESS FOR RECYCLING OF EOL-LIB

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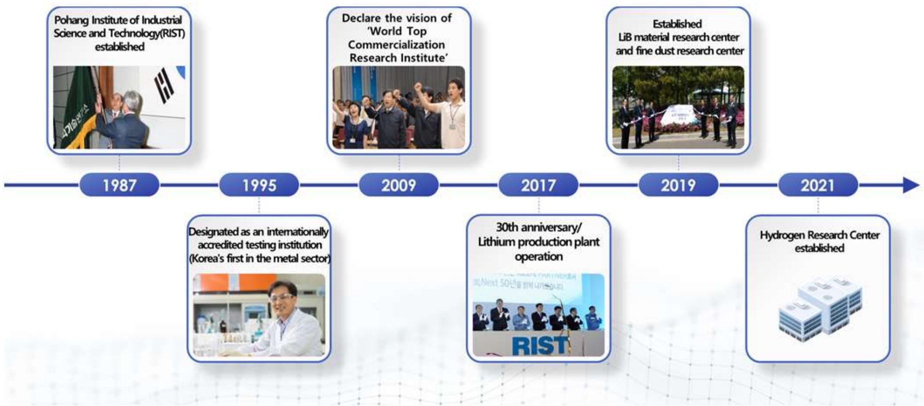
I. Background

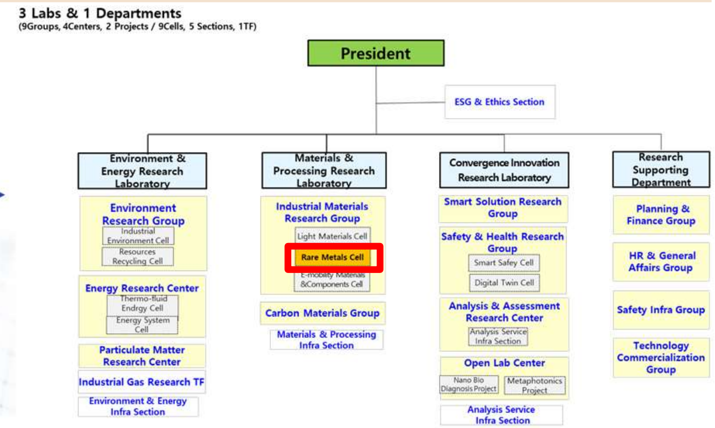
I-(1). RIST Introduction

I-(2). Research Objective

I-(1). Introduction (RIST)

RIST is Korea's first private research institute established in 1987 for the purpose of "Development of national industrial technology and dissemination of achievements".



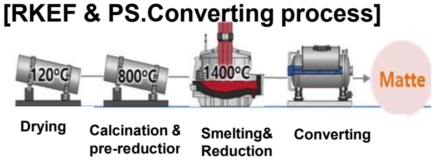


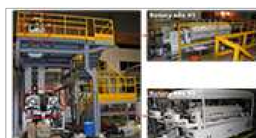
○ Main research contents and facilities

[Nickel extraction process]

[LIB recycling process]

[RKEF & PS.Converting process]





- **Rotary kiln simulator**
  - Specifications
    . indirect heating, temperature Max. 900℃,
    . Capacity Max. 2kg/hr,
    . Hydrogen/nitrogen atmosphere
  - Field of use: raw material drying/sintering/reduction

- **Submerged arc furnace (SAF)**
  - Specifications
    . DC single phase 280kW(70V, 4000A),
    . Capacity Max. 150~200kg
    . Continuous operation
  - Field of use : ferrous alloys reduction smelting

- **Mix-settler for Solvent Extraction**
  - Specifications
    . 20 stages : mixing zone 2L, settling zone 4L
    . Mixed saponification/pH control
  - Field of use: Purification of LiB BP, Matte, MHP/MSP

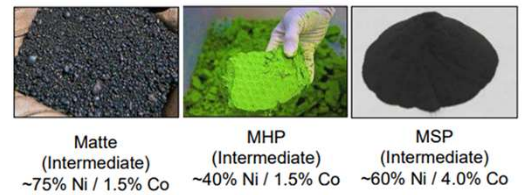
I-(1). Introduction (RIST)

I-(1). Introduction (RIST)

Different smelting processes are required depending on the type of ore.

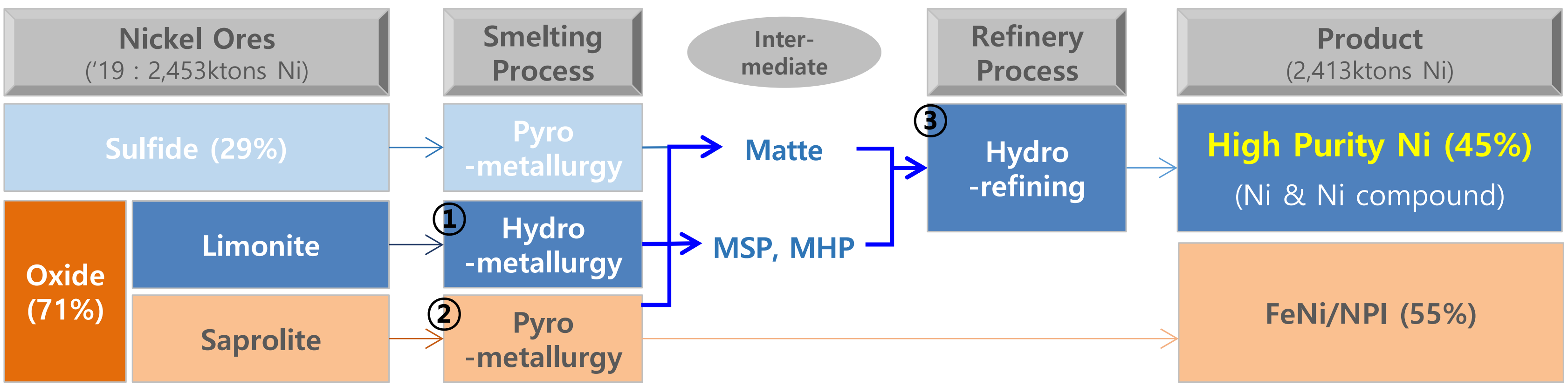
○ **High purity Nickel is manufactured through refinery process from Nickel intermediate**

- Nickel Sulfide : Classical method (smelting+converting) to Matte intermediate
- **Limonite (Oxide)** : Hydrometallurgy to MHP, MSP intermediate
- **Saprolite (Oxide)** : Pyrometallurgy to Matte intermediate
  (RKEF‡ to FeNi, NPI → using in STS) ‡ Rotary Kiln, Electric Furnace



