Recent Technological Progress in Metals' Recovery from Spent NCM Battery Promoted by New Separation Reagents

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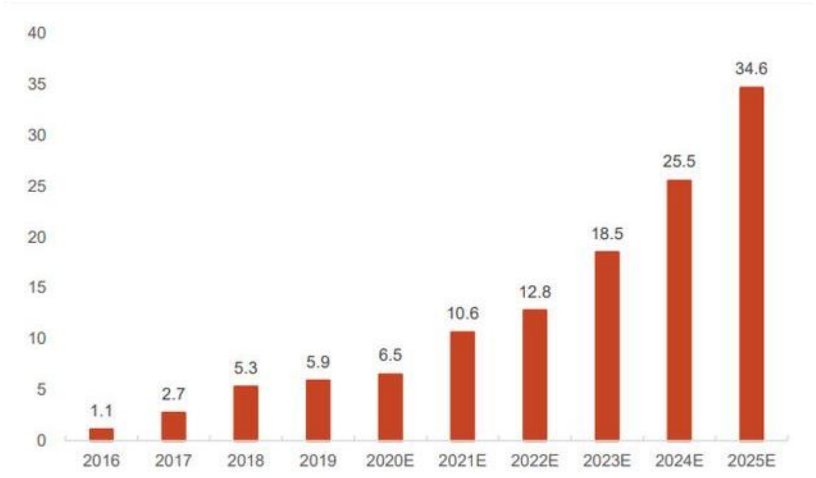
1、Importance of metal recovery from the spent LIBs

2、 Key challenges presented in traditional processes

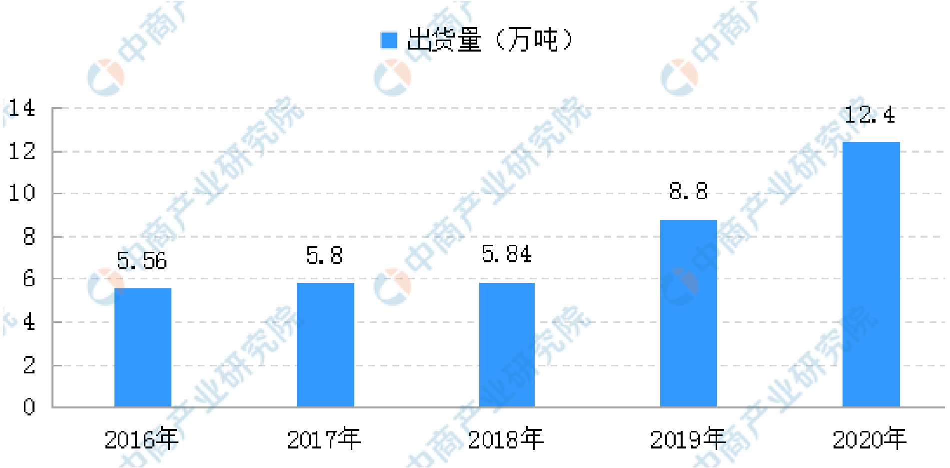
3、 Ideal technique solutions for the challenges

4、Perspectives for the recovery of metals from other wastes

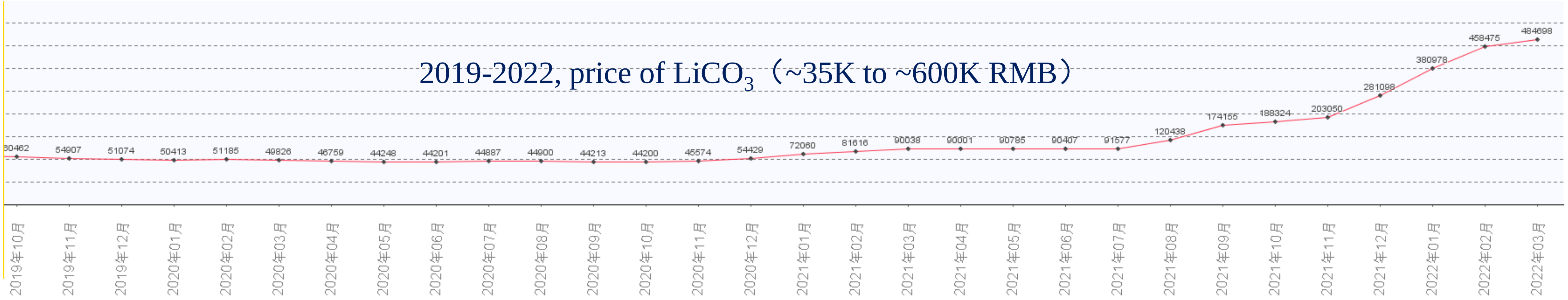
1、Importance of metal recovery from the spent LIBs



Global expansion in NCM materials



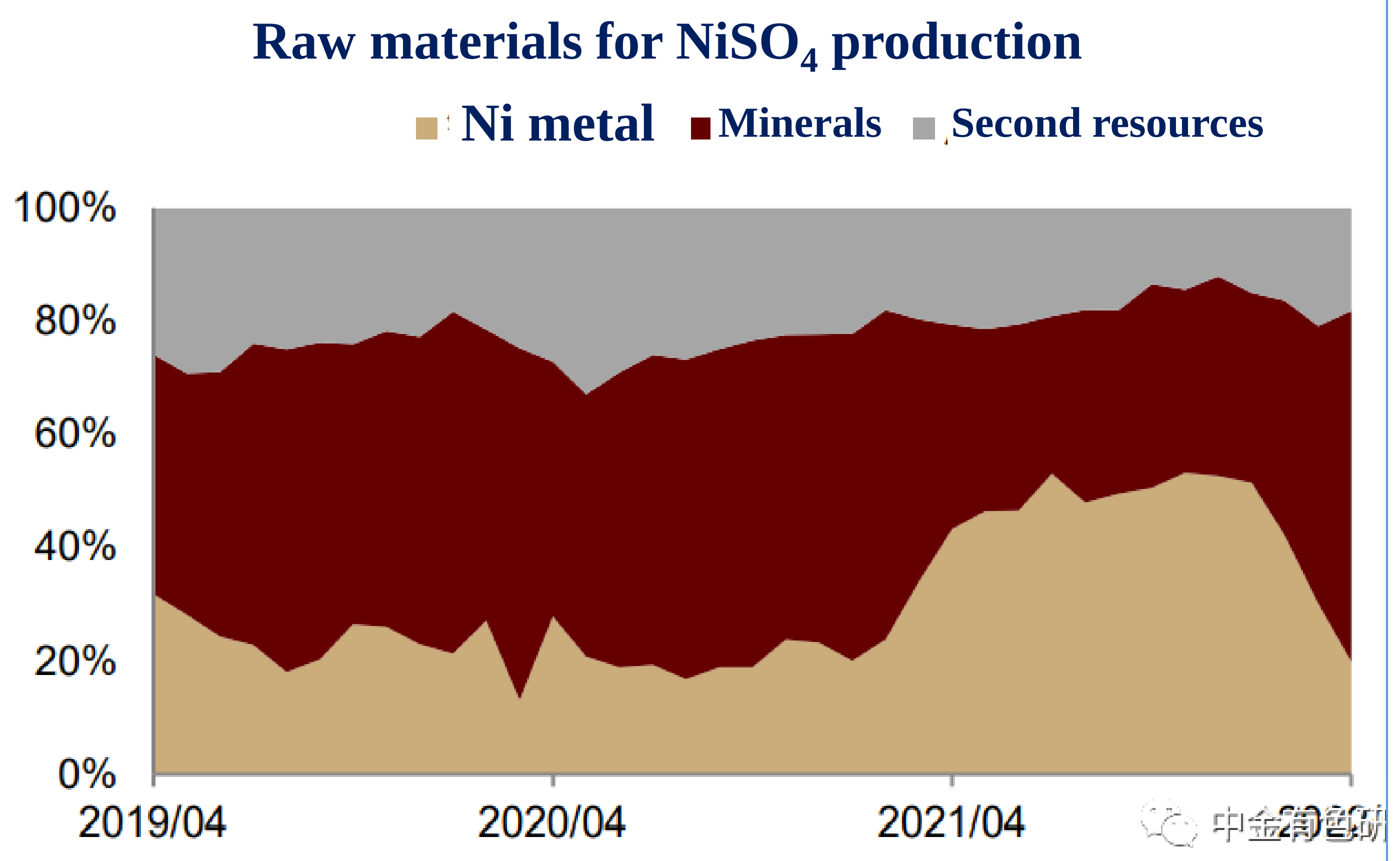
Production of $LiFePO_4$ from 2016-2020 in China

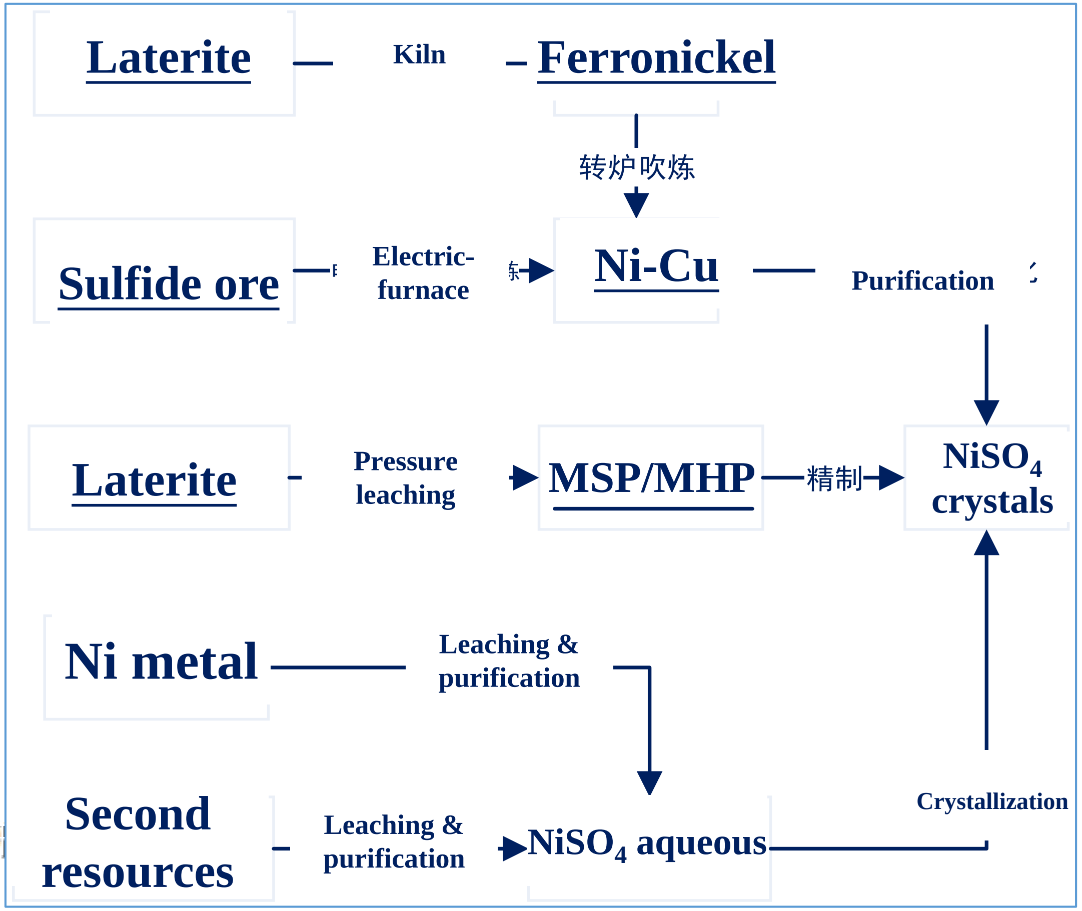


2019-2022, price of $LiCO_3$（~35K to ~600K RMB）

The rapid development of EV/LIBs industry brings huge material demand and rise in price

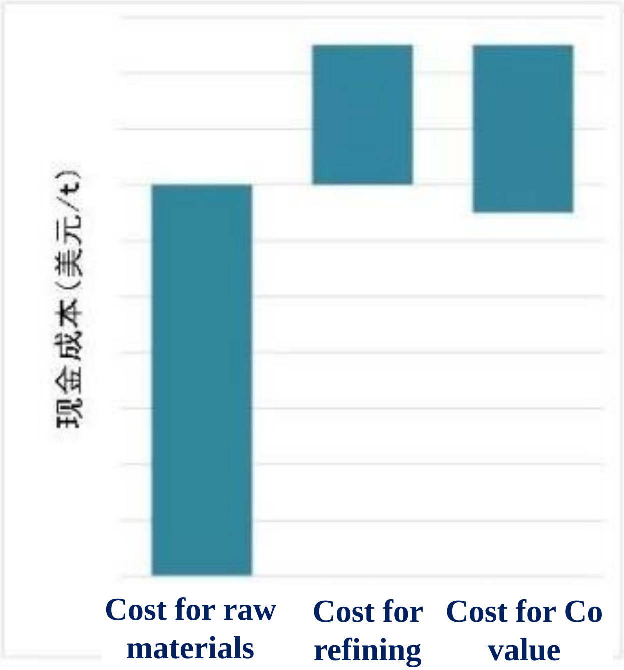
1、Importance of metal recovery from the spent LIBs.

