Selective co-extraction of Ni&Co from high Ca/Mg solutions

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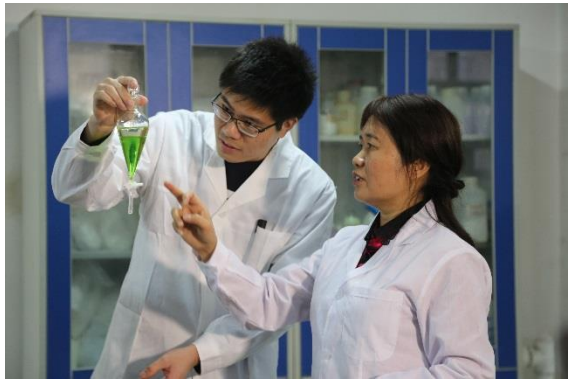
Self introduction of Shengxi Wu/ Dr. Wu or Shengxi

Shengxi Wu, born in February 1991, from Fujian China, Ph. D. in engineering, now as a associate professor in Central South University (personal page: https://faculty.csu.edu.cn/wushengxi/zh_CN/index.htm)

In the past about four years, published 41 papers, 20 patents and built up 12 leaching and extraction production lines and finished 10 pilot scale line tests (treating >500L solution per day)









中南大學 CENTRAL SOUTH UNIVERSITY

冶金分离科学与工程重点实验室 Key Laboratory of Metallurgical Separation Science & Engineering

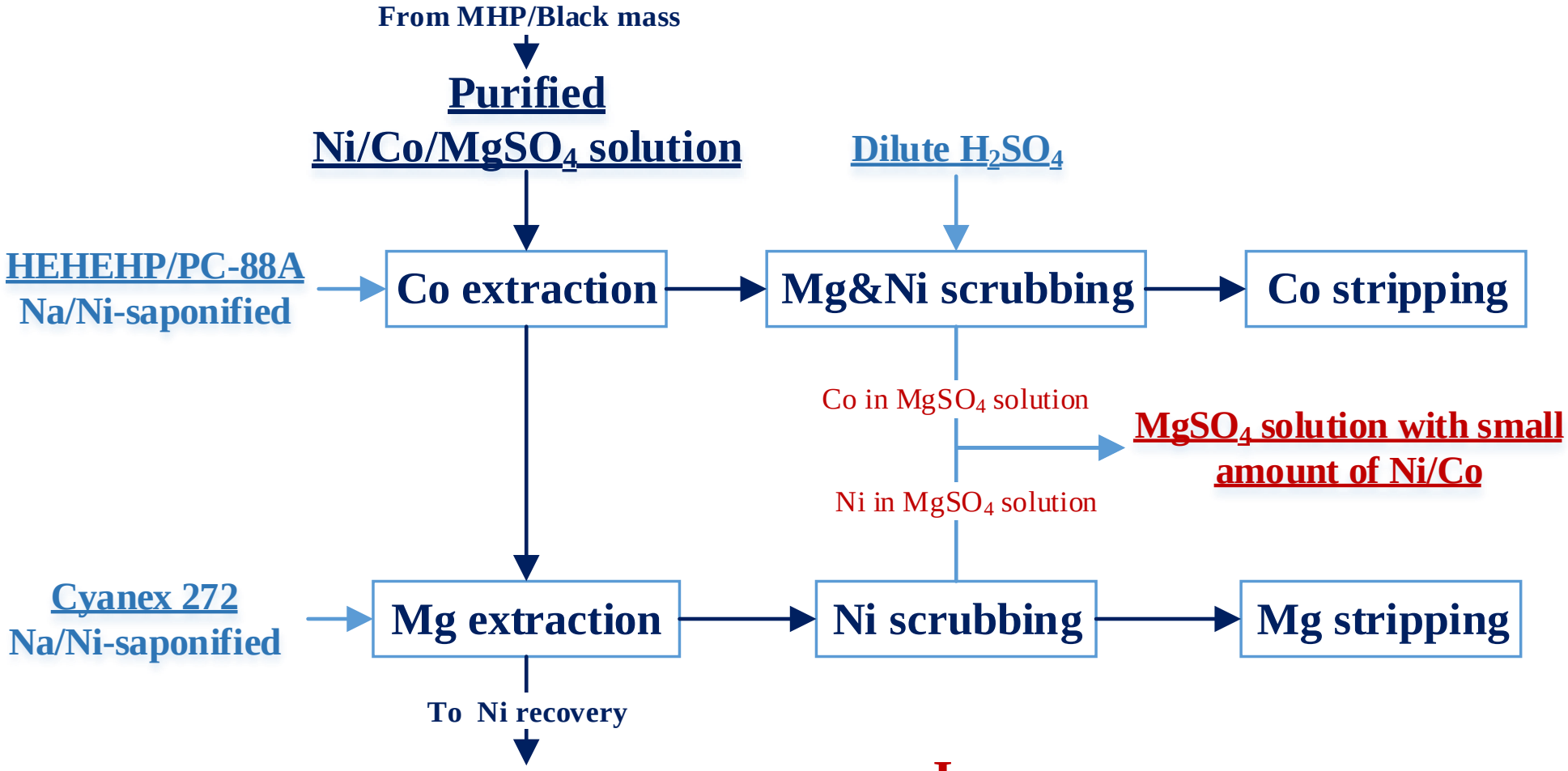
1. Research Background

2. Technological solution for Ni&Co co-extraction

3. Experimental and industrial progress

4. Summary of Ni&Co co-extraction technology

1. Research Background



Issues:

- Difficult in Ni/Co separation from massive Mg; High cost of sulfide precipitation, [Ni] unable to 1mg/L, Toxic gas emission; Extra pressure oxidation leaching is needed;

plus: Basic conceptions and principles in solvent extraction

Reagent Cost Structure for metal recovery from spent LIBs

- **Alkali for saponification;**
- **Acid for stripping and scrubbing**
- **CaO/Na_2S for trace heavy metal and As/P/F precipitation in wastewater**
- **NaOH for pH adjusting (neutralization)**

Seponification: $2NaOH+2\overline{(HL)_2} \leftrightarrow \overline{Na(L{\cdot}HL)_2} + H_2O$