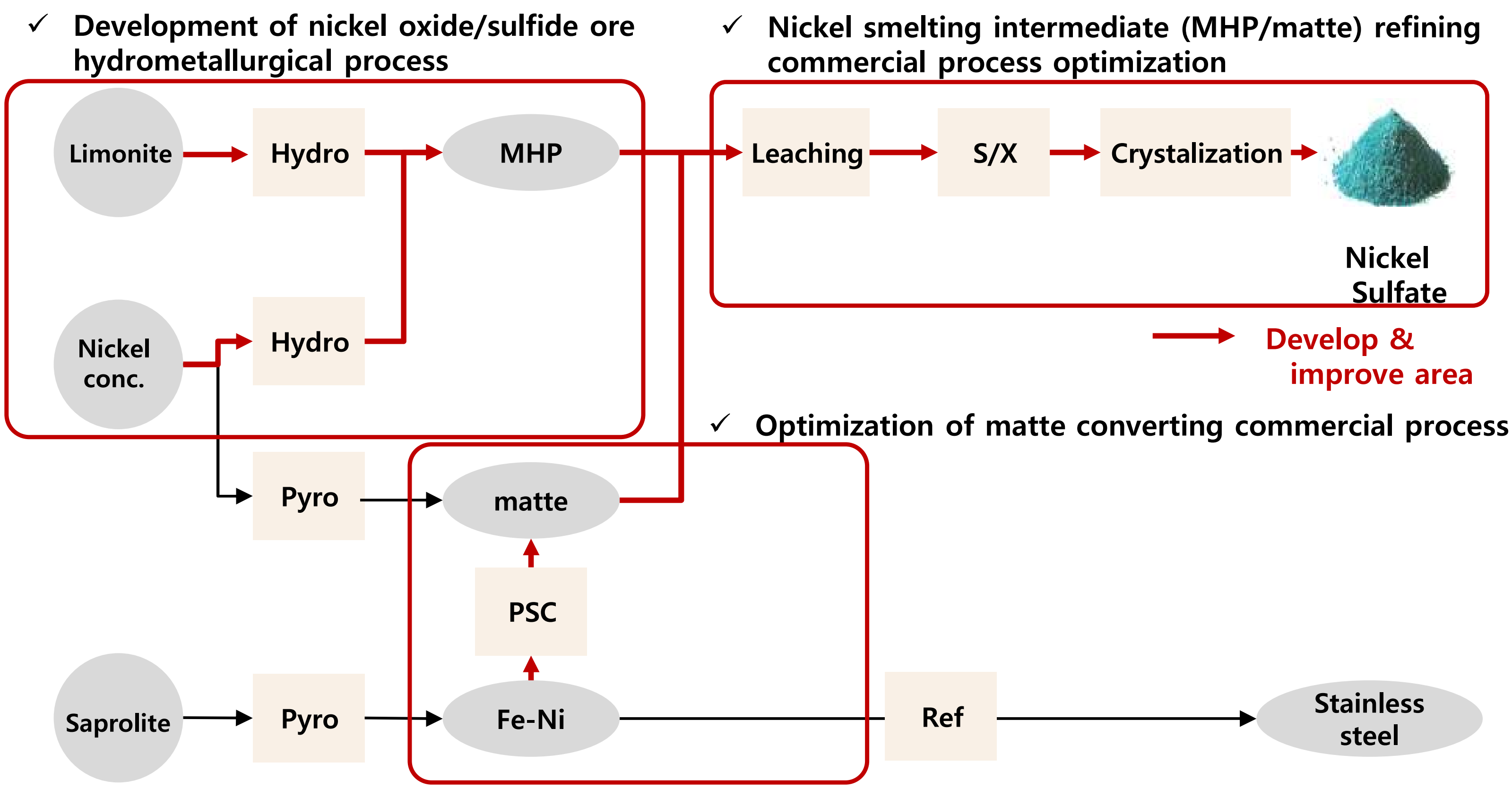
○ **Nickel intermediate**

- **Matte** : High grade Nickel sulfide (Ni_3S_2), Nickel content around 75% (Ni matte : Ni 72%)
- **MHP**(Mixed Hydroxide Precipitate) : Ni, Co mixed hydroxide ($Ni(OH)_2$), Nickel content around 40% (MHP : Ni 42%)
- **MSP**(Mixed Sulfide Precipitate) : Ni, Co mixed sulfide (Ni_3S_2), Nickel content around 60%



I-(1). Introduction (RIST)

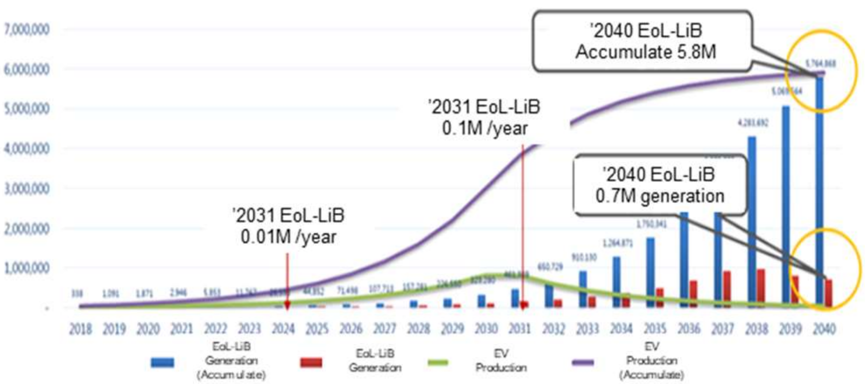
Development of eco-friendly nickel smelting technology and optimization of commercial smelting/refining process



I-(2). Research Objective

■ Current status of low-quality circulating resources

○ **EoL-LiB market outlook :** As demand for lithium ion batteries (LiB) such as EV and ESS increases, the amount of **EoL-LiB generated increases rapidly.**



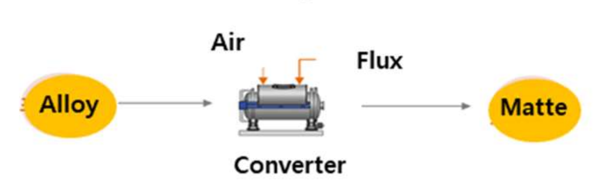
【EoL-LiB Market Outlook】

- As the amount of EoL-LiB is rapidly increasing, the recycling process is also changing from a hydrometallurgy to a pyrometallurgy that can solve **environmental problems and mass production,** or to **a hybrid metallurgy process (pyro & hydro).** (Umicore, Sumitomo, etc.)

■ Development of smelting process for recycled resources

○ **Recovery of rare metals :** Aims to develop an economical and eco-friendly process through high-temperature concentration of rare metals (Ni, Co, etc.) utilizing **collected metals (Fe, FeNi, etc.)**

【Smelting Process】



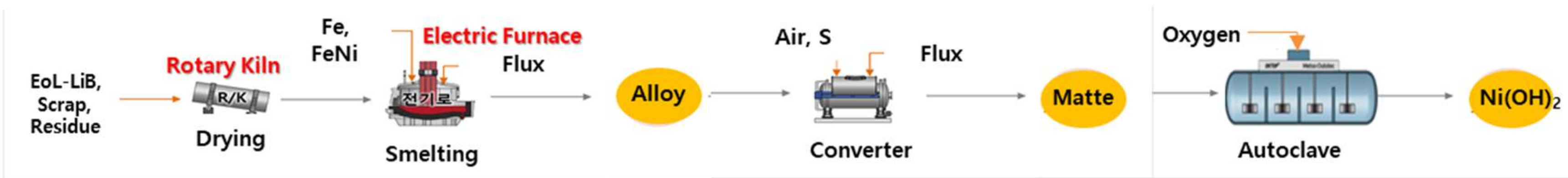
【Converting Process】

- Optimization of process conditions **(temperature, flux additive, captured metal ratio)** is required through thermodynamic review and experiment of smelting-converter-purification process

I-(2). Research Objective

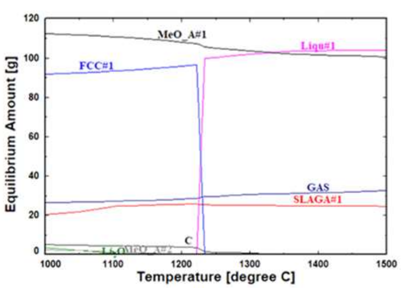
■ **Recycling of EoL-LiB through hybrid metallurgy (Smelting-Converting-Purification)**

○ **Objective :** Technology that collects valuable metals such as Ni and Co from recycled resources in the molten state by using low-cost Fe capture metals and then selectively oxidizes and separates iron using air (oxygen) to concentrate valuable metals.

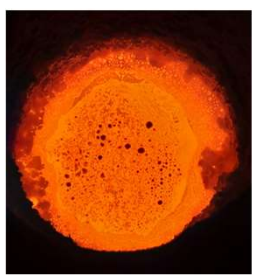


○ **Research** :

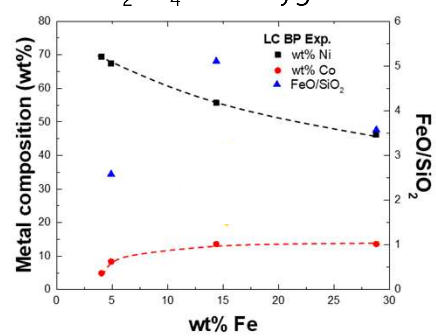
- **Smelting Process :** Recovery of metal using hot metal (Fe, FeNi)
- **Converting Process :** Concentration of metal using Air and sulfur (+ slag recycling)
- **Purification Process :** Purification of metal using autoclave with H_2SO_4 and oxygen



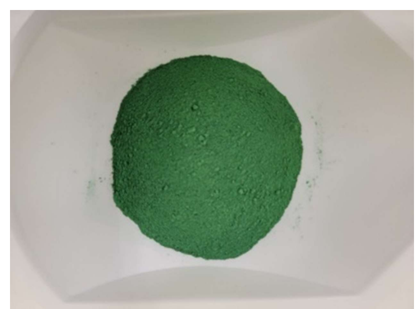
【Thermodynamic Consideration】



【Smelting Process】



【Converting Process】



【Purification Process】

I-(2). Research Objective

■ Recycling of EoL-LiB through hybrid metallurgy (Smelting-Converting-Purification)