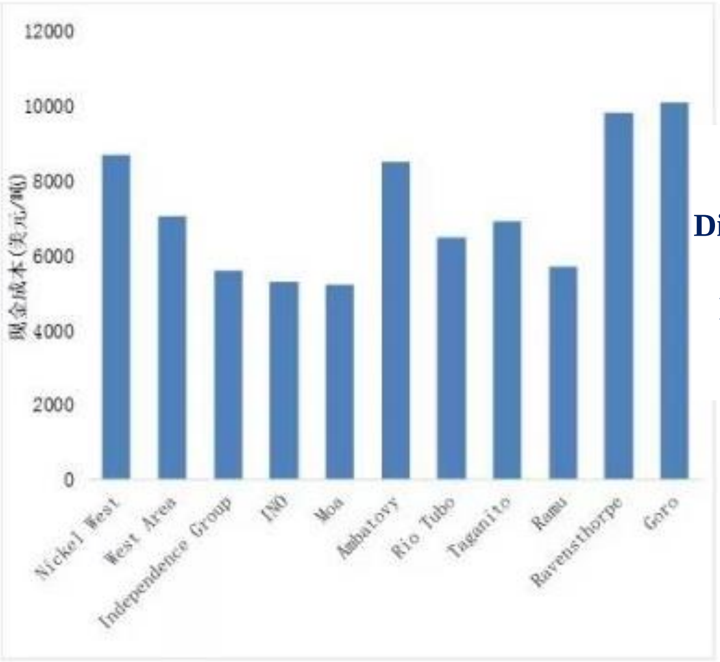


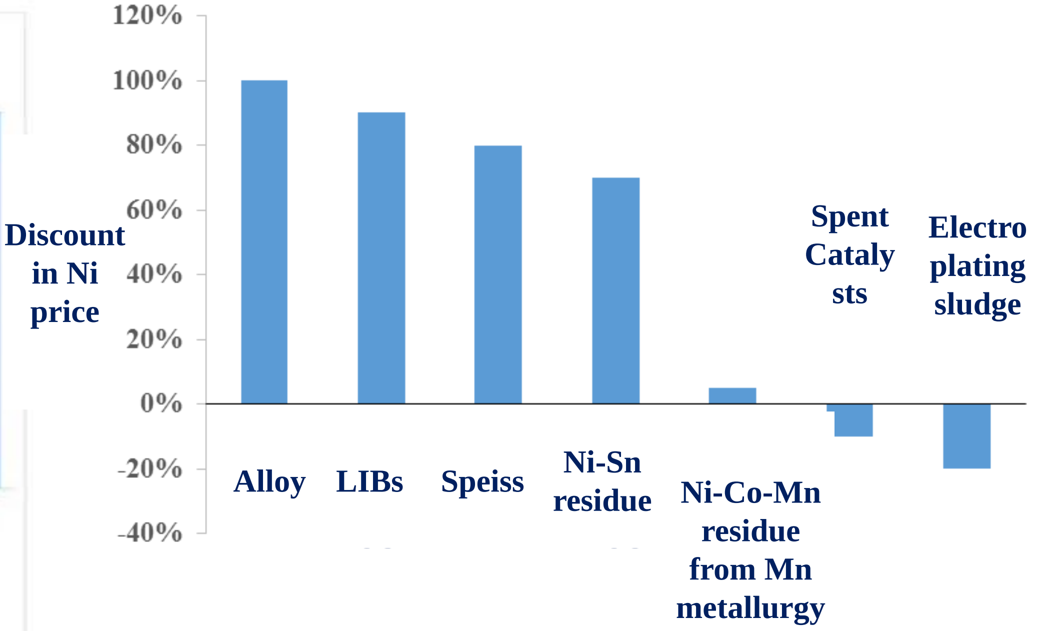


Processes for $NiSO_4$ from various sources require an hydrometallurgical purification operation-deeply separation of impurities (Ca/Mg/Fe/Al/Mn/Cu)

1、Importance of metal recovery from the spent LIBs.







Using MHP/MSP or Ni metal to produce $NiSO_4$ is a short process, **but with a high raw material cost** (the production cost is about 6000-10000$/t)

By contrast, recovery Ni from wastes save the material cost but via a complex purification

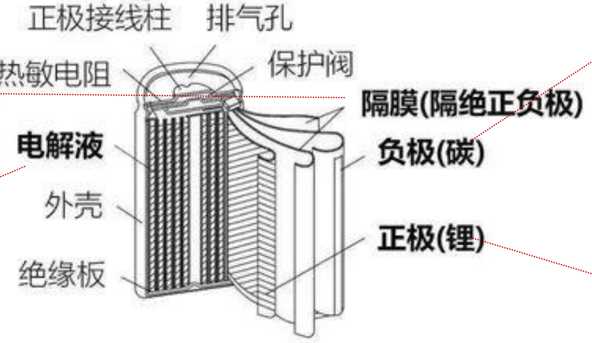
Ultimate Goal: Green, Efficient, Economic impurity separation technologies

1、Importance of metal recovery from the spent LIBs.

☐ Hazardous of spent lithium battery

Diaphragm organic wastes

Electrolyte $LiPF_6$ toxic wastes



Anode： Cu foil and graphite

Cathode： Ni/Co/Mn heavy metals

☐ Critical elements presented in spent LIBs

中华人民共和国自然资源部
Ministry of Natural Resources of the People's Republic of China

能源矿产	石油、天然气、页岩气、煤炭、煤层气、铀
金属矿产	铁、铬、铜、铝、金、**镍**、钨、锡、钼、锑、**钴**、**锂**、稀土 、锆
非金属矿产	磷、钾盐、晶质石墨、萤石

中国发布24种战略性矿产目录(2016)

Europeiska kommissionen

Critical raw materials

Antimony	Fluorspar	LREEs	Phosphorus
Baryte	Gallium	Magnesium	Scandium
Beryllium	Germanium	graphite	Silicon
Bismuth	Hafnium	rubber	Tantalum
Borate	Helium	Niobium	Tungsten
Cobalt	HREEs	PGMs	Vanadium
Coal	Indium	Phosphate rock	

欧盟发布27种关键矿产清单(2017)

U.S. Department of the Interior

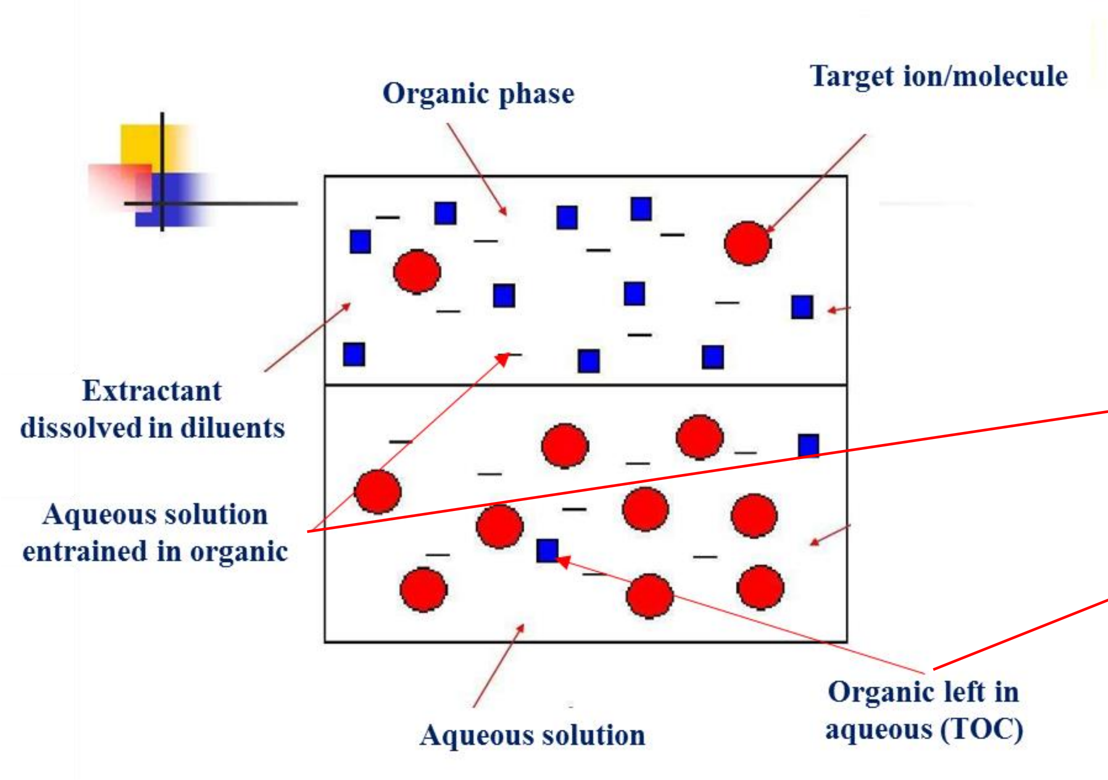
Final List of Critical Minerals 2018

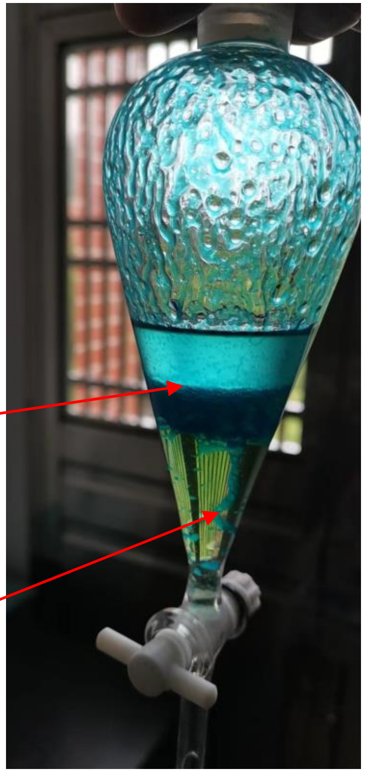
Aluminum (bauxite), antimony, arsenic, barite, beryllium, bismuth, cesium, chromium, cobalt, fluorspar, gallium, germanium, graphite (natural), hafnium, helium, indium, lithium, magnesium, manganese, niobium, platinum group metals, potash, the rare earth elements group, rhenium, rubidium, scandium, strontium, tantalum, tellurium, tin, titanium, tungsten, uranium, vanadium, and zirconium.