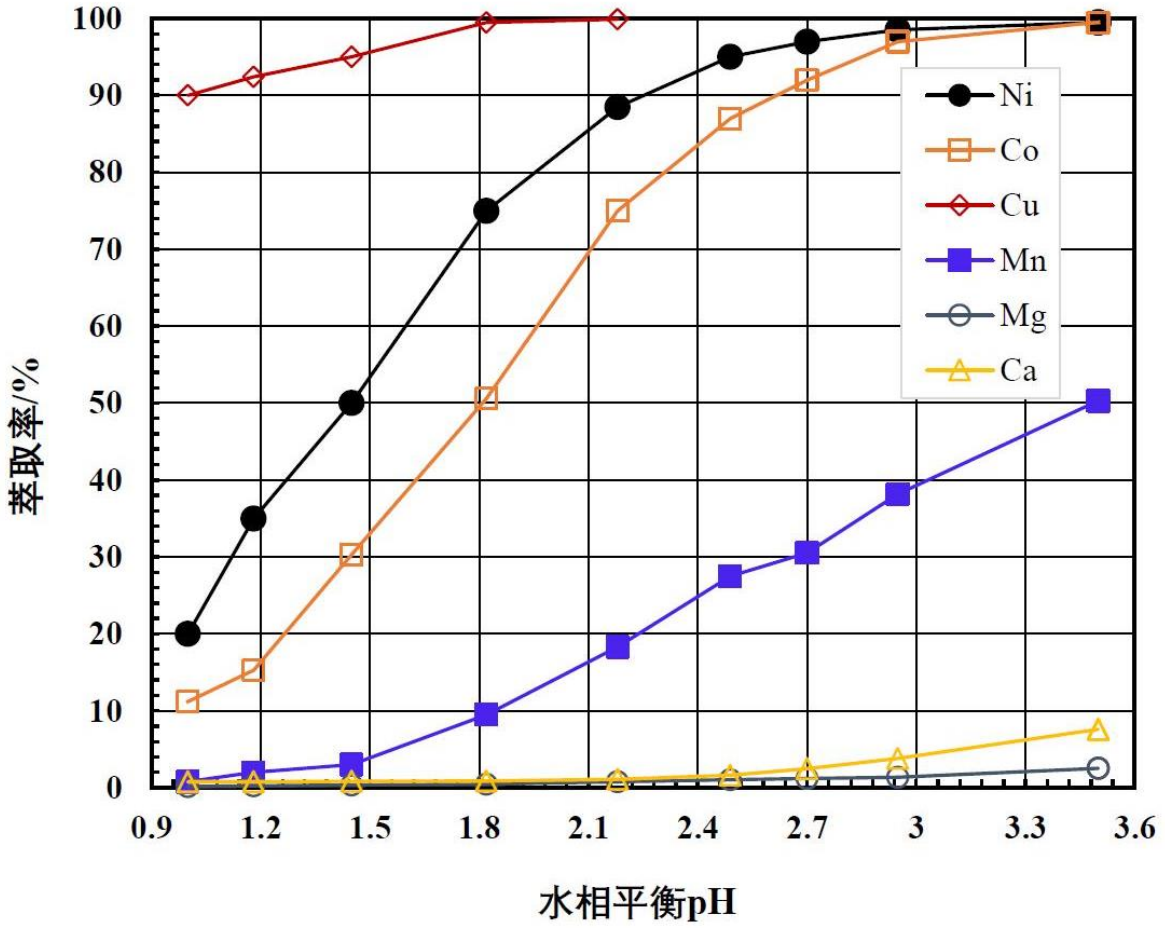
Extraction: $Me^{2+} +2\overline{Na(L.HL)_2} \leftrightarrow \overline{Me(L{\cdot}HL)_2} + 2Na^{+}$

Scrubbing: $\overline{Me(L{\cdot}HL)_2} + 2H^{+} \leftrightarrow Me^{2+} +2\overline{(HL)_2}$

Stripping: $\overline{Me(L{\cdot}HL)_2} + 2H^{+} \leftrightarrow Me^{2+} +2\overline{(HL)_2}$

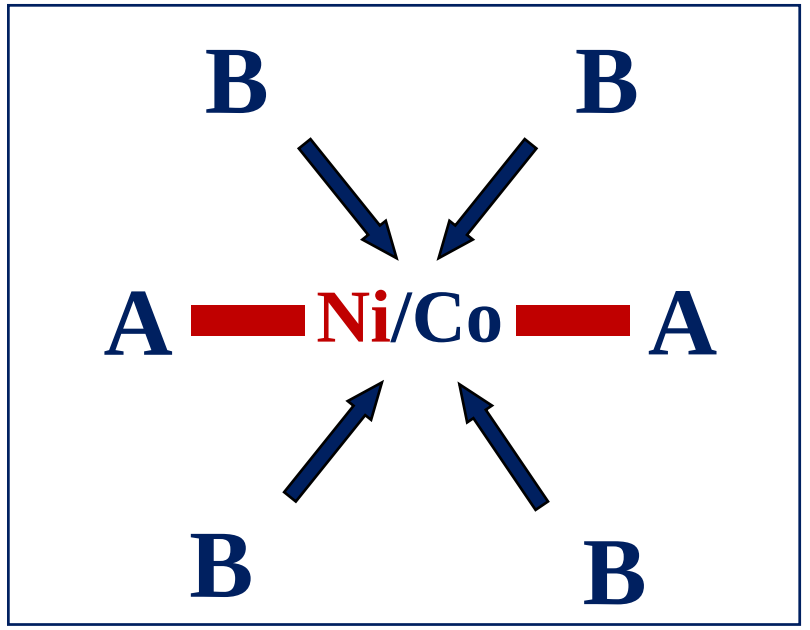
Principle 1st: Extracting small amount of elements from huge body element is economic

1. Extraction basis for Ni/Co from high Ca/Mg concentration solutions



Effect of pH on extraction efficiency of metal caions

20% HBL116；Feed（g/L）：1.71 Ni^{2+}, 0.12 Co^{2+}, 15.7 Mg^{2+}, 0.11 Ca^{2+}, A/O 1:1；30 ℃



A: Cation exchanger; B: Steric hindrance provider

Ni and Co can be selectively extracted by HBL-116 (HT-059) from high Ca/Mg concentration solutions

1. Extraction basis for Ni/Co from high Ca/Mg concentration solutions

1.1 batch extraction experiments

Five-stage countcurrent extraction of Ni/Co from high Ca/Mg concentration solutions

Elements	Co	Ni	Mg	Ca
Feed（g/L）	0.115	1.68	15.7	0.112
Raffinate（g/L）	0.0009	0.0038	16.1	0.127
Loaded organic（g/L）	0.141	4.36	0.0364	0.0041
Extraction efficiency（%）	99.8	99.8	0.093	1.47

Stripping efficiency of Ni/Co from loaded organic by 0.75mol H_2SO_4 via 5 stages

Elements	Co	Ni	Mg	Ca
Scrubbed organic（g/L）	0.140	4.35	0.0067	0.0011
Stripping solutions（g/L）	1.41	42.2	0.0801	0.0203
Regenerated organic（g/L）	0.0001	0.0131	---	---
Stripping efficiency（%）	99.5	99.9		
Impurity removal efficiency（%）	---	---	99.97	99.26

Organic： 20% HBL116 + 80% diluent；Feed（g/L）：0.115 Co^{2+}，1.68 Ni^{2+}，15.7 Mg^{2+}，0.112 Ca^{2+}，O/A =1:2.5；30 ℃；saponification ratio：50%；stripping O/A 10:1

1. Extraction basis for Ni/Co from high Ca/Mg concentration solutions

Five-stage countcurrent extraction of Ni/Co from high Ca/Mg concentration solutions

Rows	Co in raffinate (g/L)	Ni in raffinate (g/L)	Mg in raffinate (g/L)	Equibrium pH
1	1.723	0.903	13.17	3.48
2	0.007	0.003	13.10	4.43
3	0.005	0.001	13.12	4.33
4	0.0008	0.0005	13.15	4.32
5	ND	ND	13.11	4.36
6	ND	ND	13.15	4.29
7	0.0009	0.0004	13.18	4.31
8	0.0012	0.0006	13.35	4.28
9	0.0014	0.0008	13.40	4.23
10	ND	0.0005	13.19	4.26
11	**0.0011**	**0.001**	13.12	4.31
12	**0.001**	**0.0004**	13.15	4.35
13	**0.0009**	**0.0008**	13.11	4.32