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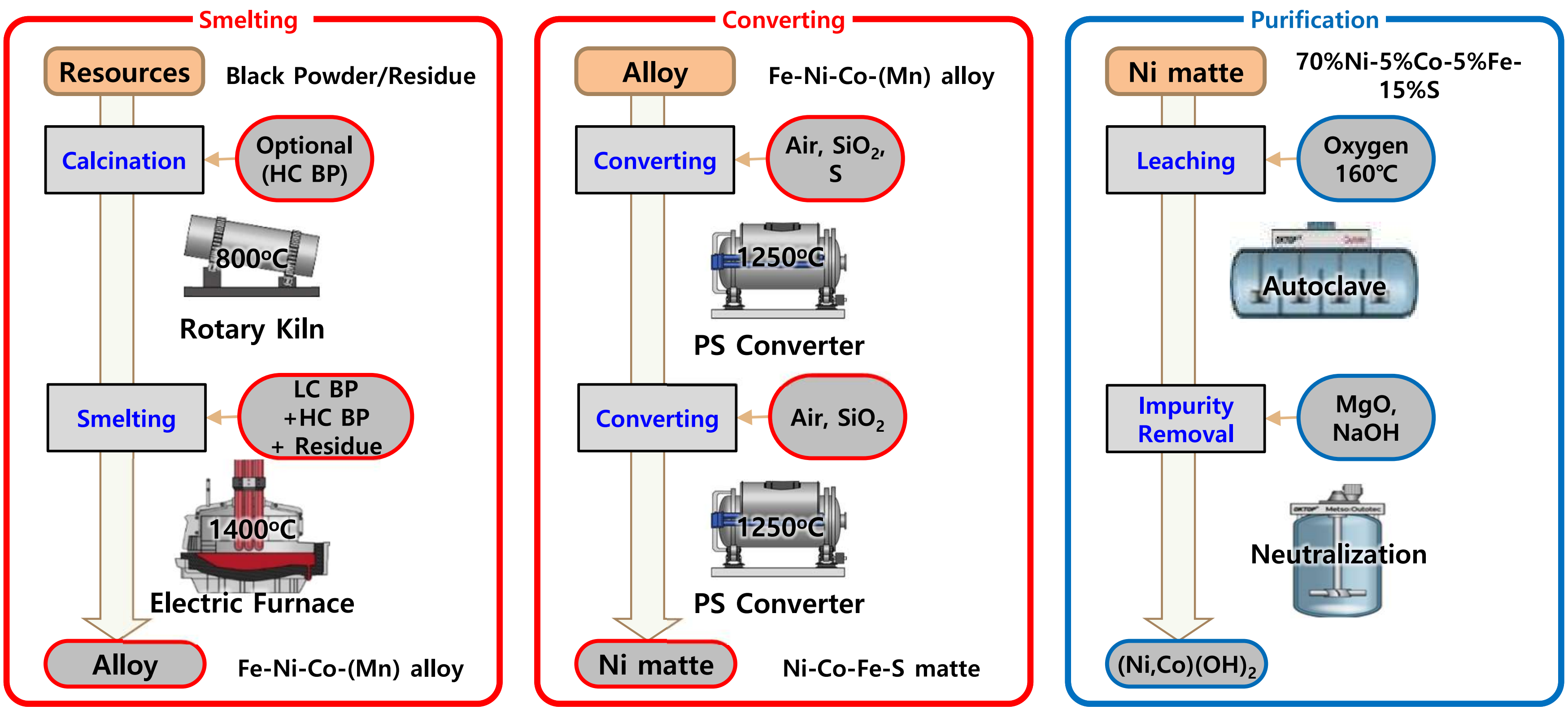


I-(2). Research Objective

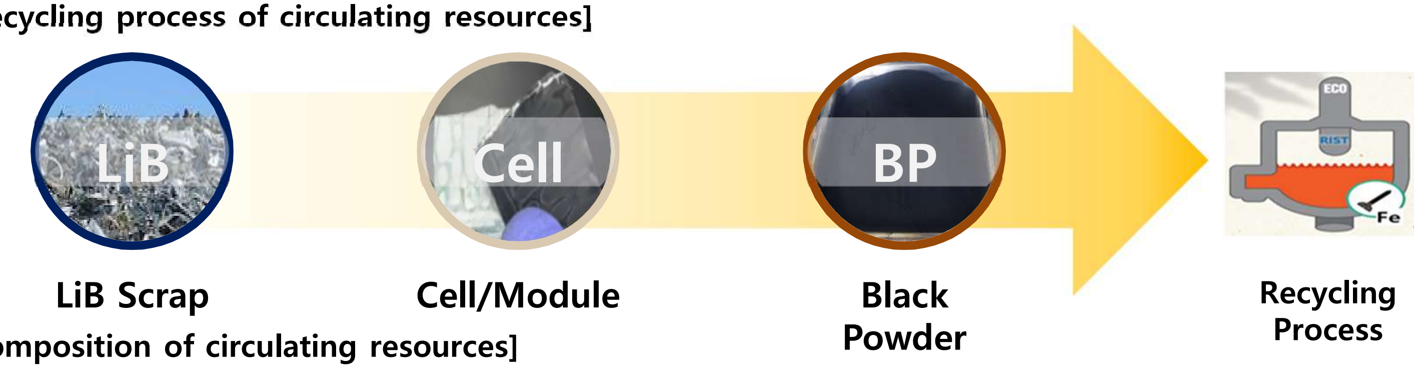
■ **Circulating resources**

① Low Carbon Black Power (LC BP)

② High Carbon Black Power (HC BP)

③ Residue (Petroleum catalyst residue)

[Recycling process of circulating resources]



[Composition of circulating resources]

	Oxide (wt%)						
	Li_2O	NiO	CoO	MnO_2	Al_2O_3	C	sum
LC BP	15wt%	40wt%	10wt%	10wt%	-	2wt%	-
HC BP	10wt%	20wt%	10wt%	10wt%	5wt%	30wt%	-
Residue	-	8wt%	1wt%	-	80wt%	-	-

[Research Method]

① Thermodynamic Calculation (FactSage^{TM}) ② Smelting & Converting process (Pyro-Lab test)

③ Purification process (Hydro-Lab test) ④ Process Simulation (METSIM & HSC chemistry)