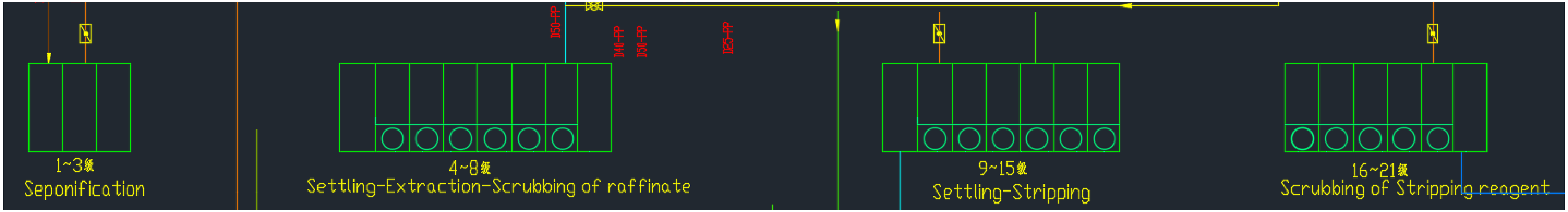
美国公布35种关键矿物目录（2018）

1、Importance of metal recovery from the spent LIBs.

1.plus: Basic conceptions and principles in hydrometallurgy







1.plus: Basic conceptions and principles in hydrometallurgy

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

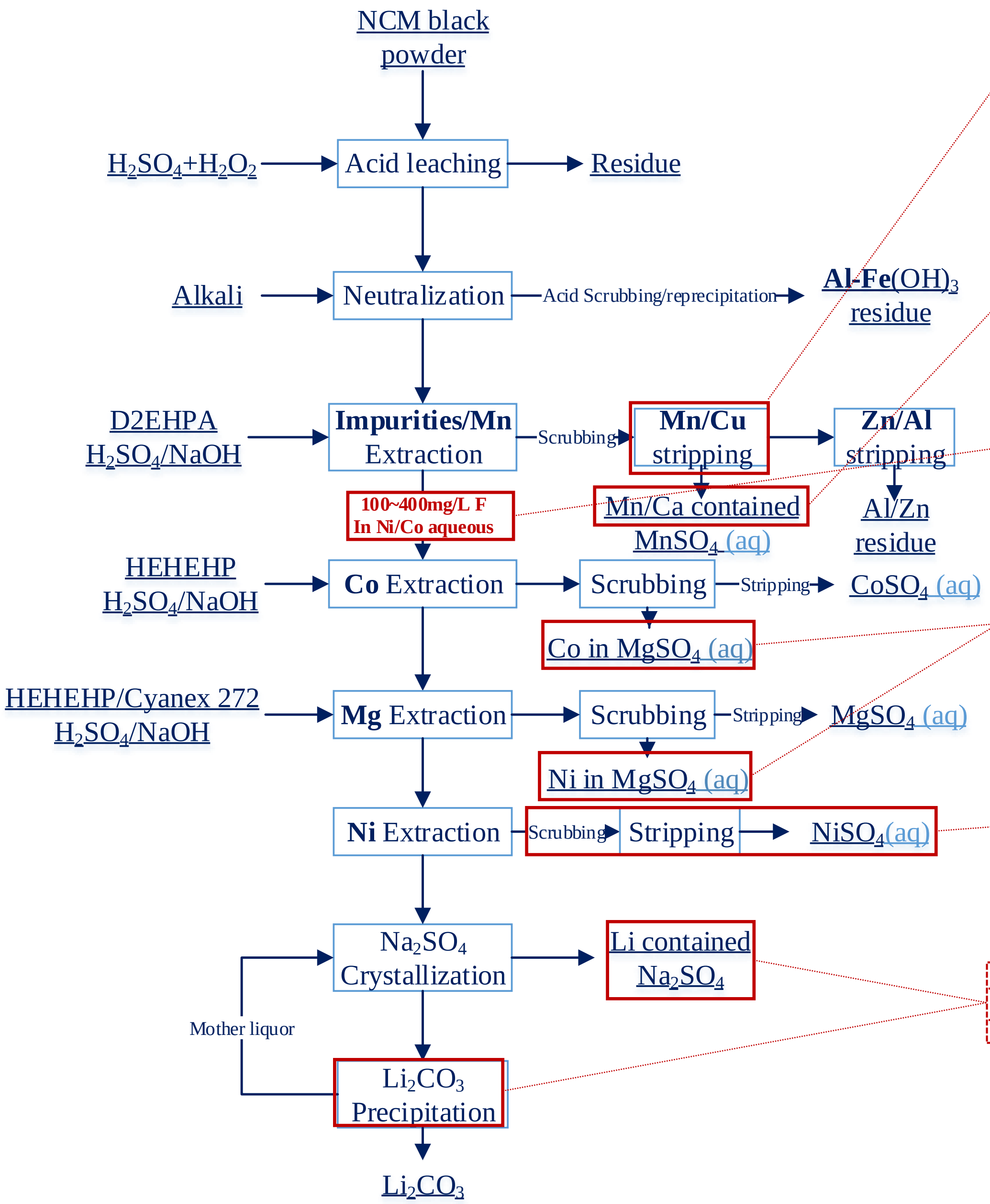
Extraction: $Me^{2+} + 2\,\overline{Na(L.HL)_2} \leftrightarrow \overline{Me(L{\cdot}HL)_2} + 2Na^{+}$

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: <u>Extracting small amount of elements from huge body element is economic</u>

Key challenges presented in the present recovery processes



Issue 1 Scaling of CaSO4 during the Mn/impurities stripping

Issue 2 Separation difficulty of trace Ca^{2+} from $MnSO_4$ aqueous

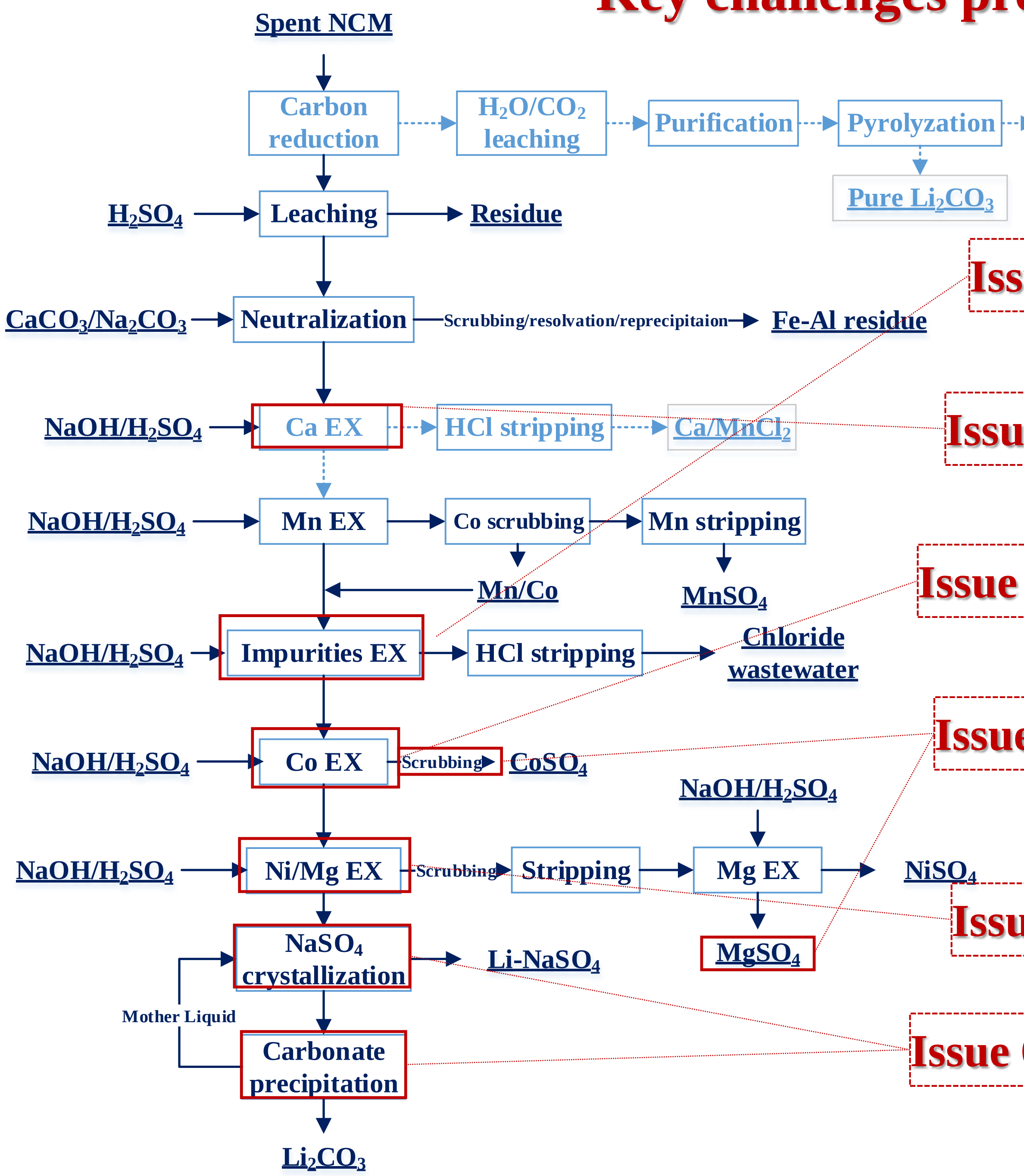
Issue 3 Small amount of F, Equipment corrosion and purity reduction

Issue 4 Small amount of Ni/Co in $MgSO_4$ solution, hard to recover

Issue 5 Massive Li^+ loss in $NiSO_4$ extraction due to co-extraction

Issue 6 Li-end-recover, diluted and significant loss in front operations

Key challenges presented in the present recovery processes



Issue 1 CaSO$_4$ scaling in the impurities extraction with D2EHPA

Issue 2 Separation difficulty of trace Ca^{2+} from MnSO$_4$ aqueous

Issue 3 Small amount of F, Equipment corrosion and purity reduction

Issue 4 Small amount of Ni/Co in MgSO$_4$ solution, hard to recover

Issue 5 Massive Li$^+$ loss in NiSO$_4$ extraction due to co-extraction

Issue 6 Li-end-recover, diluted and significant loss in front operations

Key challenges presented in the present recovery processes

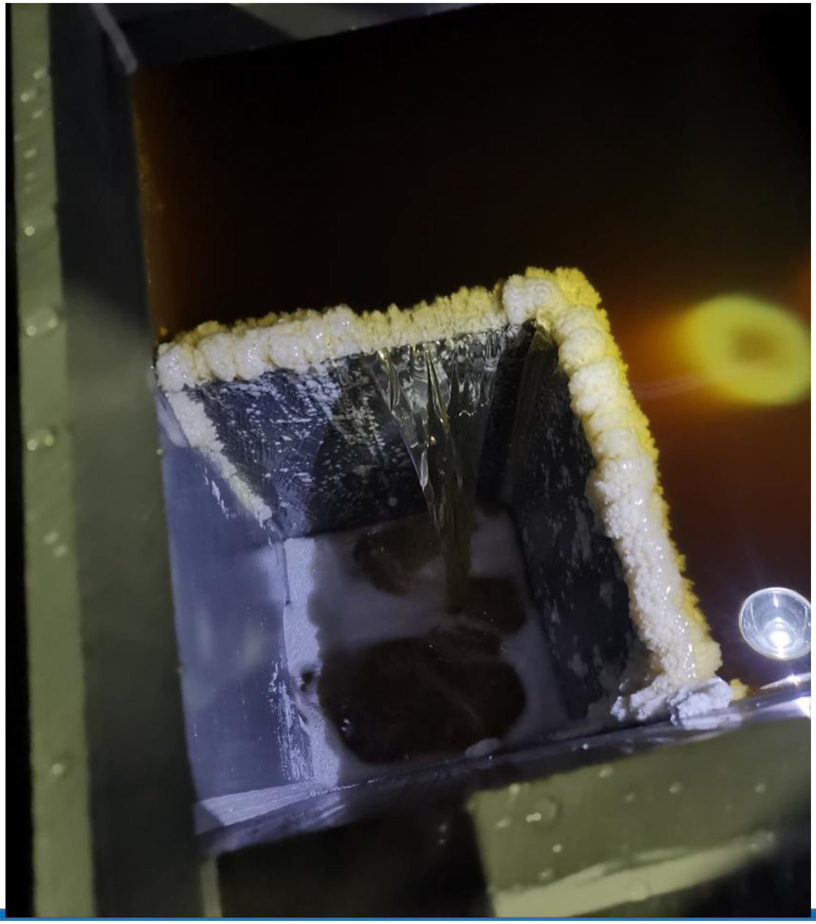
Issues faced by preferential Lithium leaching the carbon reduction calcination process