E_{Ni}>99.99%， E_{Co}>99.99%

Feed：Co 8.50 g/L；Ni 9.70 g/L；Mg 14.2 g/L；pH 5.0

20%（v/v）HBL116 , O/A=2.8:1，225 rpm，t=10 min，T=25℃

1. Extraction basis for Ni/Co from high Ca/Mg concentration solutions

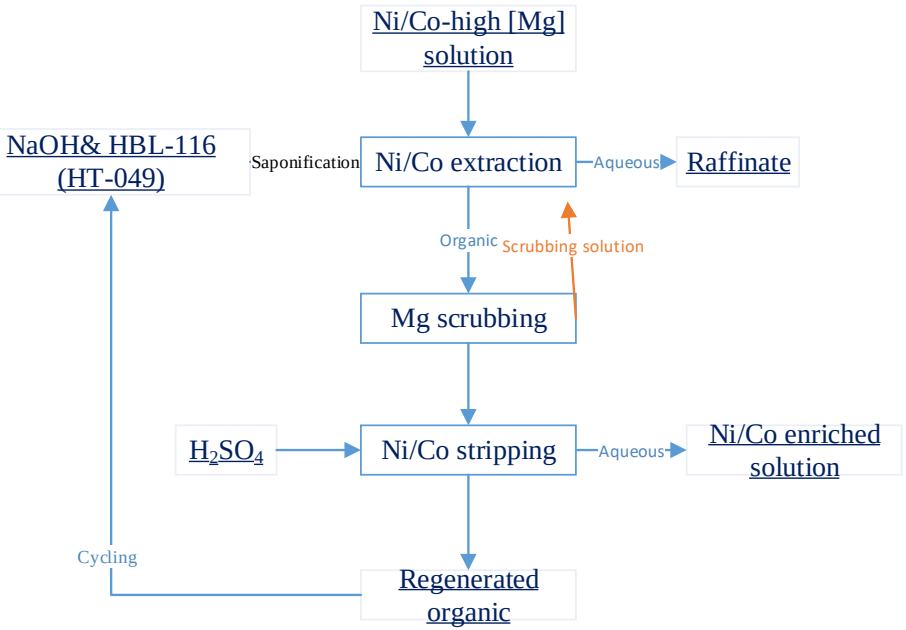
Phase segregation performance

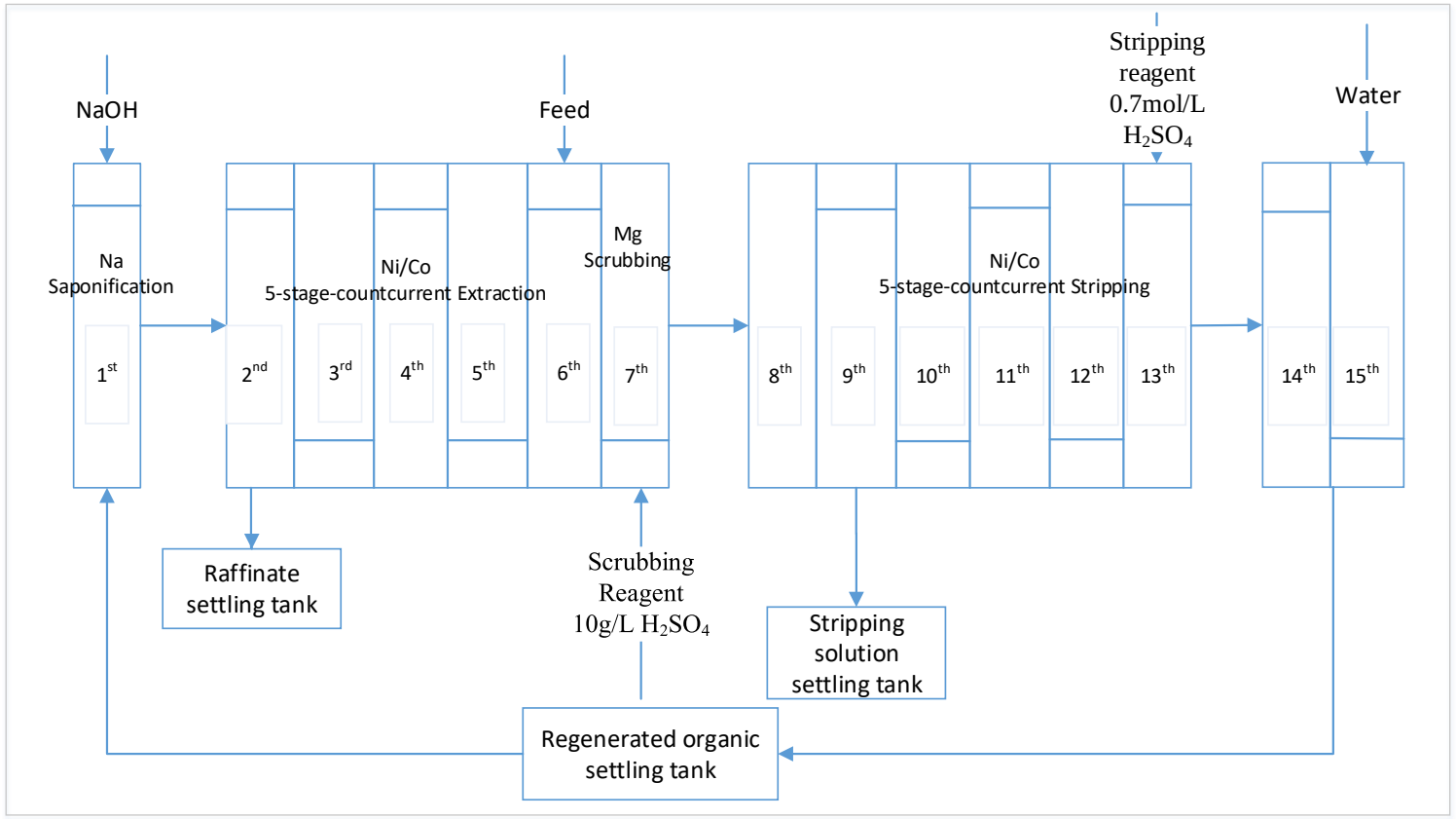
Photos of phase segregation row 13 (50s after stop mixing), stage 1st to stage 5th, excellent phase segregation excellent

2. Pilot test and industrial application of Ni/Co extraction from high Ca/Mg solutions

2.1 Guangdong Fangyuan New Material Group Co., LTD

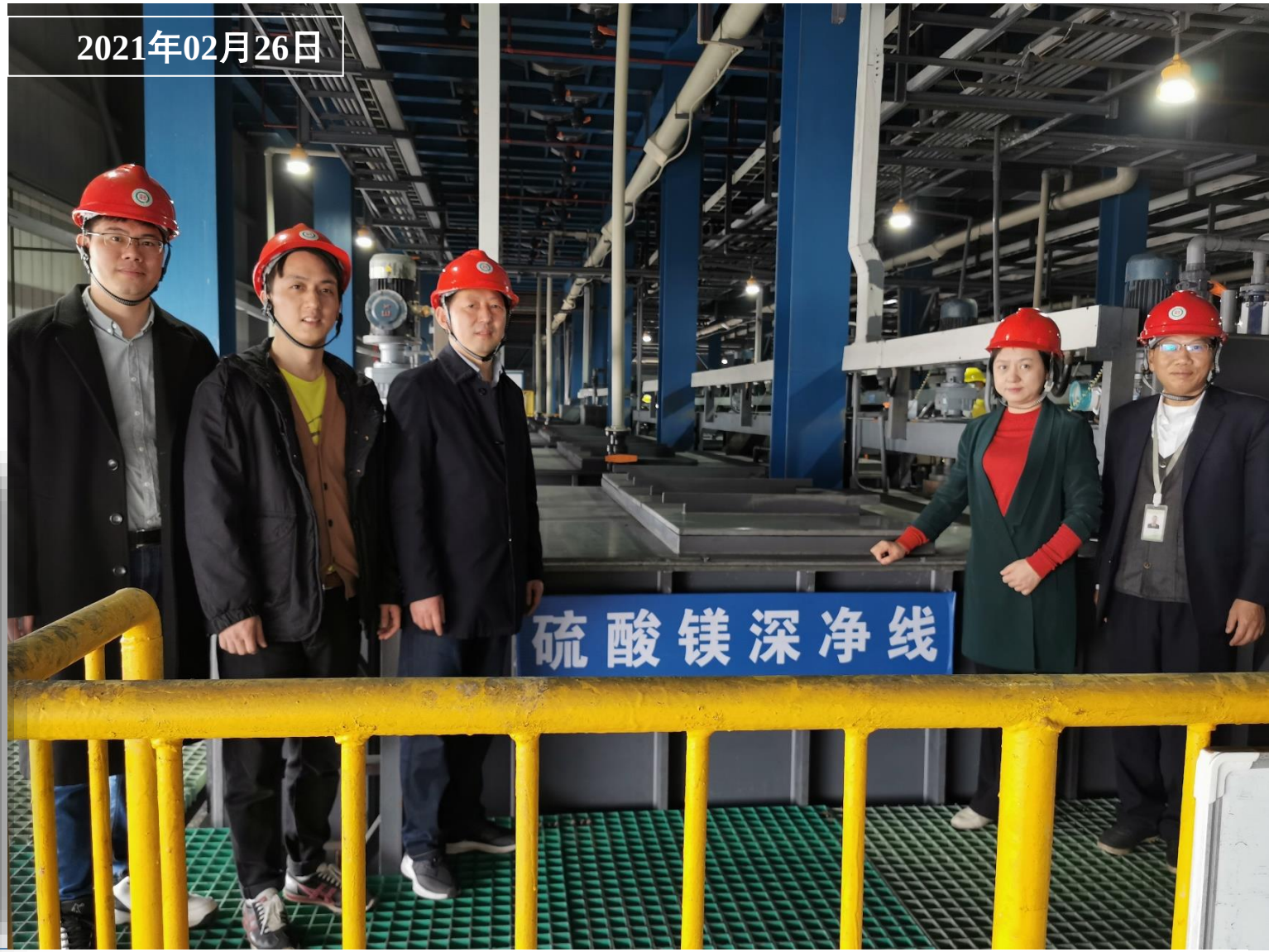
廣東芳源新材料集團股份有限公司
Guangdong Fangyuan New Materials Group Co., Ltd.