II. Research

II-(1). Smelting Process of EoL-LiB

II-(2). Converting Process of EoL-LiB

II-(3). Purification Process of EoL-LiB

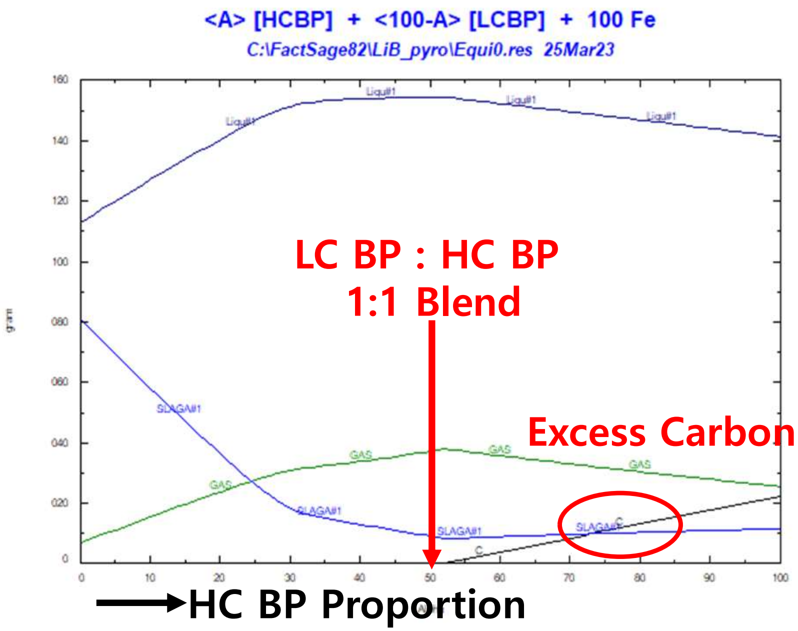
II-(4). Process Design using Simulation

II-(1). Smelting Process of EoL-LiB

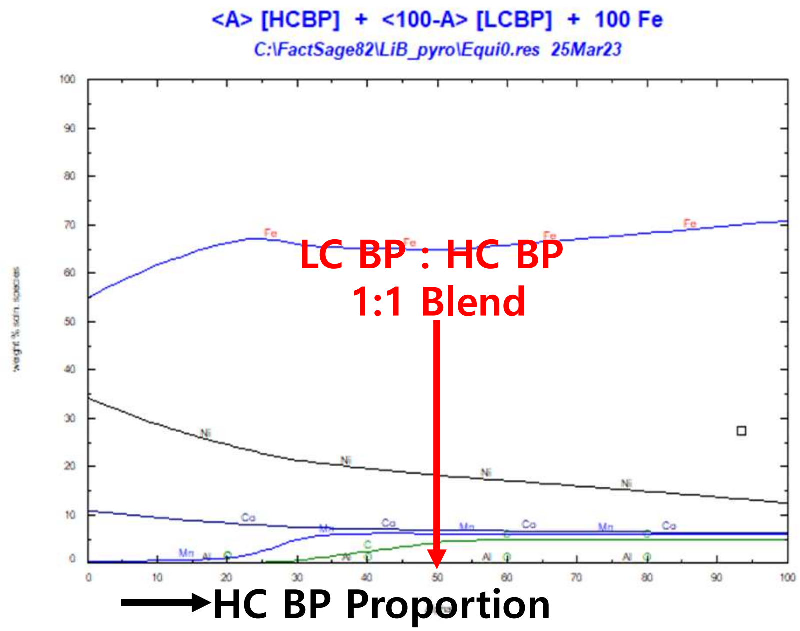
■ **Smelting Process of EoL-LiB**

○ **Thermodynamic Calculation (FactSage™)** : <A>g LC BP & <100-A>g HC BP + **Fe 100g**

- LC BP : HC BP = 1:1 Blending → Recovery of metal (Ni, Co, Mn) in Fe (65%Fe-18%Ni-7%Co-6%Mn-3%C)
- Carbon saturated iron due to the high carbon content in HC BP



【Mixture of Black Powder (LC BP & HC BP)】



【Alloy composition (LC BP & HC BP)】

II-(1). Smelting Process of EoL-LiB

■ Smelting Process of EoL-LiB

○ Experimental Condition

- Input : Fe 2.5kg, LC BP 1.25kg, HC BP 1.25kg, flux SiO_2 250g
- Apparatus : 10kg induction melting furnace
- Temperature : 1500~1600℃
- Procedure : Fe melting → Input LC BP + HC BP + Flux (SiO_2) → ••• → Alloy production

【Furnace】

【Input B.P & flux】

【Smelting of B.P in Fe】

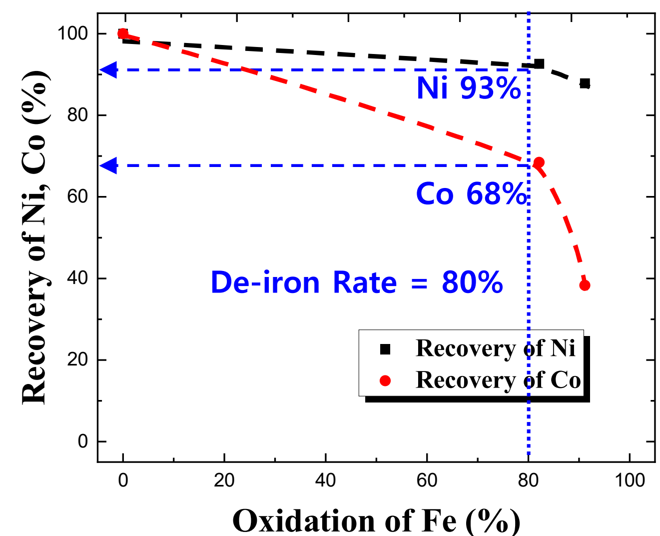
【Alloy production】

II-(2). Converting Process of EoL-LiB

■ Converting Process of EoL-LiB

○ **Experimental Condition**

- **(smelting test) Recovery of metal in B.P blending using Fe hot metal**
  → (Ni+Co)>20% Alloy (Fe-Ni-Co)
  → Li_2O-SiO_2 Slag (100% Li recovery in slag)
- **(smelting test) Recovery of metal in B.P using Fe and FeNi hot metal**
  → (Ni+Co)>70% Alloy (Fe-Ni-Co)
  → Li_2O-FeO-MnO-SiO_2 Slag (100% Li, 100% Mn recovery in slag)
- **(converting test) Removal of Fe and concentration of metal using Air (O_2)**
  → (Ni+Co)> 75% Matte (Ni-Co-S)
  → As decreased the Fe content, the recovery of Co decreases
- **Recovery Rate**
  = (Metal weight in alloy)/[(Metal weight in alloy)+(Metal weight in slag)]

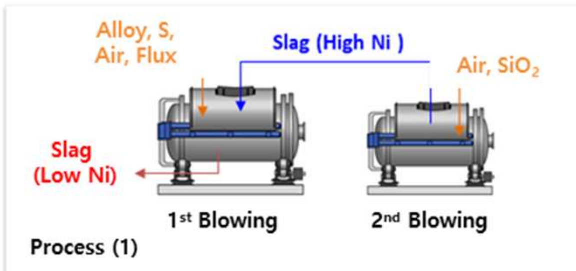


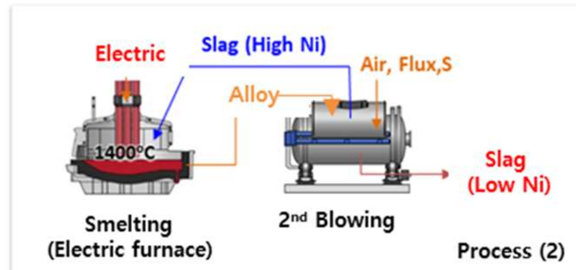
【Concentration of Ni, Co in Converting Process】

Recovery [%]	Ni	Co	(Ni+Co)	Mn	(Li) (slag)	Metal Composition	Slag composition
LC BP & HC BP Smelting	99.7	99.90	**99.76**	93.28	100	66%Fe-16%Ni-7%Co-5%Mn	Li_2O-(FeO-MnO)-SiO_2-(MgO)
LC BP Smelting	97.53	91.20	**96.03**	0.44	78.49	50%Fe-38%Ni-11%Co	Li_2O-FeO-MnO-SiO_2-MgO
LC BP Smelting (FeNi)	97.5	88.44	**95.9**	0.79	100	28%Fe-60%Ni-11%Co	Li_2O-FeO-MnO-SiO_2-(MgO)
LC BP & HC BP Converting	96.73	87.91	**94.32**	-	-	33%Fe-34%Ni-12%Co-S	FeO-SiO_2-MnO-(MgO)
LC BP Converting	89.69	25.92	**76.48**	-	-	5%Fe-68%Ni-5%Co-S	FeO-SiO_2-MgO
LC BP Converting (FeNi)	89.03	41.60	**80.75**	-	-	2%Fe-70%Ni-5%Co-S	FeO-SiO_2-MgO

II-(2). Converting Process of EoL-LiB

■ Converting Process of EoL-LiB





[Final slag (High Ni)]

Slag Composition (wt.%)							FeO/SiO_2 ratio
FeOx	NiO	CoO	MgO	SiO_2	Al_2O_3	S	
41.8	**10.96**	**11.52**	7.69	22.04	2.40	0.19	1.90

① Process (1) : step converting

○ **Experimental condition**

- Sample : FeNi matte(Fe 40%) 2kg+ **Final slag 200g**
- Temperature : 1400℃, 30min, N_2 gas bubbling(3L/min)

[Step converting : Recovery rate]

	Ni	Co	(Ni+Co)
Ni, Co recovery (%)	72.72	96.13	84.72
Total Recovery	96.11	97.44	96.82