Explosive applications in Chinese Battery recycling plants in 2021~2022 due to the high lithium price

- 7~9% active carbon powder addition;
- 550~700 ^{o}C calcination at least for 1h;
- Easy to sinter, Reducing Ni/Co/Mn leaching efficiency
- Over reduction of NCM and form alloys
- Low utilization efficiency of CO_2 (~20%) due to the limited solubility of $LiHCO_3$ (6~7g/L Li)
- High total cost: about 800~1200 RMB per ton black mass treatment;
- Low recovery of Li, only 70~85%, with ~1.0% Li left in leaching residue (NCM);

3.1 Selective extraction of Ca from NCM leaching solution

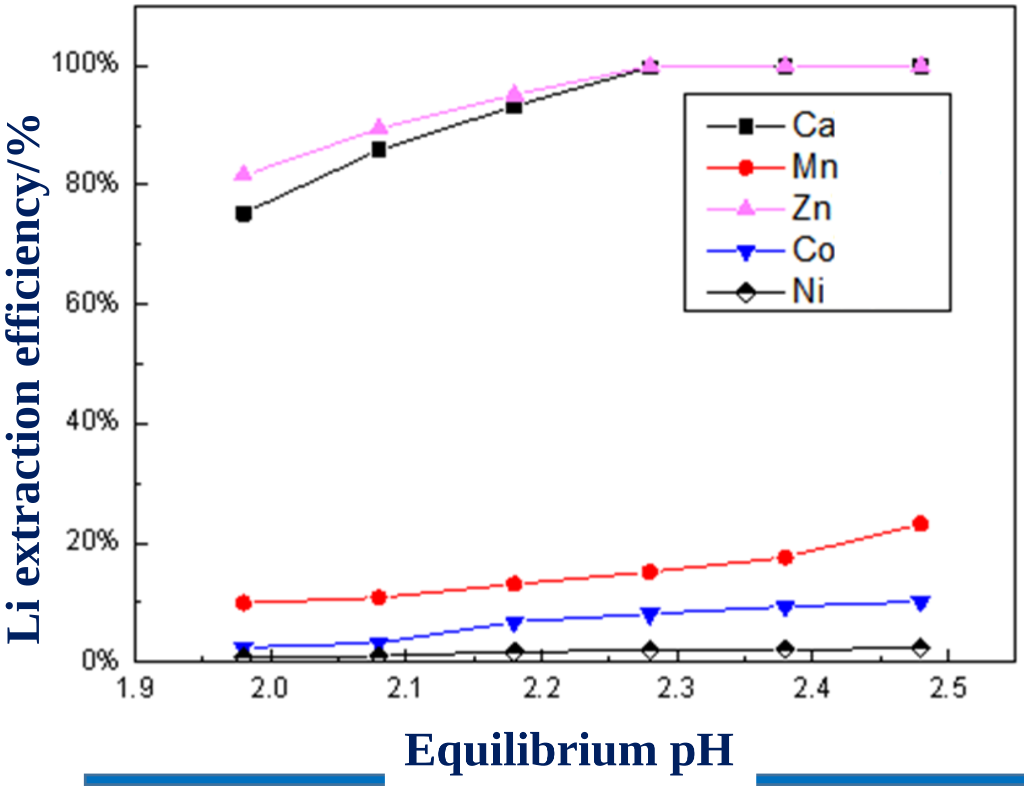
Small amount of 100~500mg/L Ca^{2+} in black mass leaching solution, leading to severe scaling during the scrubbing and stripping section in Mn/Cu/Zn/Al extraction by D2EHPA



Similar cases in Co-medium product recovery

3.1 Selective extraction of Ca from NCM leaching solution

Ca^{2+}/Zn^{2+} can be selectively extracted by HBL-120(HT-040), eliminating the scaling issue during the scrubbing and stripping section in Mn/Cu/Zn/Al extraction by D2EHPA

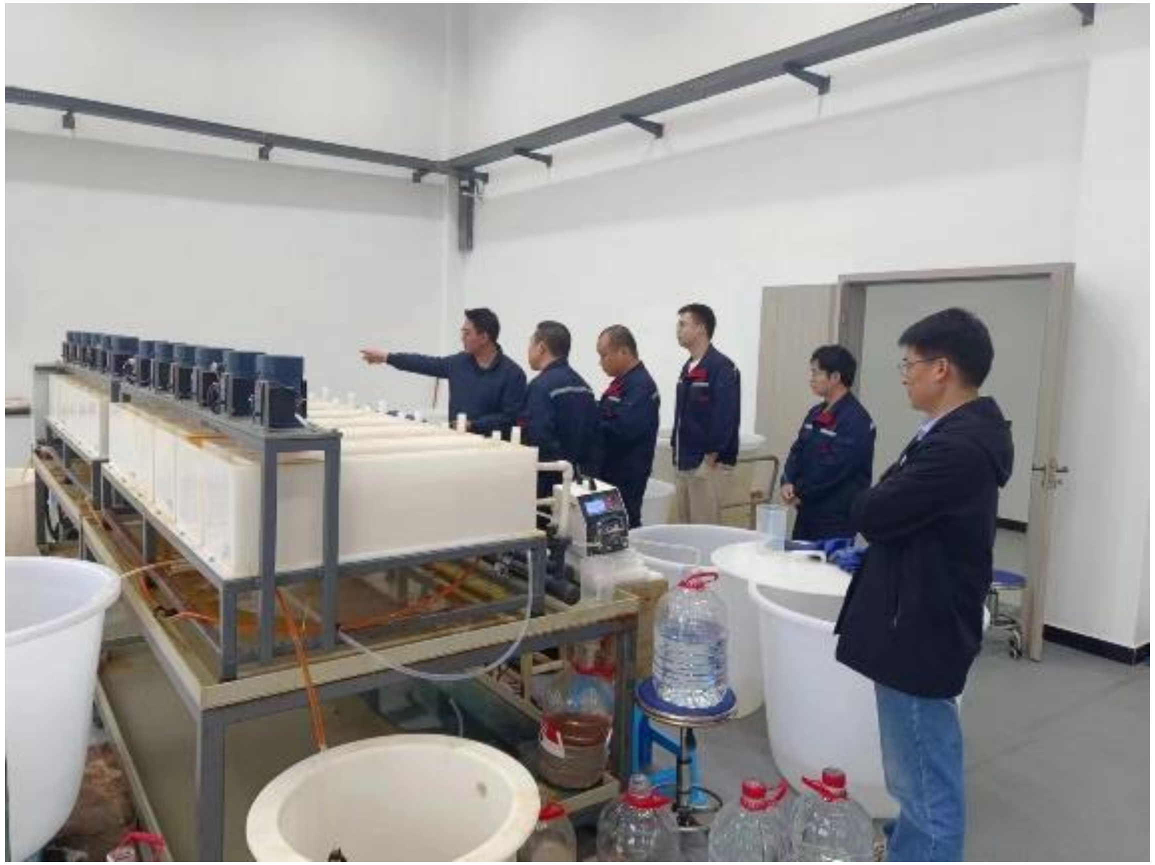


Five-stage of count-current extraction with HT-019-D-Ca

Rows	Equilibrium pH	Cation in raffinate 离子浓度（g/L）				Extraction Efficiency/%			
		Ca	Zn	Co	Mn	Ca	Zn	Co	Mn
Feed	1.15	1.5212	0.0482	1.0674	56.4085	/	/	/	/
Row 13	1.97	0.0463	0.0005	1.0330	55.4325	96.96%	98.96%	3.22%	1.73%
Row 14	1.98	0.0423	0.0008	1.0337	55.6725	97.22%	98.34%	3.16%	1.30%
Row 15	1.97	0.0417	0.0003	1.0324	55.6113	97.26%	99.38%	3.28%	1.41%

3.1 Selective extraction of Ca from NCM leaching solution

Ca^{2+}/Zn^{2+} can be selectively extracted by HBL-120 (HT-040), eliminating the scaling issue during the scrubbing and stripping section in Mn/Cu/Zn/Al extraction by D2EHPA



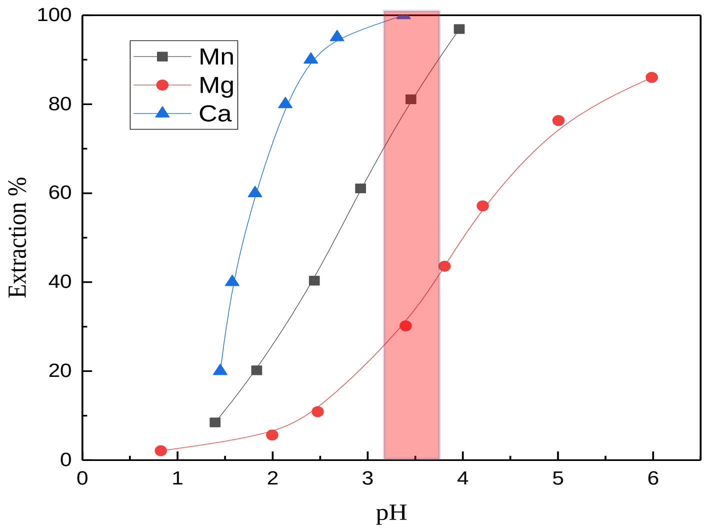
中冶瑞木新能源科技有限公司
MCC RAMU NEW ENERGY TECHNOLOGY CO.,LTD

Pilot Test Line 1 Selectively extraction of Ca^{2+} from NCM black mass leaching solution

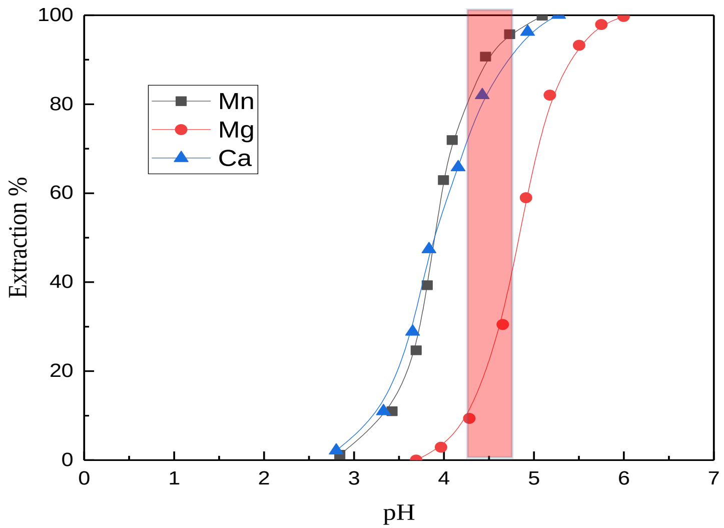
Reagents	NaOH (32%)	H_2SO_4	Solvent Loss	Waste Treatment
Dosage (kg)	0.086	0.18	0.02	0.02

3.2 Deeply removal of trace Ca^{2+} from concentrated $MnSO_4$ solution

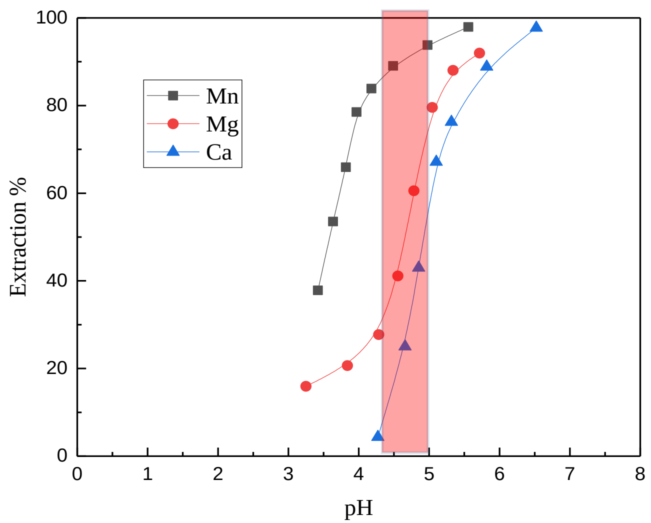
$MnSO_4$ stripped from loaded D2EHPA contains about 100~200mg/L Ca^{2+}, for NCM synthesis, Ca^{2+} should be less than 30mg/L at least