Production Lines: Selectively extraction of Ni/Co from $MgSO_4$ solutions by HBL-116(HT-059).
（launched in June 2020 ）

2. Pilot test and industrial application of Ni/Co extraction from high Ca/Mg solutions



Pilot test & Production Lines: Selectively extraction of Ni/Co from $MgSO_4$ solutions by HBL-116(HT-059).
Feed solution treating Scale: 400m^3/day（launched in June 2020 ）

2. Pilot test and industrial application of Ni/Co extraction from high Ca/Mg solutions

2.2 Continuous Running Data

表 3 HB116 镁水深净线皂化-萃取-萃洗-反萃-反洗连续稳定运行试验结果

时间	萃取			萃洗		反萃		反洗		皂化		萃余液				反萃液					
												Ni		Co		Ni		Co		Mg	
	有机 L/h	水相 L/h	萃余 pH	流量 L/h	出口 pH	流量 L/h	反萃 pH	流量 L/h	出口 pH	皂化率/%	碱量 L/h	mg/L	萃取率/%	mg/L	萃取率/%	g/L	反萃率/%	g/L	反萃率/%	g/L	除去率
01-09:00	3600	2800	6.76	150	5.15	750	1.1	530	1.55	70	63	未测出	99.99	0.8	99.94	3.81	99.95	11.55	99.99	0.023	>99.99%
01-11:00	3600	2800	6.64	150	5.2	800	0.93	560	1.77	70	63	未测出	99.99	0.1	99.99	3.98	99.97	10.33	99.99	0.014	>99.99%
01-13:00	3300	3300	6.98	150	5.47	800	0.93	560	1.82	73	60	0.4	99.99	0.3	99.97	3.12	99.98	10.15	99.99	0.007	>99.99%
02-09:10	3500	3500	7.55	150	5.68	800	0.99	560	1.92	71	62	0.07	99.97	0.8	99.94	3.19	99.97	10.76	99.95	0.010	>99.99%
02-11:00	3500	3500	6.98	150	5.61	800	1.01	560	1.91	70	65	未测出	>99.99	未测出	99.99	2.8	99.52	9.26	99.96	0.008	>99.99%
02-13:00	3700	3500	6.74	150	5.66	800	1.01	560	1.81	70	65	未测出	>99.99	未测出	99.99	4.14	99.52	11.88	99.96	0.012	>99.99%
03-09:00	3900	3500	6.29	150	5.22	800	0.96	560	2.13	70	68	0.06	99.98	0.27	99.98	4.29	99.89	14.5	99.97	0.012	>99.99%
03-11:00	3900	3500	6.27	150	5.25	800	1.02	560	1.97	70	68	0.74	99.72	0.19	99.99	3.84	99.87	15.74	99.97	0.013	>99.99%
03-13:00	3900	3500	6.57	150	5.49	800	1.17	560	2.09	70	68	0.42	99.85	0.13	99.99	3.24	99.86	15.19	99.97	0.006	>99.99%
04-09:00	3900	3500	6.31	150	4.85	750	1	530	2.02	70	68	0.43	99.84	0.35	99.97	4.29	99.86	14.5	99.97	0.012	>99.99%
04-11:00	4200	3500	6.27	150	4.9	750	1	530	1.82	70	73	0.74	99.03	0.19	99.88	3.84	99.87	15.74	99.97	0.013	>99.99%

The content of Ni/Co in raffinate was kept less than 1mg/L after 4 days of test running

2. Pilot test and industrial application of Ni/Co extraction from high Ca/Mg solutions

2.2 Continuous Running Data

时间	萃取			萃洗		反萃		反洗		皂化		萃余液				反萃液					
												Ni		Co		Ni		Co		Mg	
	有机 L/h	水相 L/h	萃余 pH	流量 L/h	出口 pH	流量 L/h	反萃 pH	流量 L/h	出口 pH	皂化率/%	碱量 L/h	mg/L	萃取率/%	mg/L	萃取率/%	g/L	反萃率/%	g/L	反萃率/%	g/L	除去率
25-09:00	6500	2000	5.05	100	3.68	900	1.24	630	1.89	70	113	未测出	100	0.48	99.89	25.1	99.95	7.56	99.88	0.008	>99.99%
25-13:00	6200	2200	5.31	100	3.84	950	1.12	660	1.76	70	105	0.68	99.85	0.58	99.87	23.77	99.96	7.77	99.89	0.005	>99.99%
26-17:00	5600	2200	5.53	100	3.77	920	0.73	660	1.75	70	98	未测出	100	未测出	99.99	17.8	99.97	5.34	99.92	0.015	>99.99%
26-19:00	5300	2200	5.46	120	3.98	900	0.71	630	1.82	70	92	未测出	100	未测出	99.99	17.78	99.97	6.23	99.92	0.015	>99.99%
26-21:00	4700	2200	5.21	130	3.97	870	0.61	609	1.79	70	81	0.79	99.88	0.26	99.97	15.37	99.97	4.86	99.92	0.012	>99.99%
27-09:00	4700	2500	7.78	150	4.27	810	0.71	560	1.91	70	81	0.26	99.99	0.35	99.95	20.99	99.97	6.15	99.92	0.009	>99.99%
27-11:00	4700	2700	5.86	150	4.44	810	0.82	560	1.89	70	81	0.28	99.99	0.36	99.95	21.53	99.96	7.98	99.92	0.02	>99.99%
28-13:00	4700	3000	-	170	4.15	810	1.01	560	1.81	70	81	0.88	99.86	0.31	99.98	23.91	99.96	10.79	99.92	0.012	>99.99%
30-09:00	4800	2500	5.97	170	4.21	810	0.88	810	1.83	70	83	未测出	100	0.73	99.96	16.9	99.95	10.89	99.92	0.014	>99.99%
30-11:00	5100	2700	5.46	170	4.33	780	0.73	780	1.76	69	88	未测出	100	0.59	99.96	15.39	99.95	10.71	99.94	0.005	>99.99%
30-13:00	5100	2700	5.43	170	4.31	750	0.72	750	1.7	69	88	未测出	100	未测出	99.99	16.61	99.95	12.56	99.94	0.016	>99.99%
平均	4671	2935	6.09	177	4.34	774	0.98	556	1.80	69	81	**0.40**	**100**	**0.49**	**99.96**	**12.89**	**99.92**	**14.36**	**99.94**	0.081	>99.99%