② Process (2) : smelting & slag recycling

○ **Experimental condition**

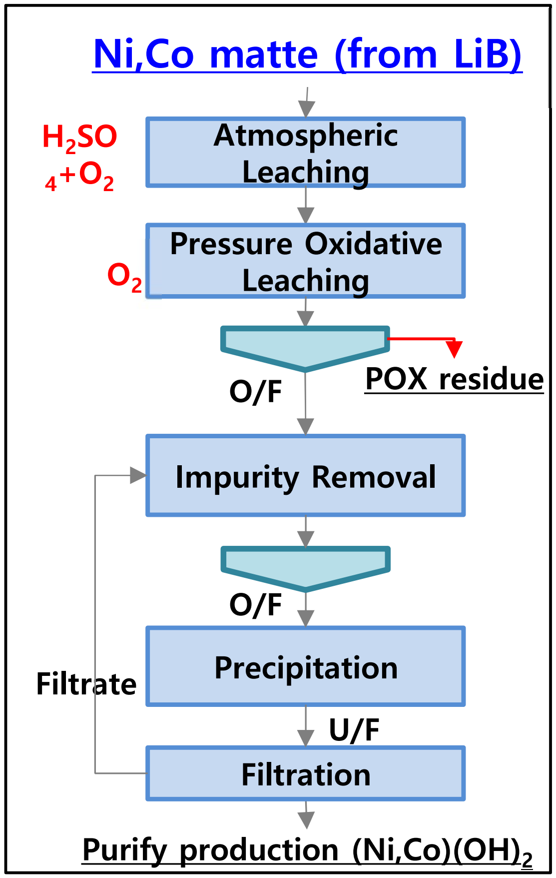
- Sample : Fe 2kg+ **Final slag 200g**
  + LC BP 200g + SiO_2 200g (flux)
- Temperature : 1400℃

[Smelting & slag recycling : Recovery rate]

	Ni	Co	(Ni+Co)
Ni, Co recovery (%)	78.47	80.46	79.49
Total Recovery	98.41	93.84	97.81

II-(3). Purification Process of EoL-LiB

■ Purification Process of EoL-LiB



○ **Leaching Condition (Ni 94%, Co 87% recovery & Si, Fe 99% removal)**

- **POX Leachate (PLS) :** 84g/L Ni – 4.6g/L Co – 0.3g/L Fe
- **POX residue (waste) :** Fe_2O_3-SiO_2-NiS compound (6% Ni-7%Si-41%Fe)

[Leaching Condition]

	Temperature	Atmosphere	H_2SO_4	pH	ORP	Time
Atmospheric Leaching	90℃	Air + O_2	60g/L	0.4→1.3	-200mV	Total 8h
Pressure Oxidative Leaching	160℃	O_2 10~15bar	-	1.3→1.9	500mV	Total 7h

○ **Neutralization Condition (47% Ni-3.2%Co precipitate)**

- **Neutralization solution (Impurity removal) :** 81.5g/L Ni – 4.5g/L Co – 1.4g/L Na
- **Purify production :** $(Ni,Co)(OH)_2$ **(Purity > 99.5%)**

[Neutralization Condition]

	Temperature	Neutralization reagent	Amount of reagent	pH	ORP	Time
Impurity Removal	25℃	1M NaOH	Leachate 1.3%	1.8~5.5	496 →202mV	Total 3h
Precipitation	25℃	1M NaOH	Leachate 126%	5.5~7.7	202 →167mV	Total 3h

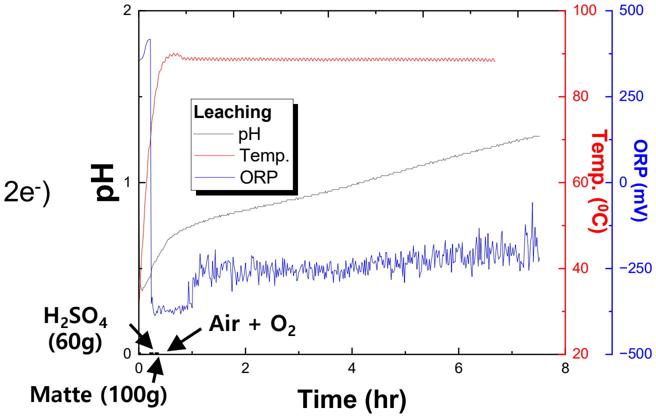
II-(3). Purification Process of EoL-LiB

■ Purification Process of EoL-LiB

○ Leaching test (90℃)

- **pH :** pH 0.5 reached then increased the pH 1.3 due to the leaching reaction
- **ORP** : decreased the ORP at initial reaction (300mV → -370mV) (H_2SO_4)
  increased the ORP at final reaction (-370mV → -200mV) ($Ni^0 = Ni^{2+} + 2e^-$)
- Leaching the metals (Ni, Co, Fe) in matte (from LiB)

[Leaching test (90℃)]

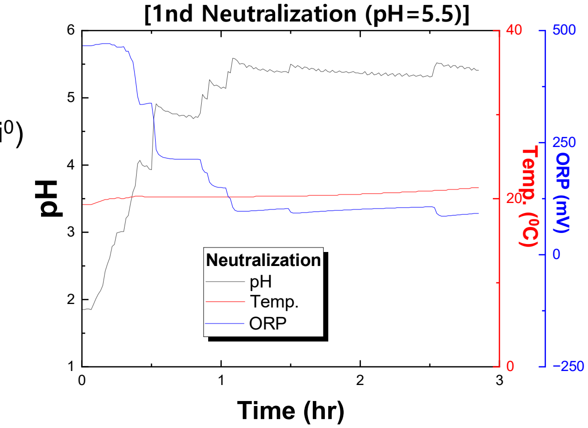


Atmospheric Leaching	pH	H_2SO_4	Sol.//Liq.
Condition	0.5~2.0	60g/L	1:8

○ Neutralization test (25℃)

- **pH :** 1st Neut. (pH 5.5), 2nd Neut. (pH 7.5) <Reagent : NaOH>
- **ORP** : decreased the ORP as the neutralization reaction (~90mV) ($Ni^{2+} + 2e^- = Ni^0$)

[1nd Neutralization (pH=5.5)]



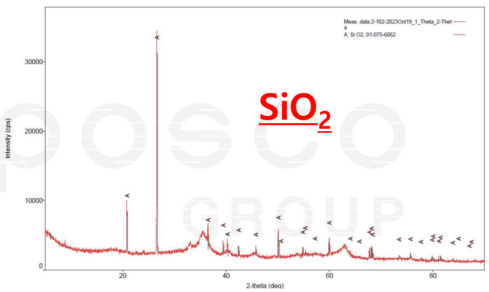
	pH	ORP	1M NaOH	Residue weight
1st Neutralization	5.5	202mV	4.63g	66.77g
2nd Neutralization	7.5	167mV	458.4g	29.76g

II-(3). Purification Process of EoL-LiB

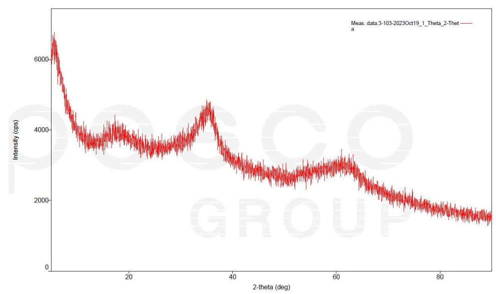
■ Purification Process of EoL-LiB

○ **Precipitation production (Purify = 99.5%)**

6.62%Ni-0.2%Co-41.8%Fe-7.57%Si

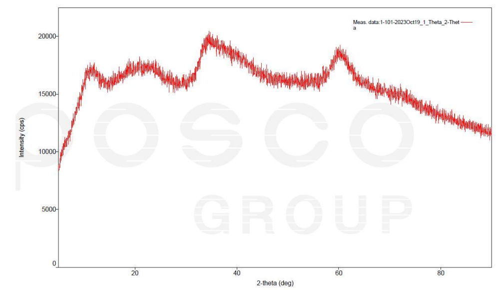


[POX residue]



[1st Neut. residue]

47%Ni-3.3%Co



[2nd Neut. precipitate]

[POX residue]

[2nd Neut. precipitate]