Extraction efficiency of Ca/Mg/Mn vs. pH value by D2EHPA



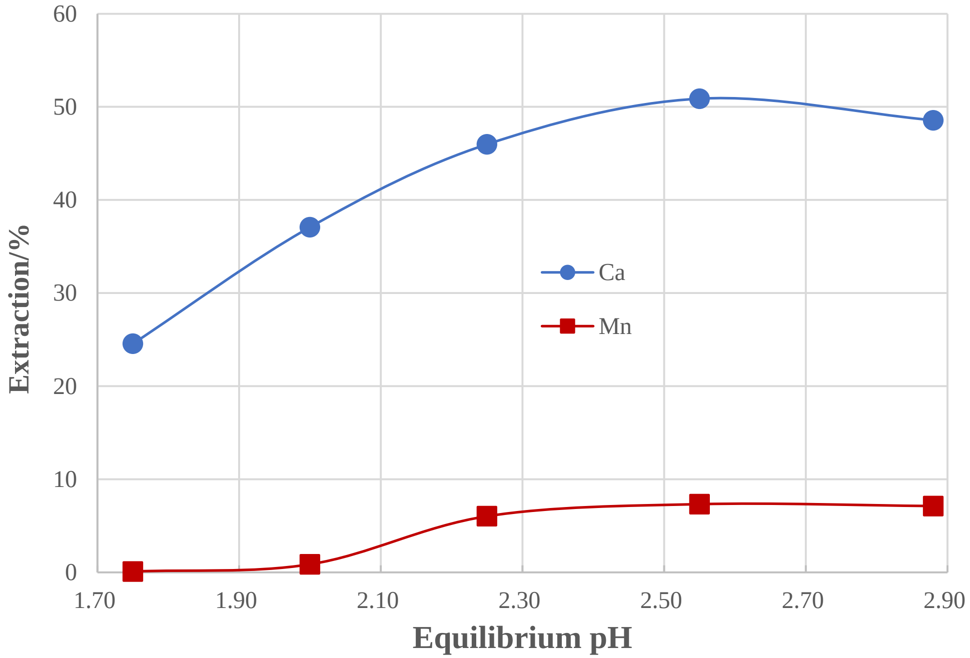
Extraction efficiency of Ca/Mg/Mn vs. pH value by HEHEHP



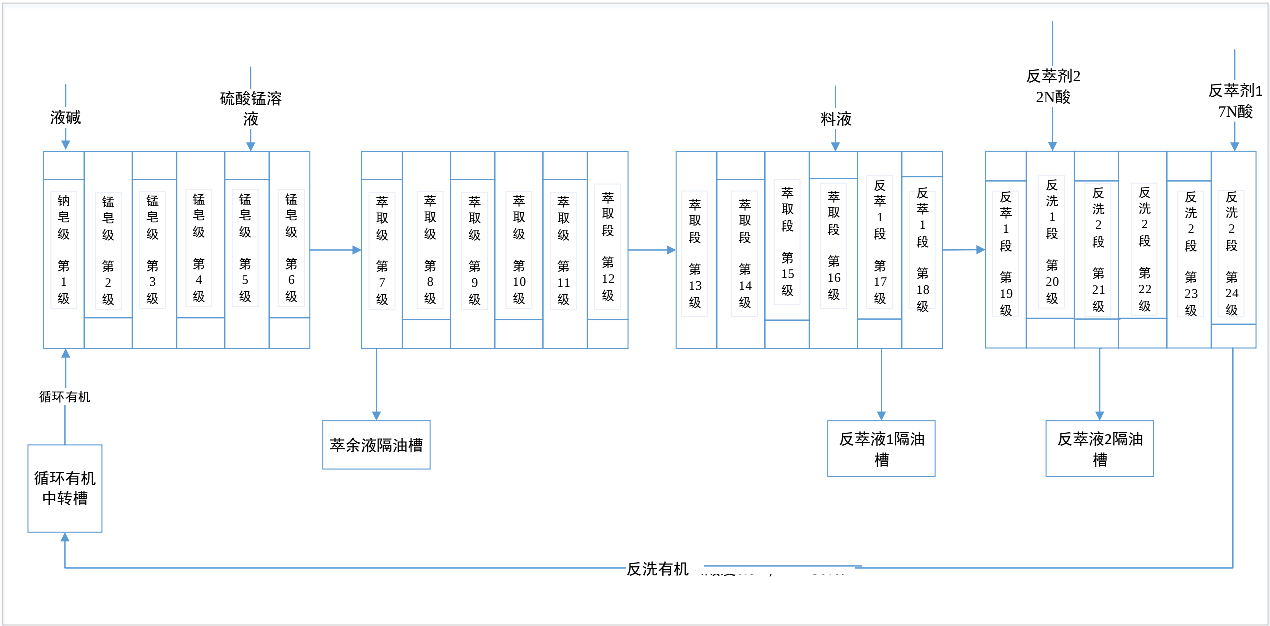
Extraction efficiency of Ca/Mg/Mn vs. pH value by Cyanex272

Traditional extractants can hardly separate Ca/Mg from $MnSO_4$ stripping solutions

3.2 Deeply removal of trace Ca^{2+} from concentrated $MnSO_4$ solution



Extraction efficiency of Ca/Mg/Mn vs. pH value by HT-040

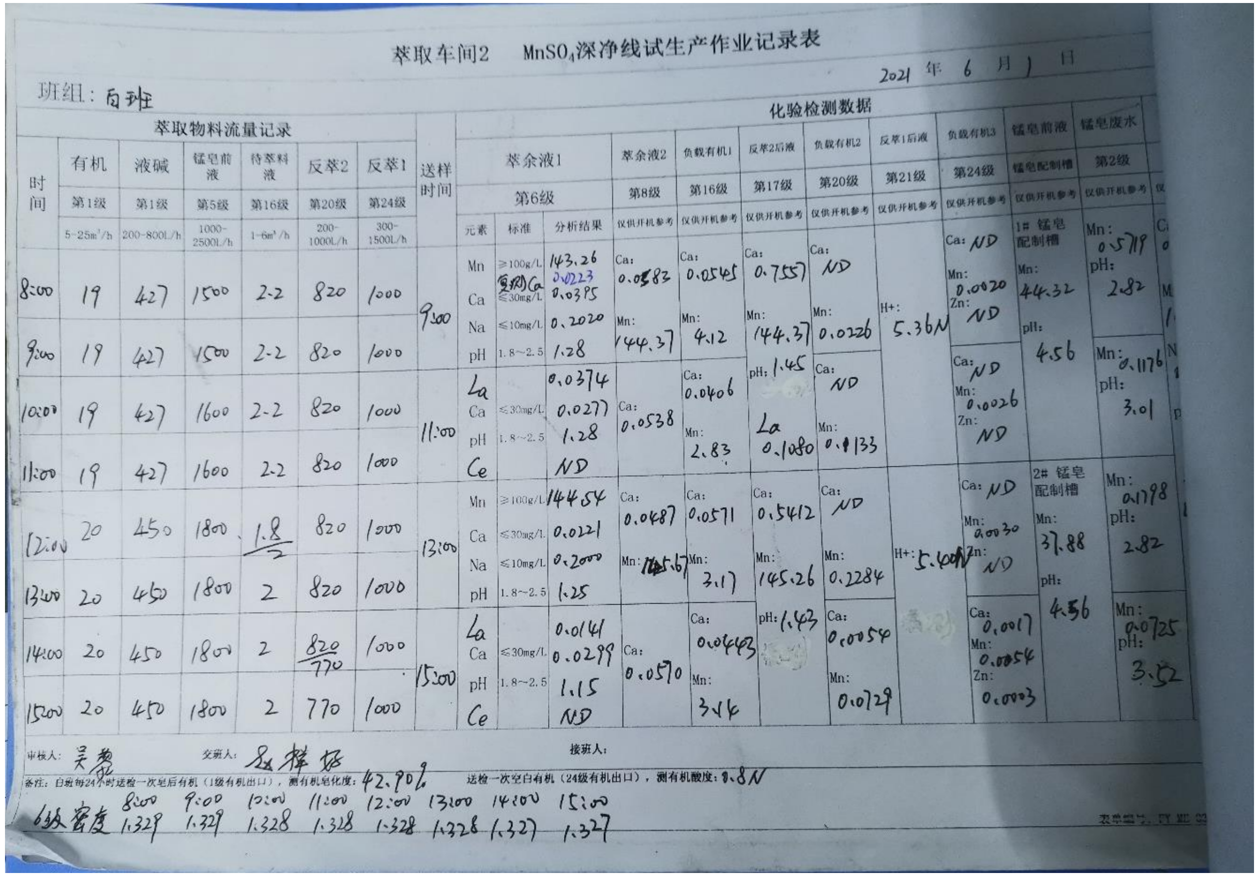


Selective extraction of Ca^{2+} from $MnSO_4$ solution by HT-040

Guangdong Fangyuan New Materials Co., LTD

HBL-120 (HT-040) extraction did reduce the Ca^{2+} in $MnSO_4$ stripping solution from ~100mg/L to <ins><10mg/L</ins> which can be directly used for NCM synthesis (with 0.15% of Mn loss)

3.2 Deeply removal of trace Ca^{2+} from concentrated $MnSO_4$ solution



Production Line 1 Deeply purification of Ca from $MnSO_4$ stripping solution（Launched in Oct. 2020 ）

Guangdong Fangyuan New Materials Co., LTD

3.2 Deeply removal of trace Ca^{2+} from concentrated $MnSO_4$ solution

Production Line 2 Deeply purification of Ca from $MnSO_4$ stripping solution in Fangyuan Cycling plant

（Launched in June. 2022）

3.3 Deeply removal of Fluorine from Ni/Co/Mn sulfate solutions

Leaching solutions of spent LIBs contains 100~400mg/L fluorine originated from $LiPF_6$ and PVDF

And fluorides were introduced to reduce the massive Mg/Ca, left about 3~5g/L of F.