The content of Ni/Co in raffinate was still kept less than 1mg/L after 45 days of production running

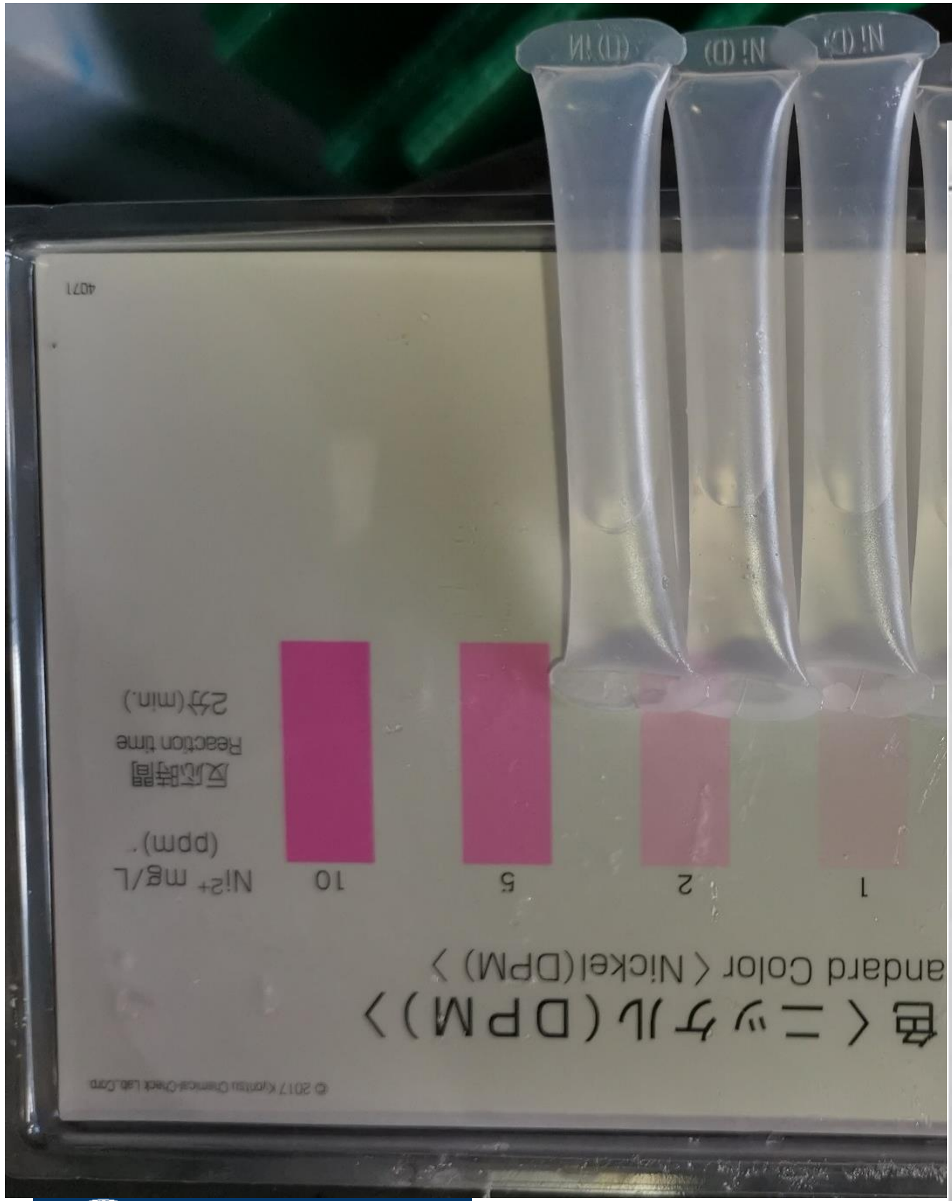
2. Pilot test and industrial application of Ni/Co extraction from high Ca/Mg solutions

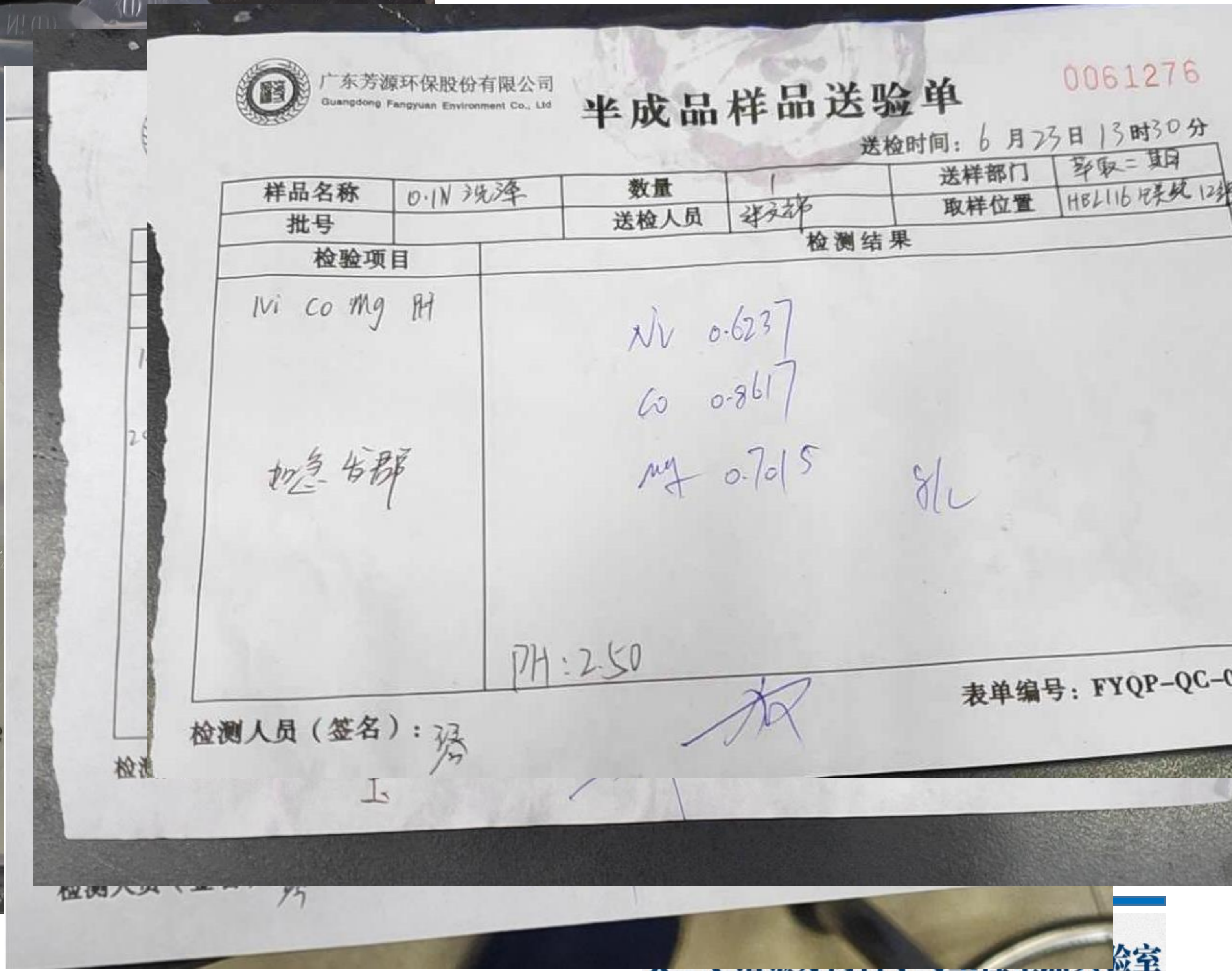
2.2 Continuous Running Data

Elements	Ni	Co	Mg
Feed（g/L）	0.1~3	1~5	25~60
Stripping（g/L）	1~4.5	10~15	1.07
Raffinate（mg/L）	<1	<1	>32
Extraction efficiency/%	99.9	99.9	---
Mg removal efficiency/%	---	---	99.7

Oil content in raffinate：8.14-16.06ppm，COD：59.43-96.68ppm

Oil content in stripping：4.19-10.97ppm，COD：28.04-40.67ppm




广东芳源环保股份有限公司
Guangdong Fangyuan Environment Co., Ltd

0061276

半成品样品送验单

送检时间：6 月 23 日 13 时 30 分

样品名称	0.1N 洗涤	数量	1	送样部门	萃取二班
批号		送检人员	叶文部	取样位置	HBL116 ...