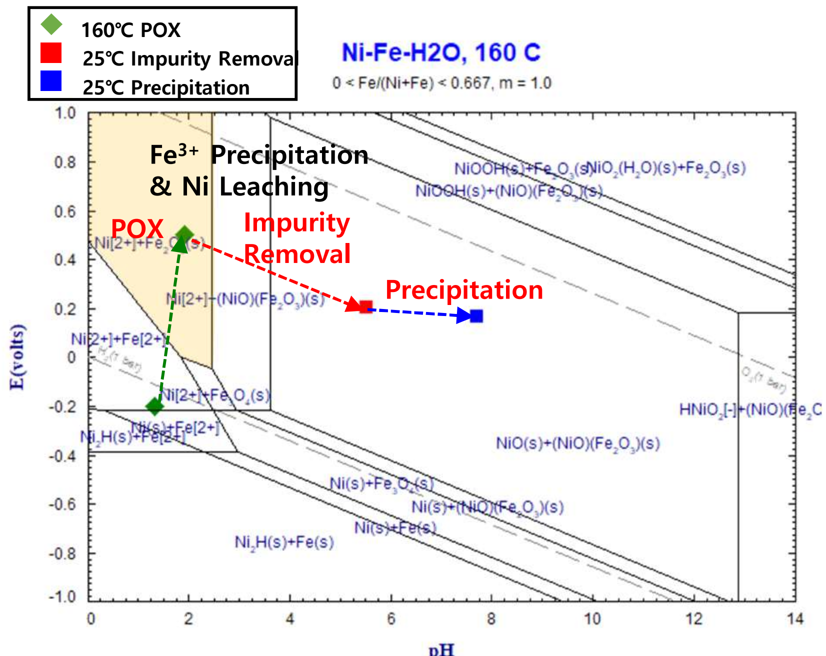
	Composition (wt%)												
	Ni	**Co**	**Mn**	**Al**	**Mg**	**Si**	**Ca**	**Fe**	**Na**	**P**	**Li**	**C**	**S**
Production	47.1	3.23	0.01	0.011	<0.01	0.255	0.016	<0.01	0.039	0.01	0.01	0.065	5.17

II-(3). Purification Process of EoL-LiB

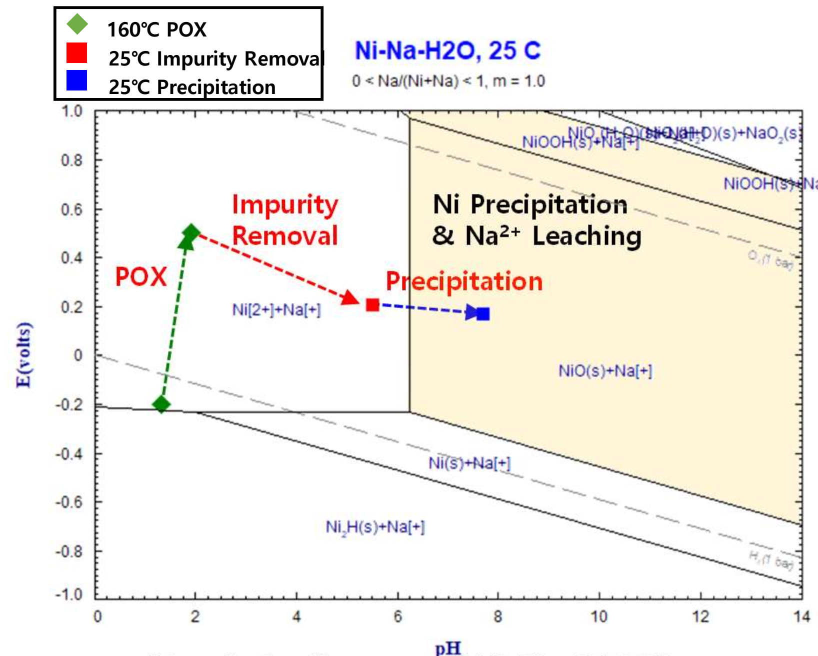
■ Purification Process of EoL-LiB

○ Pourbaix Diagram (E-pH)

- **POX** : pH 1.3~1.9 & ORP 500mV → Fe_2O_3 (hematite) precipitate & Ni Leaching
- **Impurity Removal** : pH 1.9~5.5 Neutralization → Fe^{3+}, Al (pH 2.0), Si (pH 4.5) remove & Ni loss
- **Precipitation** : pH 5.5~7.7 Neutralization → Ni precipitation & Na, Si co-precipitation



[Pourbaix diagram of Ni-Fe (160℃)]



[Pourbaix diagram of Ni-Na (25℃)]

II-(3). Purification Process of EoL-LiB

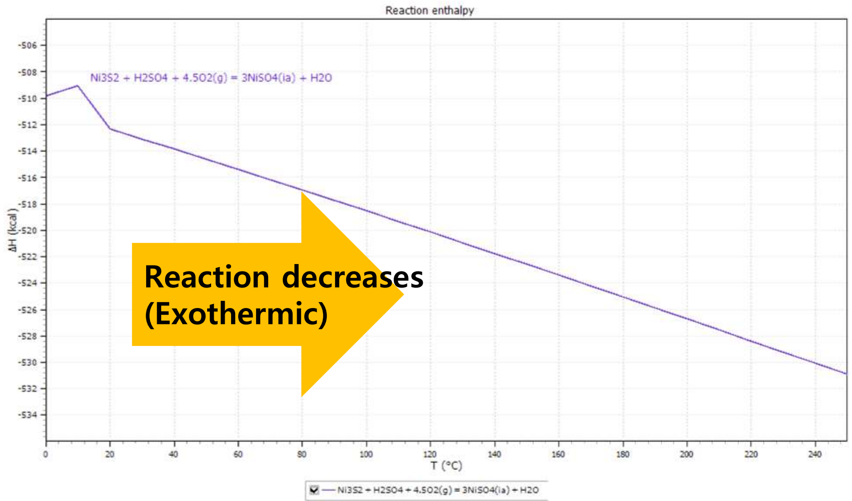
■ Purification Process of EoL-LiB

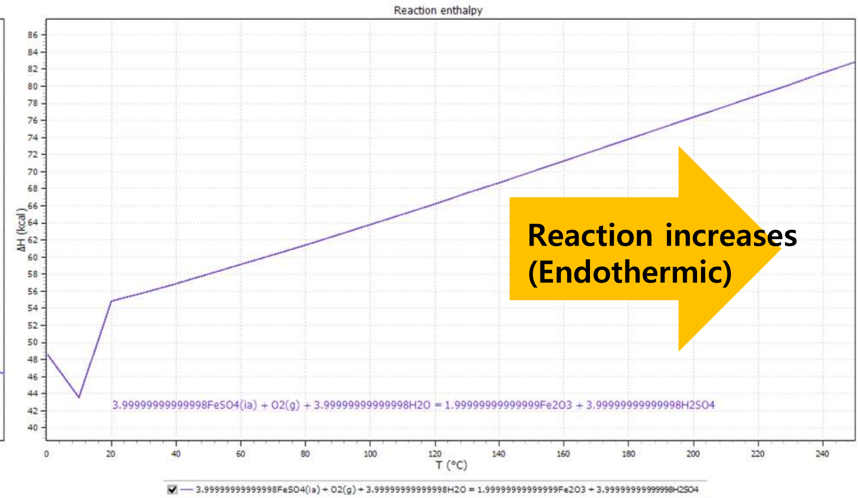
○ Sulfide Leaching Reaction (POX)

: $Ni_3S_2(s) + H_2O + 4.5O_2(g) = 3NiSO_4(aq) + H_2SO_4$

○ Fe Precipitation (HPAL)

: $4FeSO_4(aq) + O_2(g) + 4H_2O = 2Fe_2O_3 + 4H_2SO_4$





Reaction Equation					
Ni3S2 + H2SO4 + 4.5O2(g) = 3NiSO4(ia) + H2O					
Reaction Data					
T °C	ΔH kcal	ΔS cal/K	ΔG kcal	K	Log K
150.000	-522.565	-378.910	-362.229	1.262E+187	187.101

Reaction Equation					
4FeSO4(ia) + O2(g) + 4H2O = 2Fe2O3 + 4H2SO4					
Reaction Data					
T °C	ΔH kcal	ΔS cal/K	ΔG kcal	K	Log K
160.000	71.241	232.051	-29.272	5.898E+014	14.771