表 1 电池级硫酸钴溶液主要化学成分

项 目	指 标	
	优等品	一等品
钴（Co）g/L	110.00～130.00	
钠（Na）g/L	≤0.0100	≤0.1000
镁（Mg）g/L	≤0.0050	≤0.0100
铅（Pb）g/L	≤0.0020	≤0.0050
氟（F）g/L	≤0.0040	≤0.0100
氯（Cl^-）g/L	≤0.050	≤0.080
油分 g/L	≤0.0100	
pH	2.00～6.00	
磁性异物 g/L	≤0.00002	≤0.0001

表 1 电池级硫酸锰溶液主要化学成分

项 目	指 标	
	优等品	一等品
锰（Mn）g/L	110.00～130.00	
钠（Na）g/L	≤0.0500	≤0.1000
镁（Mg）g/L	≤0.0050	≤0.0100
铅（Pb）g/L	≤0.0020	≤0.0050
氟（F^-）g/L	≤0.0500	≤0.1000
氯（Cl^-）g/L	≤0.0500	≤0.1000
油 g/L	≤0.0100	≤0.0500
pH	1.00～5.00	
磁性异物 g/L	≤0.00002	≤0.00008

表 1 电池级硫酸镍溶液主要化学成分

项 目	指 标	
	优等品	一等品
镍（Ni）g/L	115.00～125.00	
钠（Na）g/L	≤0.5000	≤1.0000
氟（F）g/L	≤0.0040	≤0.0150
氯（Cl^-）g/L	≤0.0100	≤0.1000
油分 g/L	≤0.0050	≤0.0120
pH	2.50～6.00	
磁性异物 g/L	≤0.00002	≤0.00008
水不溶物 w/%	≤0.0040	≤0.0080

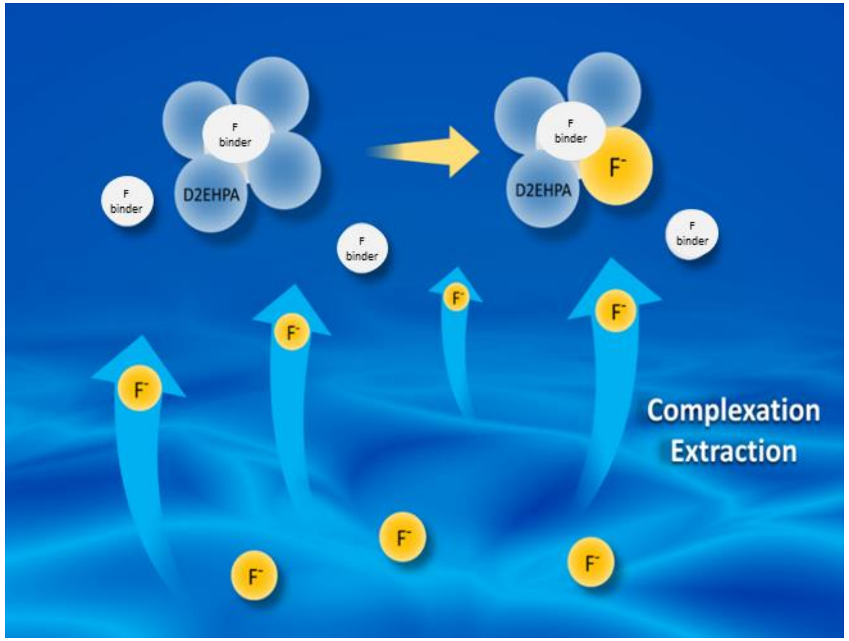
- **Latest battery grade standard (1st class product) requires [F] in Ni/Co/Mn solutions less than 10、15、50mg/L**
- **MVR/MED for Na_2SO_4 evaporation requires the [F] in aqueous less than 50mg/L，generally <10mg/L**
- **Industrial wastewater discharge limits the [F] in final less than 6mg/L**

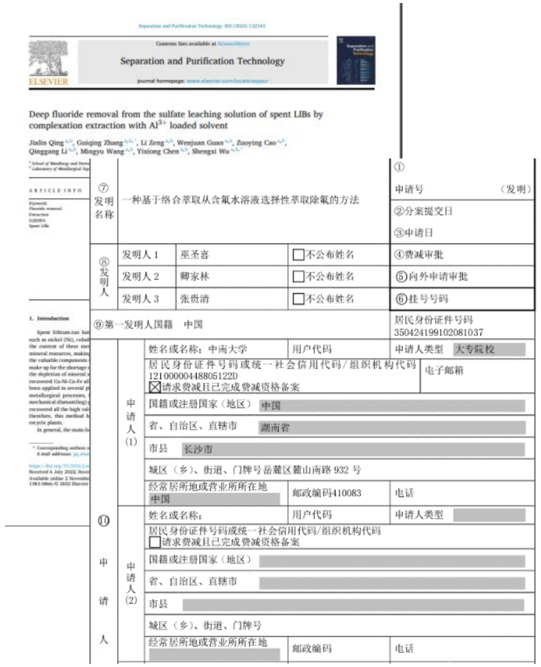
3.3 Deeply removal of Fluorine from Ni/Co/Mn sulfate solutions

Processes	Reagents	Advantages	Disadvantages
Chemical/Flocculation precipitation	Ca/Al salts：Limestone/Calcium chloride/Calcium carbide slag	Simple operation、Economic	Huge amount of wet residue, slow settle rate, high residual F
Adsorption	Rare earth/Al/Zr… based inorganic adsorbents	Recyclable and easy segregation	Limited cycle times、metal loss、secondary hazardous、impurities introduced
Solvent Extraction	Neutral Extractant	Recyclable and Economic	Only HF can be extracted and limited impurities in aqueous solution
Ion Exchange	Amino phosphate resin, Al-loaded resins	Simple operation and Economic	Strict TOC limit in aqueous、limited loading capacity、large amount of wastewater
Other methods	Electrocoagulation, reverse osmosis, crystallization, etc	Simple operation and no waste generation	Fragile film、High power consumption、high residual F

The existing mature defluorination technologies from Ni/Co/Mn sulfate solutions limited by economy, impurities introduction and environmental protection

3.3 Deeply removal of Fluorine from Ni/Co/Mn sulfate solutions




Separation and Purification Technology

ELSEVIER

Deep fluoride removal from the sulfate leaching solution of spent LIBs by complexation extraction with Al^{3+} loaded solvent

Jialin Qing, Guiqing Zhang, Li Zeng, Wenjuan Guan, Zuoying Cao, Qinggang Li, Mingyu Wang, Yixiong Chen, Shengxi Wu

ARTICLE INFO

1. Introduction

⑦发明名称 一种基于络合萃取从含氟水溶液选择性萃取除氟的方法

①申请号 （发明）

②分案提交日

③申请日

⑧发明人 发明人1 巫圣喜 □不公布姓名 ④费减审批

发明人2 卿家林 □不公布姓名 ⑤向外申请审批

发明人3 张贵清 □不公布姓名 ⑥挂号号码

⑨第一发明人国籍 中国 居民身份证件号码 350424199102081037

⑩申请人 申请人(1) 姓名或名称：中南大学 用户代码 申请人类型 大专院校

居民身份证件号码或统一社会信用代码/组织机构代码 12100000448805122D 电子邮箱

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经常居所地或营业所所在地 中国 邮政编码410083 电话

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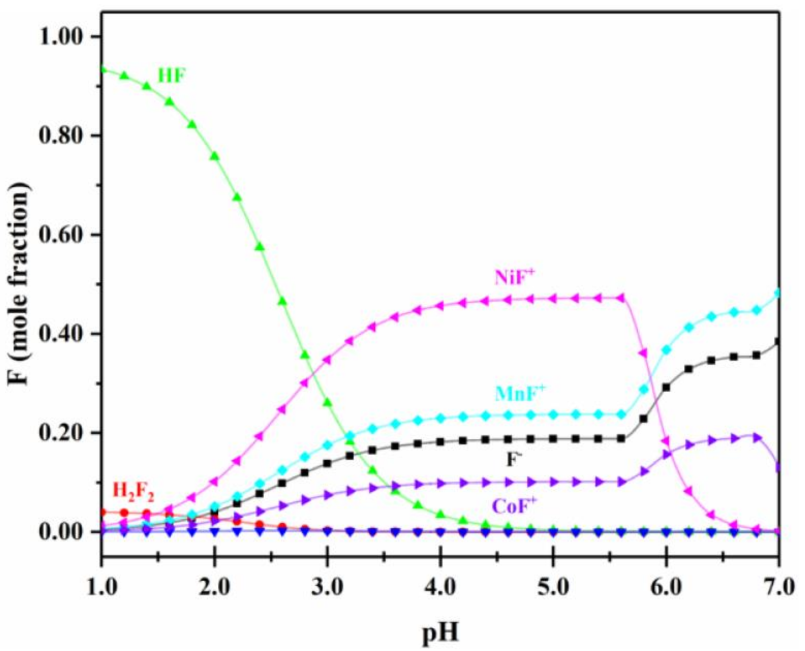
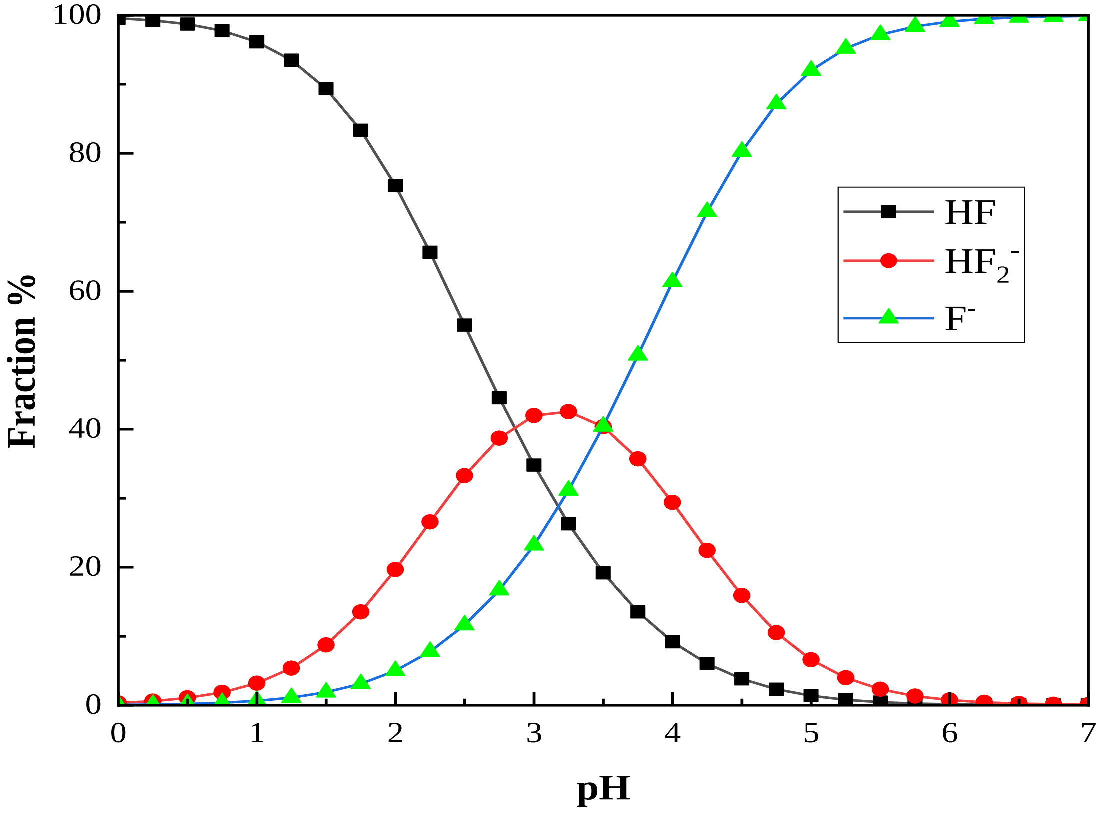