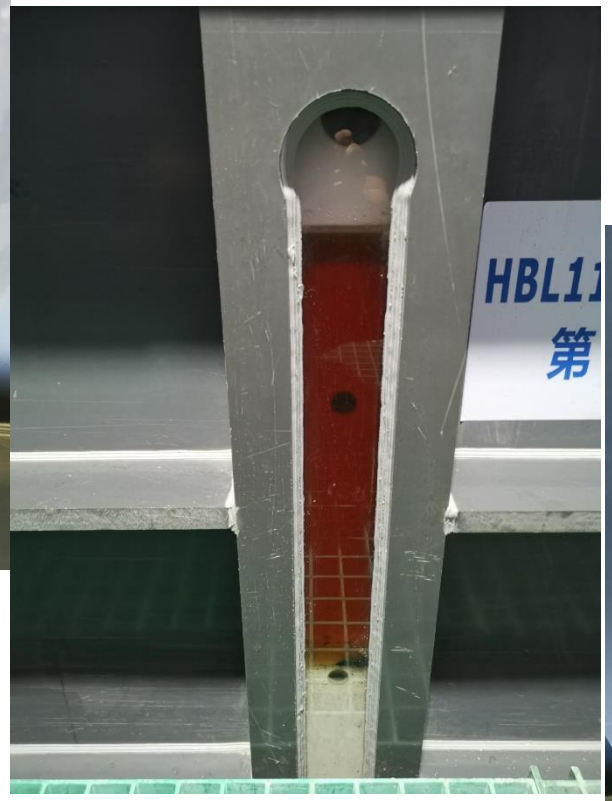
检验项目	检测结果
Ni Co Mg PH 加急 化郡	Ni 0.6237 Co 0.8617 Mg 0.7015 g/L PH:2.50

表单编号：FYQP-QC-

检测人员（签名）：

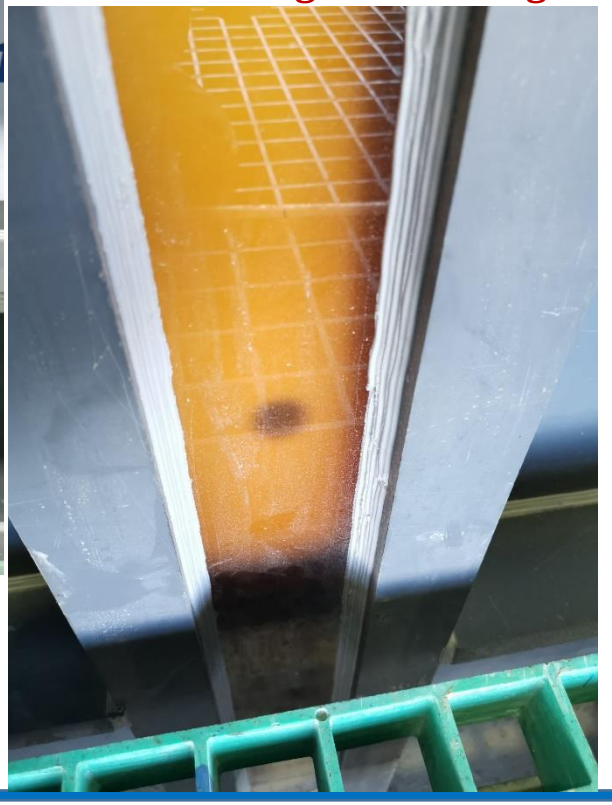
Segregation in 1st stage

Loaded organic



Stripping segregation

Regenerated organic



3 month after test running

12 month after test running

2. Pilot test and industrial application of Ni/Co extraction from high Ca/Mg solutions

廣東芳源新材料集團股份有限公司
Guangdong Fangyuan New Materials Group Co., Ltd.

Reagent consumption for Ni/Co extraction from high Ca/Mg solutions

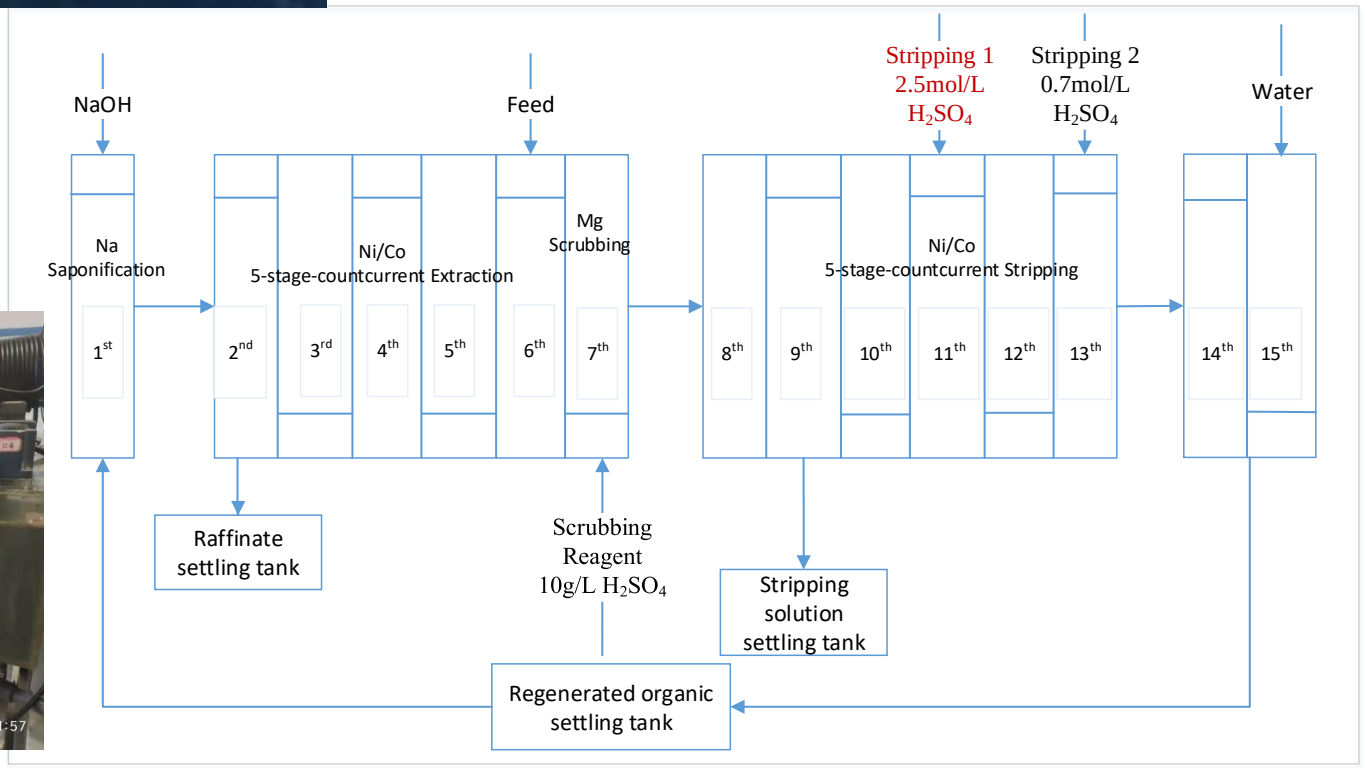
Reagent	Sulfuric acid consumption (98%H_2SO_4)			Alkali (100%NaOH)	
	Scrubbing Acid	Stripping Acid	Acid in total	Saponified alkali	**Total**
Theoretical consumption (t/t Ni&Co)		1.66		**1.36**	
Dosage (kg/m^3) feed solution	0.59	19.41	20.01	10.04	**10.04**
Dosage (t/t) Ni/Co metal	**0.09**	**2.92**	**3.01**	**1.66**	**1.66**