II-(4). Process Design using Simulation

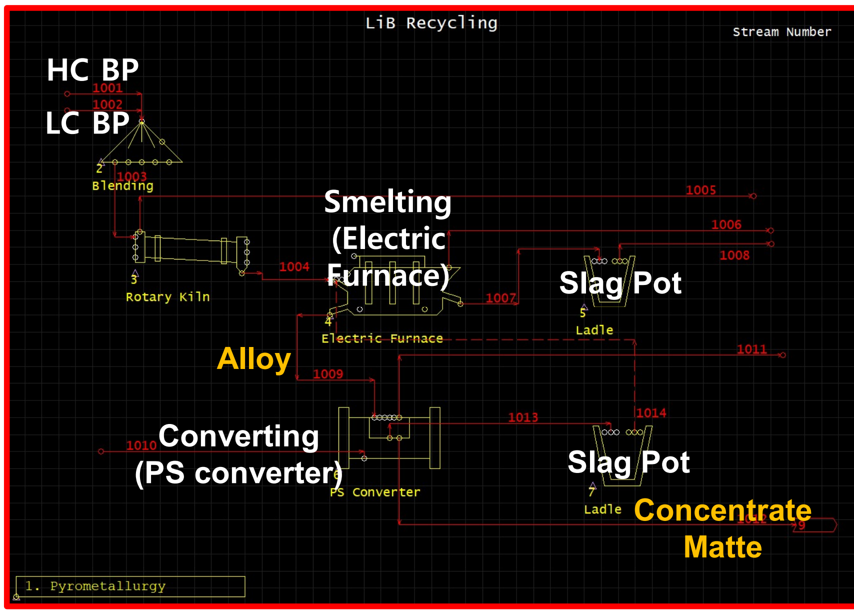
■ Process Design (METSIM)

○ METSIM simulation

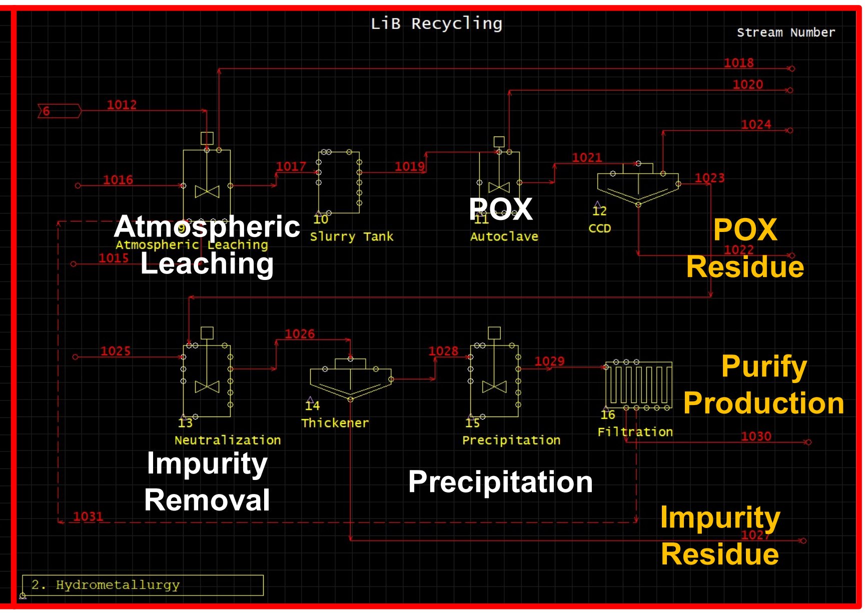
- **Pyro-smelting process** : LC BP & HC BP blending → Calcination (Rotary Kiln) → Smelting (Electric Furnace)
- **Pyro-converting process** : Converting (PS Converter) → Slag recycling (Ladle)
- **Hydro-purification porcess** : Atmospheric Leaching → Pressure Oxidative Leaching → Precipitation ($Ni(OH)_2$)

→ Process simulation based on the experimental database.

[Pyrometallurgy Process]



[Hydrometallurgy Process]



II-(4). Process Design using Simulation

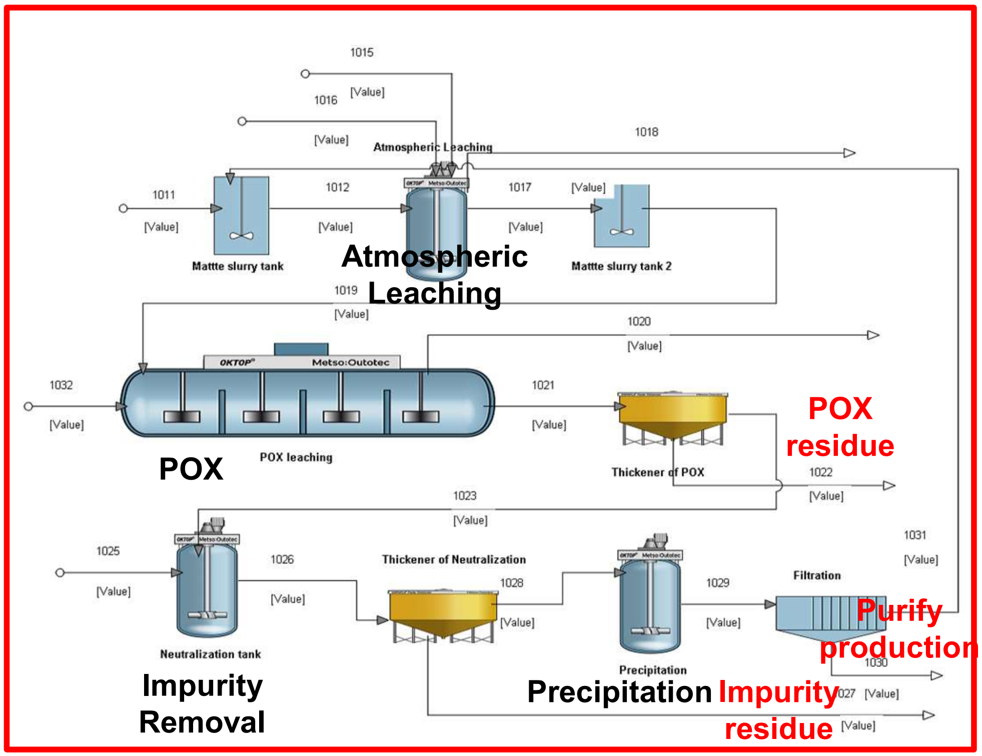
■ Process Design (HSC)

○ HSC simulation

- **Hydro-purification porcess** : Atmospheric Leaching → Pressure Oxidative Leaching → Precipitation ($Ni(OH)_2$)

→ Process simulation based on the experimental database.

[Hydrometallurgy Process]



III. Conclusion

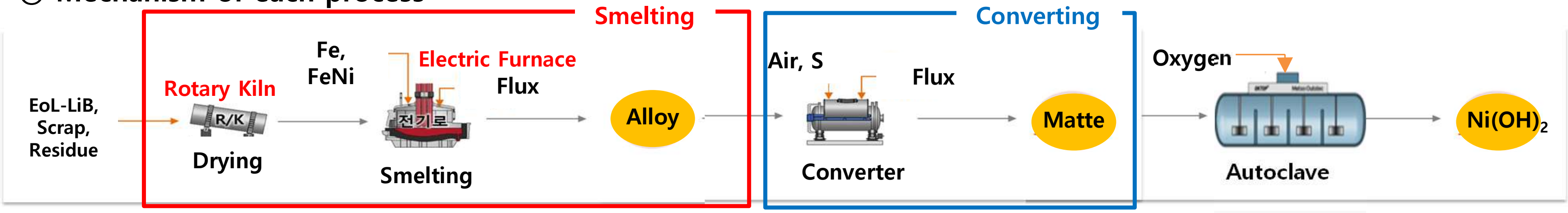
III-(1). Concluding Remarks

III-(2). Future Works

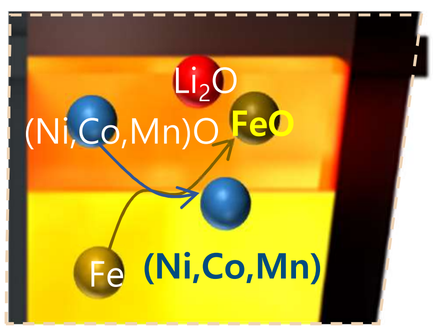
III-(1). Concluding Remarks

■ Conclusion : Process Design for recycling of EoL-LiB

○ Mechanism of each process



■ Smelting Process

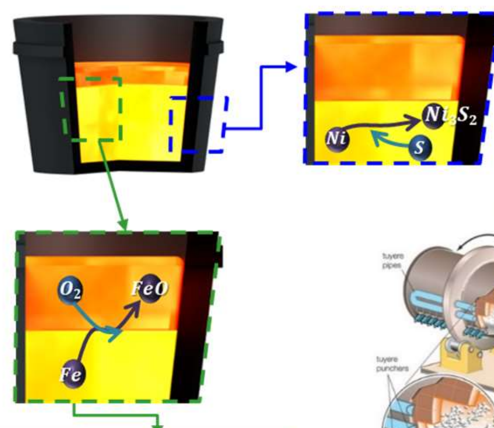


Oxidation : Fe + $\frac{1}{2}$O$_2$(g) = **FeO**

Reduction : C + **(FeO)** = Fe + **CO**

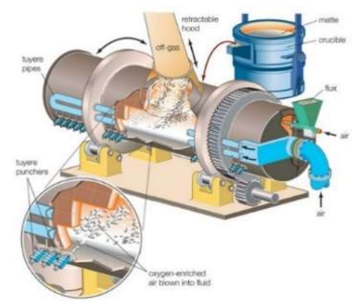
Fe + **(Ni,Co,Mn)O** = FeO + **(Ni,Co,Mn)**