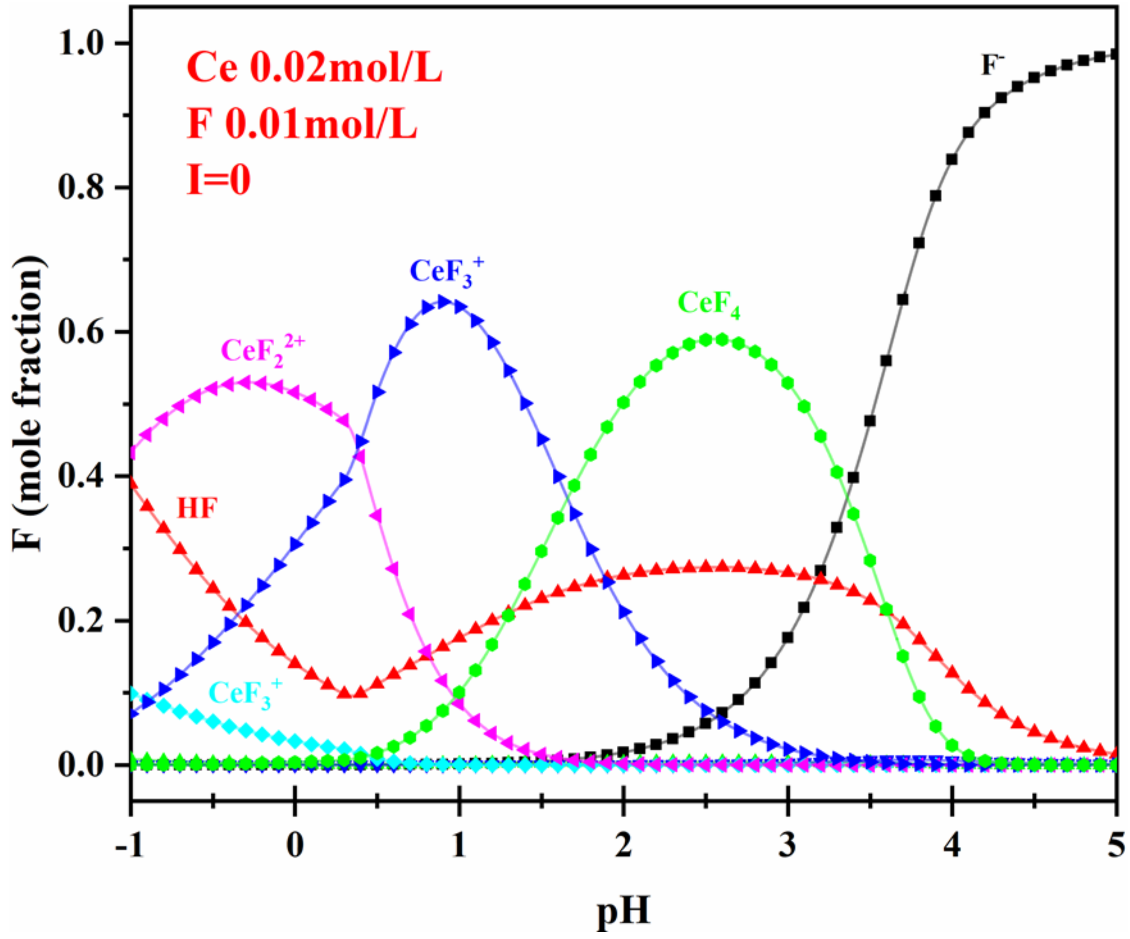
HBL-222 (HT-19-R): Loading F-binder on the carbon chain to complexing F and take the binding complexes into organic phases

HBL-221 (HT-19-D): Extracting HF molecule MeF^{+} and F^{-} by multifunctional group grafting on the carbon chain

3.3 Deeply removal of Fluorine from Ni/Co/Mn sulfate solutions

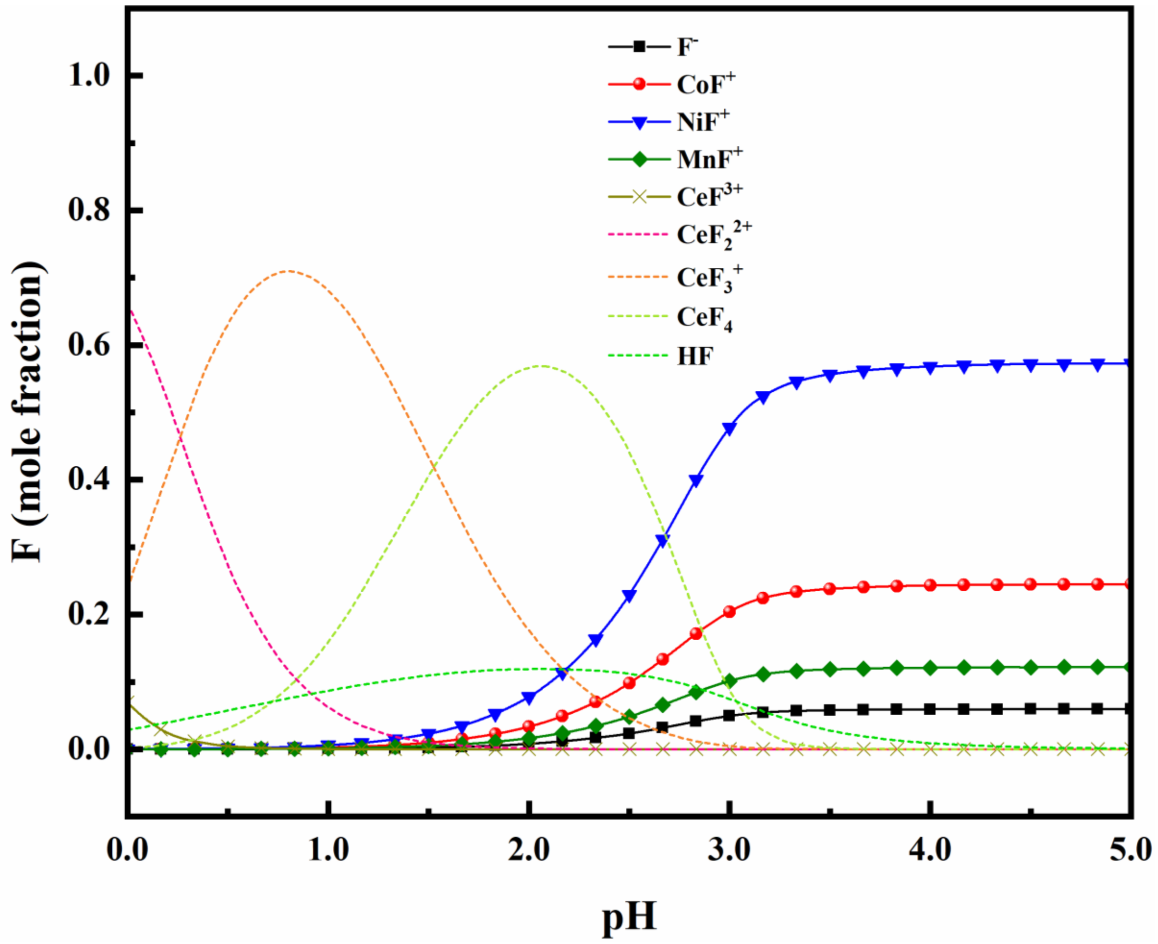


Complexation of fluorine in HF-H_2O aqueous solutions

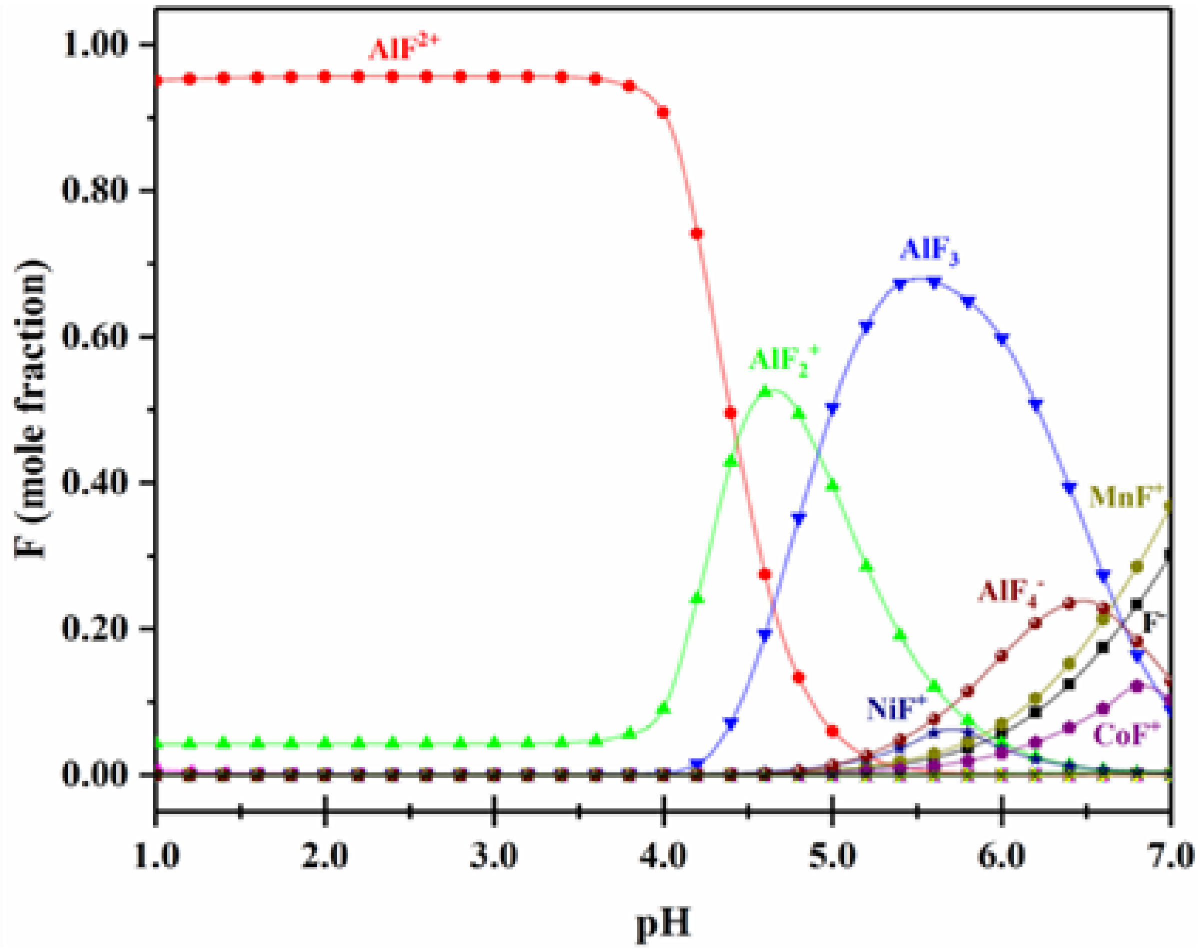


Complexation of fluorine in Ce-F-H_2O aqueous solutions

3.3 Deeply removal of Fluorine from Ni/Co/Mn sulfate solutions

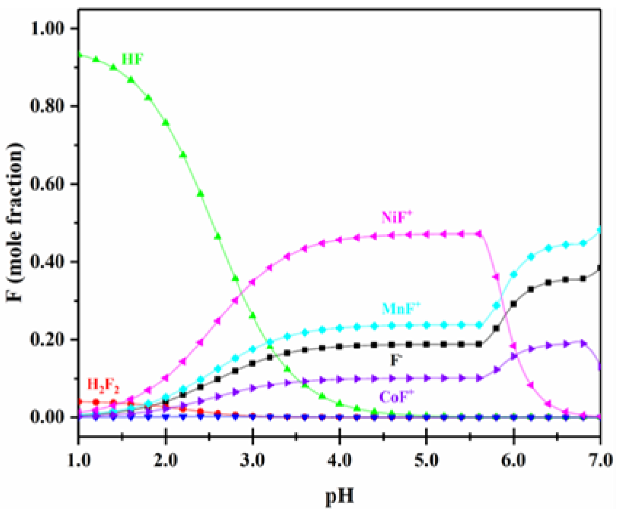


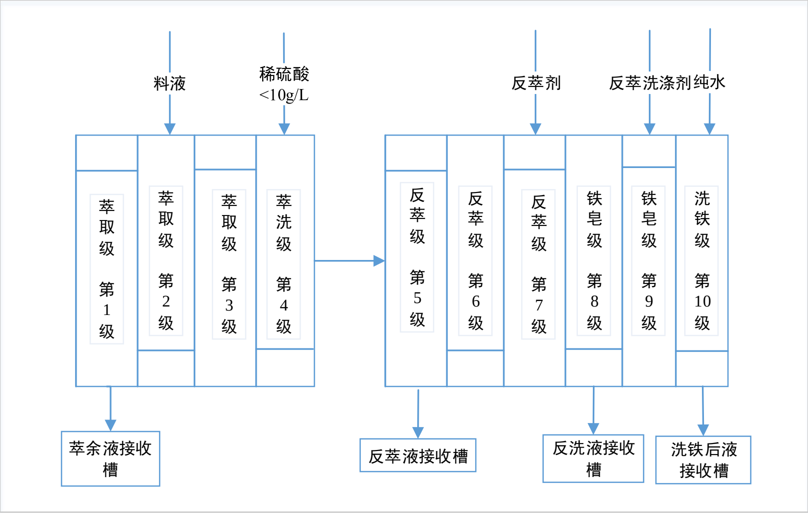
Complexation of fluorine in Ce/Ni/Co/Mn-F-H_2O aqueous solutions



Complexation of fluorine in Al-F-H_2O aqueous solutions

3.3 Deeply removal of Fluorine from Ni/Co/Mn sulfate solutions





Times	pH	$[F]_{aq}$ /(mg L^{-1})
1	2.67	106.98
2	2.46	18
…		
7	2.47	12.51
8	2.43	8.09
9	2.41	4.21
10	2.44	3.10

- HBL-121 (HT-19-D) extraction has been used for F removal from Ni/Co/Mn sulfate solutions provided by Guangdong Fangyuan New Materials Group; Hunan Brunp Recycling; Jiangxi Ruida technology and showed an excellent F removal efficiency with only <5mg/L left.
- HBL-121 (HT-19-D) which can also used for Fluorine removal from Li leaching solutions.