2. Pilot test and industrial application of Ni/Co extraction from high Ca/Mg solutions

2.2 Huayou Cobalt Group Co., LTD ---pilot test

华友钴业 HUAYOU COBALT

Goal: Ni+Co in raffinate <20ppm; Stripping solution Ni>80g/L, Mg<10ppm Ammonia<100ppm;



	Saponification	extraction	Scrubbing		Stripping		scrubbing
Flow rate(L/h)	Organic	Alkali	Feed	0.3N acid	5N acid	1.5N acid	Water
	18	0.72	48	6	1.5	0.96	3

	Raffinate				Stripping solution					
Element	Ni	Co	pH	TOC	Ni	Co	Mg	pH	NH_3-N	TOC
g/L	0.009	0.02	4.25	0.025	87.52	0.75	0.0032	1.31	0.046	0.036

2. Pilot test and industrial application of Ni/Co extraction from high Ca/Mg solutions

	Aqueous					Oragnic		
	Co	Mg	Ni	pH	NH_3-N	Co	Mg	Ni
萃取一	**0.017**	**15.39**	**0.0062**	**4.26**		0.31	4.66	0.49
萃取二	0.13	17.14	0.07	4		3.55	1.25	3.56
萃取三	1.73	16.08	1.74	3.33		2.65	0.14	6.35
萃取四	1.43	15.34	3.58	3.15		1.07	0.048	8.13
萃取五	0.87	14.91	4.66	3.18		0.44	0.046	9.83
洗涤一	1.51	0.89	10.51	2.82	0.36	**0.42**	**0.0087**	**8.77**
洗涤二	1.34	0.017	12.28	2.7	0.064	0.35	0.0026	9.00
洗涤三	0.99	0.0034	11	2.65	0.054	0.24	0.00086	9.11
洗涤四	0.58	0.0011	12.25	2.58	0.049	0.17	0.0022	9.04
洗涤五	0.27	0.0017	7.92	2.15	0.032	0.1	0.00084	7.70
反萃一	**0.78**	**0.00098**	**83.23**	**1.34**	0.055	0.047	0.00051	6.98
反萃二	0.32	0.00085	79	0.85	/	0.026	0.00041	5.46
反萃三	0.1	0.00062	51.05	0.2	/	0.029	0.00037	1.48
反萃四	0.07	0.00097	27.06	0.2	/	0.069	0.00043	1.4
反萃五	0.031	0.00073	12.97	0.1	/	0.047	0.00069	1.3

- **Ni Raffinate is less than 50ppm (meet the low limit concentration requirement);**
- **2-stage-scrubbing for loaded organic， NH_3-N was reduced to less than 64ppm;**
- **Ni concentration in stripping solution is about 80g/L with Mg <10ppm**

2. Pilot test and industrial application of Ni/Co extraction from high Ca/Mg solutions

华友钴业 HUAYOU COBALT

Reagent consumption for Ni/Co extraction from high Ca/Mg solutions

	Liquid alkali (32% NaOH)/kg	5N H_2SO_4 /m^3	Feed/m^3	Solvent loss /kg	Diluent loss /kg
Reagent t/t Ni	5297	9.89	32.17	2.81	4.22

2. Pilot test and industrial application of Ni/Co extraction from high Ca/Mg solutions

HBL-116 (HT-059) extraction production line for Ni selective extraction from Co extraction raffinate produced for the Cu-Co ore, will be launched June 2024, Brunp, Yichang, Hubei, Chine (1462m³/d)

Ni(g/L)	Co(g/L)	Mg(g/L)	NH_4^+(g/L)	SO_4^{2-}(g/L)	油分(mg/L)	Cod(g/L)	pH
1.12	0.10	3.38	27.48	93.04	40-60	1.2	5.0-5.5

HBL 116（25%）萃镍线出口水相金属浓度

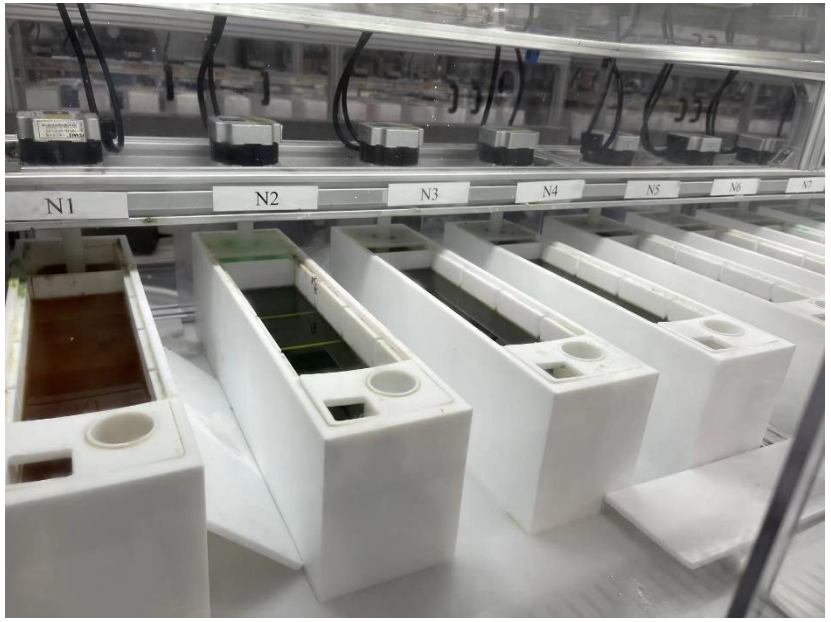
物料 / 元素	Ni(g/L)	Co(g/L)	Mg(g/L)	油分(mg/L)	Cod(g/L)	pH
萃余液	< 0.005	< 0.005	3.26	40-60	1.20	3.5-4.5
反镍液	40.42	3.61	1.22	50-60	0.60	0.5-1.5

HBL 116（25%）萃镍线级数

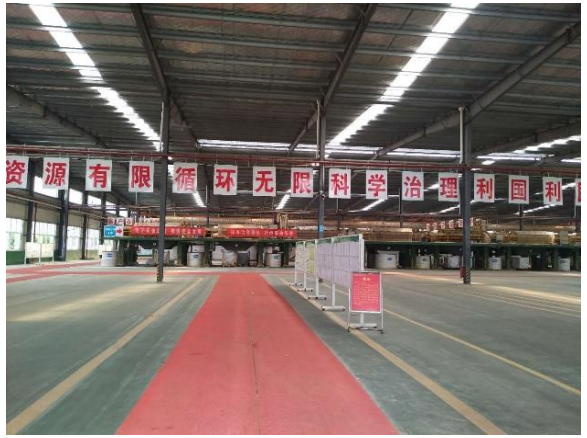
萃取功能	铵皂	萃余液澄清	萃取	洗铵镁	有机澄清	反萃	洗酸	有机澄清	总级数
级数	1	2	5	3	1	6	3	1	22
萃取槽混合室规格	φ1.8×2.65m	/	φ1.8×2.65m					/	/
萃取槽澄清室规格	7*2.1*1.3	7*4.0*1.3	7*4.0*1.3	7*2.1*1.3				7*2.1*1.3	/