■ Converting Process



Sulfidation (Step 1)
$3Ni + 2S = Ni_3S_2$

Oxidation (Step 2)
$Fe + \frac{1}{2}O_2 = FeO$

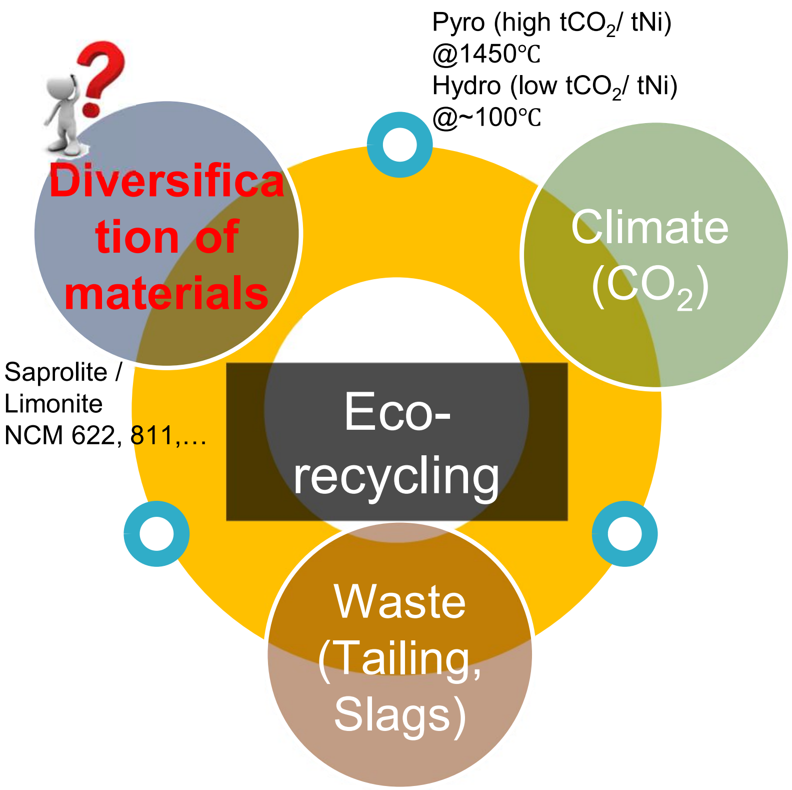


【PS Converter】

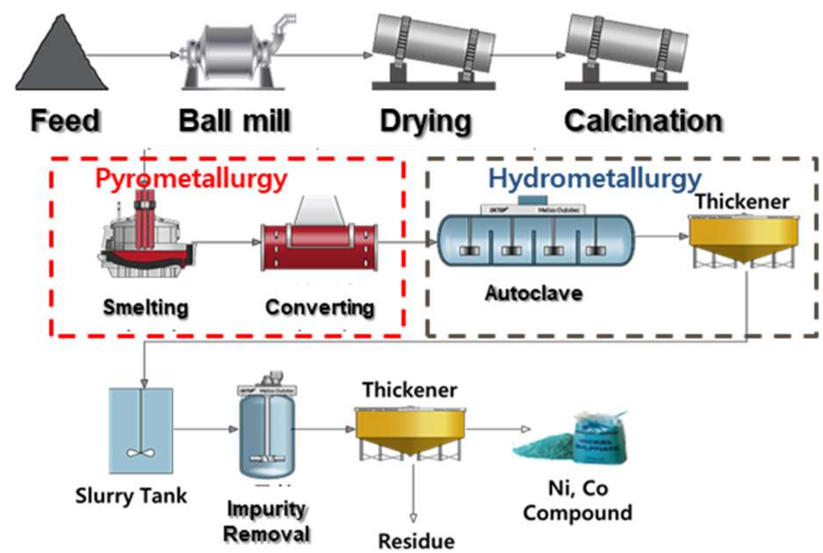
III-(1). Concluding Remarks

■ Conclusion : Process Design for recycling of EoL-LiB

○ Eco-friendly process for recycling of EoL-LiB



○ Process Design (hybrid process : pyro- & hydro-)



※Hybrid process for recycling of EoL-LiB

→ Development of **high-capacity & raw material diversification** process utilizing existing **facilities**

III-(2). Future Works

■ Conclusion & Future works

1. Smelting & Converting Process for recycling of EoL-LiB

- (smelting) Recovery of metal in B.P using Fe and FeNi hot metal

→ (Ni+Co)>70% Alloy (Fe-Ni-Co)

→ Li_2O-FeO-MnO-SiO_2 Slag (100% Li, 100% Mn recovery in slag)

- (converting) Removal of Fe and concentration of metal using Air (O_2)

→ (Ni+Co)> 75% Matte (Ni-Co-S)

→ As decreased the Fe content, the recovery of Co decreases

- (slag recycling) Recovery of Ni, Co for slag recycling

→ Smelting : (Ni+Co)>96.8% / Step converting : (Ni+Co)>97.8%

2. Purification Process for recycling of EoL-LiB

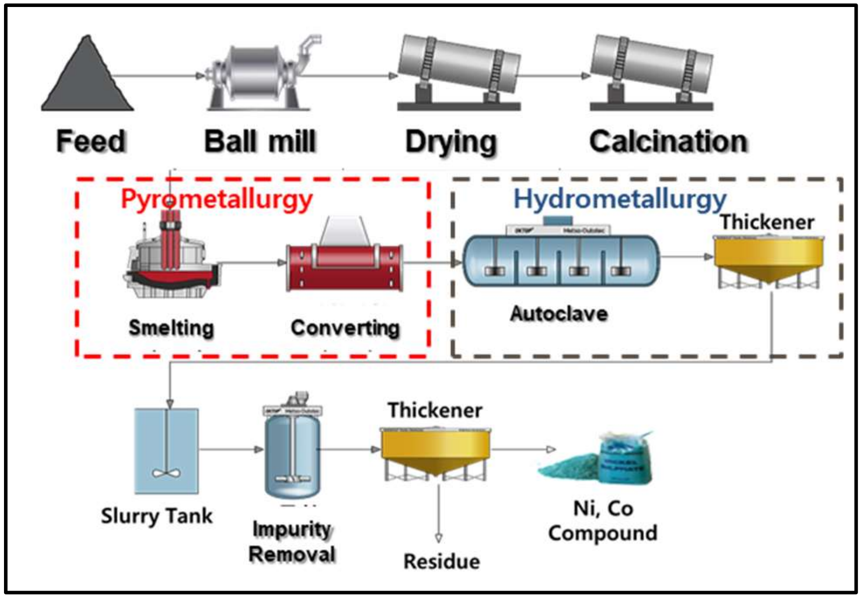
- (Purification) POX-Neutralization to purify Ni, Co

→ Purify production (Ni,Co$(OH)_2$) (Purity>99.5%)

3. Future works

○ Process design (Concept, Mass balance, Basic Flow design)

- Engineering D/B through the process cycle design & simulation
- Process design criteria through the experimental database



[Process Design for recycling of circulating resources]

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(저품위 고상 복합자원의 자원순환 오픈 플랫폼 구축을 위한 희소금속 농축회수(200kg/일) 원천기술개발)