2. Pilot test and industrial application of Ni/Co extraction from high Ca/Mg solutions

Lanzhou Jintong Energy Storage Power New Materials Co., LTD、Austin Elements (USA) pilot test for Ni&Co coextraction from Li/Ni/Co/Mg mixed solutions、Guizhou Daong Huicheng Co., LTD using HBL-110 (HT-059-2nd) to selectively co-extract Ni/Co/Mn from Ca/Mg/Fe/Al/Ni/Co/Mn mixed solutions



3. Industrial application of Ni/Co extraction from Ca/Mg/Fe/Al mixed solutions



Direct selectively extraction of Ni from acid leach solutions of stainless steel sludge, Jiuli Co. Ltd. , Zhejiang Province

$NiSO_4$: 800 ton/a，put into production in Feb, 2018

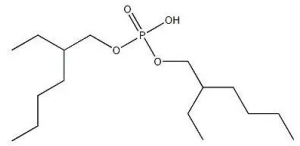
3. Industrial application of Ni/Co extraction from Ca/Mg/Fe/Al mixed solutions

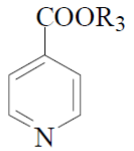
Electroplating sludge contains massive various impurities with a high concentration

Element	Zn	Ni	Ca	Mg	Al	Fe
Con.	~20g/L	5~6g/L	~0.5	~0.3g/L	~0.1g/L	<0.1g/L

production line5: Direct extraction of Ni from the leaching solution of EPS in Ruijin Shengyuan Environmental Protection Technology Co., LTD.

Using HBL110 as the extractant for Ni





式 II

Components in stripping solutions: Ni 98g/L

Zn，Ca，Mg<10ppm； Al，Fe <30ppm

3. Industrial application of Ni/Co extraction from Ca/Mg/Fe/Al mixed solutions

$NiSO_4$: 800 tonne/a
Mixer: 0.42m^3;
Put into production on Aug. 2014

DSX of Ni from acid leach solutions of electroplating sludge using HBL110 (HT-059-2nd)
Shuangneng, Ningbo, Zhejiang Province

3. Industrial application of Ni/Co extraction from Ca/Mg/Fe/Al mixed solutions

Guizhou DalongHuicheng Co. Ltd. Acid leaching solution of heavy metal sulfide precipitate that contains high Ca/Mg/Mn and considerable Ni/Co

Feed solution					
Element	Mn	Co	Ni	Ca	Mg
Con. (g/L)	50~80	4~5	2~3	0.1~0.2	0.1

Using HBL110 (HT-059-2nd) directly prepare pure NCM mixed solution

Stripping solution					
Element	Mn	Co	Ni	Ca	Mg
Con. (g/L)	~17	~25	~10	<5ppm	<5ppm

The first and the only plant that recover NCM without separation in China

4. Summary and Thanks

Summary for direct solvent of Ni/Co from high Ca/Mg solutions:

- **Short process** – omit of sulfide precipitation and pressure oxidation leaching operations
- **Excellent Ni/Co recovery - >99%,** illustrating a **>10%** increase in Ni/Co recovery;
- **Significantly reduce scrubbing solution (20~60g/L Mg, 0.5~10g/L Ni/Co)**;
- **Low Cost recovery method for Ni/Co from high Ca/Mg (even with Fe/Al solutions)**

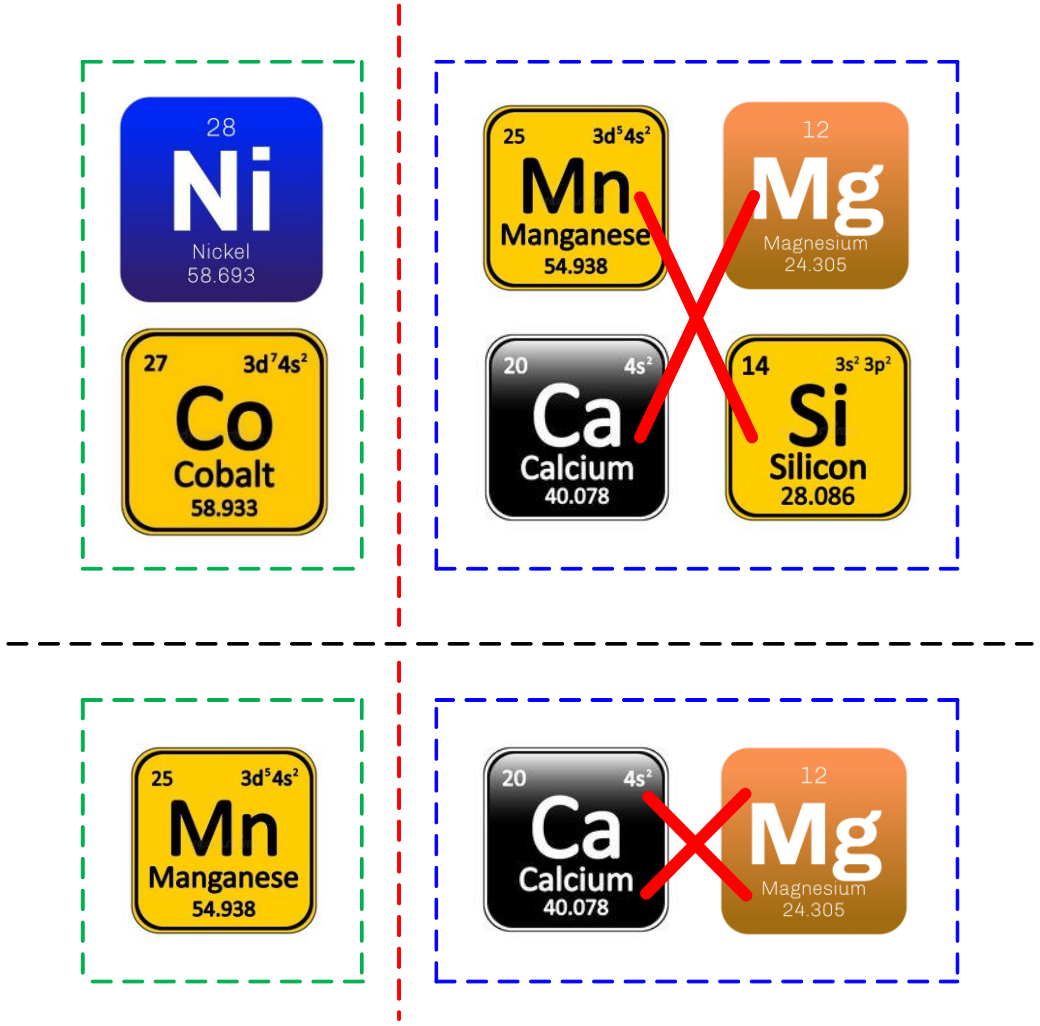
  HBL116 (HT-059) for Ni/Co separation from Ca/Mg, HBL-110 (HT-059-2nd) from Ca/Mg/Fe/Al
- **Environmental friendly, Ni/Co in raffinate was reduced to <1mg/L**

4. Summary and Thanks

Source of extractant can be guarantee：

HBL116（HT-049）annual production

capacity>3000t/y



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4、Summary

- **Core conception:** “separation as the key method、application is the final goal、achieve resource sustainable development via green and high efficient utilization”

Fundamental research

Technology development

Engineering transformation and application

4、Summary- International project solution provider in hydrometallurgy

Hydrometal Tech: International website for our group project

Pioneering Sustainable Solutions provider in Battery Recycling

Hydrometal Tech was founded from a vision to revolutionize the battery recycling technologies in industry. With over 50 years of combined experience in hydrometallurgy, our founders, a group of esteemed professors and engineers, saw the potential to make a substantial impact on the environment and the economy. Our journey began with a commitment to excellence, innovation, and sustainability, which continues to be the bedrock of our operations today.

Website: https://hydrometaltech.com/

E-mail: shengxiwu@hydrometaltech.com

4. Summary and Thanks

Thanks for your time and question are welcomed