3.3 Deeply removal of Fluorine from Ni/Co/Mn sulfate solutions

Pilot Scale Line 2 Deeply removal of F from Ni/Co/$MnSO_4$ solutions by HBL-222 (HT-019-R)(the left one, 15-stage extraction), HBL-221(HT-019-D) (the right one, 10-stage extraction) for Brunp Recycling（conducted during Oct. 2022 ）

3.3 Deeply removal of Fluorine from Ni/Co/Mn sulfate solutions

Extraction 7-stage， scrubbing 2-stage，
stripping 4-stage， scrubbing 2-stage；

Element	Ni	Co	Mn	Fe	F
Feed	20.21g/L	9.27g/L	5.87g/L	3.2mg/L	3.31g/L
Raffinate	18.90g/L	8.58g/L	5.46g/L		~0.223g/L
Stripping solution	0.004g/L	0.001g/L	0.18g/L	--	~18g/L

Reagents	H_2SO_4	NaOH (10mol/L)	Solvent	Recycled product
Consumption for treating per m^3 solution	22kg	17.8L	~40mg	6.8kg NaF， equal to 52 ¥
Price of reagent	500 ¥ /t	1080 ¥ /t	<100000 ¥ /t	
Cost	10 ¥	19.2 ¥	<4 ¥	

3.3 Deeply removal of Fluorine from Ni/Co/Mn sulfate solutions

Extraction 4-stage， scrubbing 2-stage，
stripping 4-stage， scrubbing 3-stage；

Element	pH	Ni	Co	Mn	Fe	F
Feed	5.8	31.37g/L	13.87g/L	15.49g/L	3.2mg/L	147mg/L
Raffinate	--	28.95g/L	11.88g/L	14.36g/L		~6.78mg/L
Stripping solution		0.028g/L	0.018g/L	2.29g/L	--	~1.33g/L

Reagents	H_2SO_4	Crude $AlSO_4$ (Al 15.6%)	$FeSO_4$	Solvent	CaO
Consumption for treating per m^3 solution	2.88kg	2.50kg	0.35kg	~30mg	1.98kg
Price of reagent	500 ¥ /t	600 ¥ /t	800 ¥ /t	<100000/t	600 ¥ /t
Cost	1.44 ¥	1.5 ¥	0.28 ¥	<3 ¥	1.18 ¥

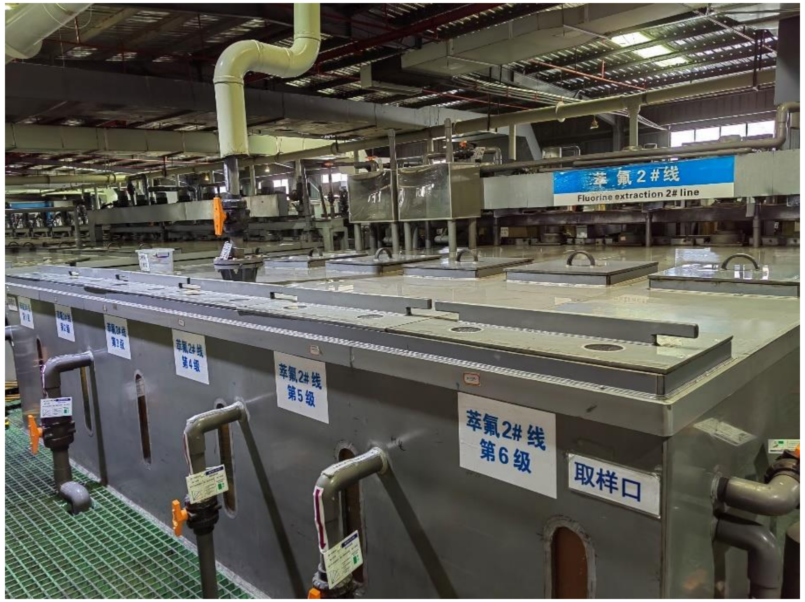
3.3 Deeply removal of Fluorine from Ni/Co/Mn sulfate solutions

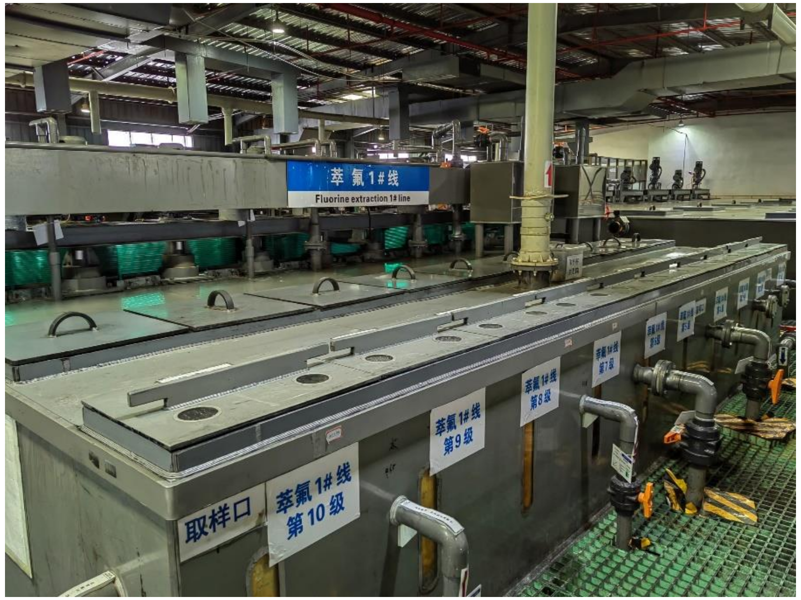
表 4-1 连续运转实验结果

2021/5/27							
萃取流比 1：1，洗涤流比 10：1，反萃流比 8：1，反洗流比 10：1（其中反洗液并入反萃液中）							
时间	料液		萃余液		氟移除率/%	反萃液	
	F(mg/L)	pH	F(mg/L)	pH		F(mg/L)	pH
流量	37.5ml/min，		41.2ml/min，			4.69ml/min，	
12:00			33.70	2.23	92.62		~1.5
13:00			21.80	2.10	95.23		
14:00	456.81	5.06	19.98	2.05	95.63		
15:00			9.96	2.13	97.82		
16:00			10.38	2.13	97.73		
17:00			9.11	2.16	98.01	435.98	
18:00			9.11	2.08	98.01	593.11	
19:00	416.80	5.40	3.98	2.13	99.05	593.11	
20:00-21:50 关机，21:50-00:10 调整反萃、反洗级液面至平衡；萃余液 Ni 39490mg/L, Co 42920, Mn 6150, Zn 612.8, Si 37.18, Fe 2							

Pilot Scale Line 3 Deeply removal of F from Ni/Co/MnSO$_4$ solutions by for Jiangxi Ruida Technology Limit.（conducted during Feb. 2021 ）

3.3 Deeply removal of Fluorine from Ni/Co/Mn sulfate solutions



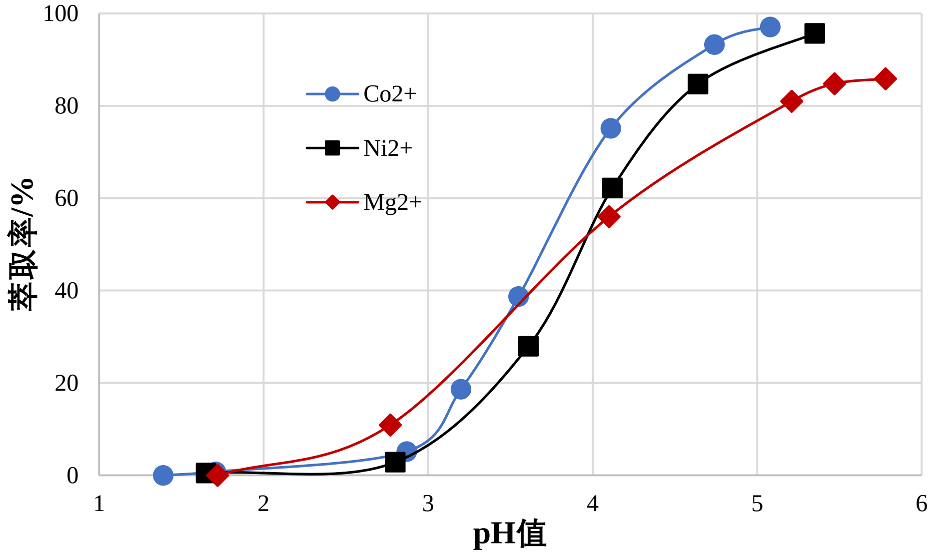


Reagents	Stripping reagent	Scrubbing acid	CaO
Consumption kg/m^3	0.5	1.7	10
Price (RMB/t)	830	500	500
Cost （RMB）	0.42	0.85	5

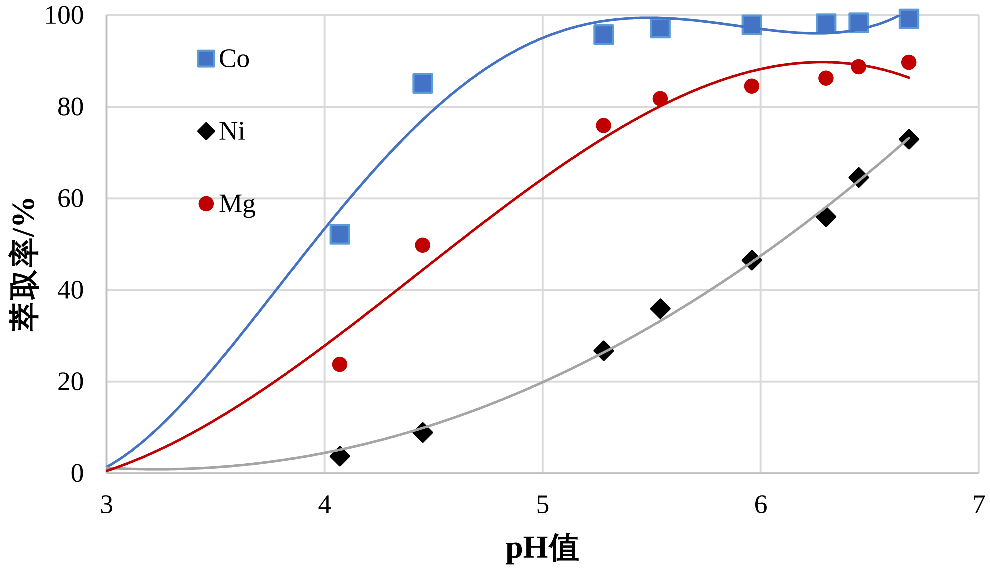
3 Production Lines: Deeply removal of F from Ni/Co/$MnSO_4$ solutions by for Jiangxi Ruida Technology Limit &Guangdong Fangyuan New Materials Co., LTD（**launched in Nov. 2021, June 2022**）

3.4 Selectively extraction of Ni/Co from $MgSO_4$ solutions

Scrubbing aqueous solutions contains Mg：30~60g/L and Ni、Co:1~5g/L. Traditional treatments: Na2S precipitation at acidic pH (H_2S gas) and produces Ni/CoS solid that is difficult to recover.



Extraction efficiency of Ni/Co/Mg vs. pH by D2EHPA

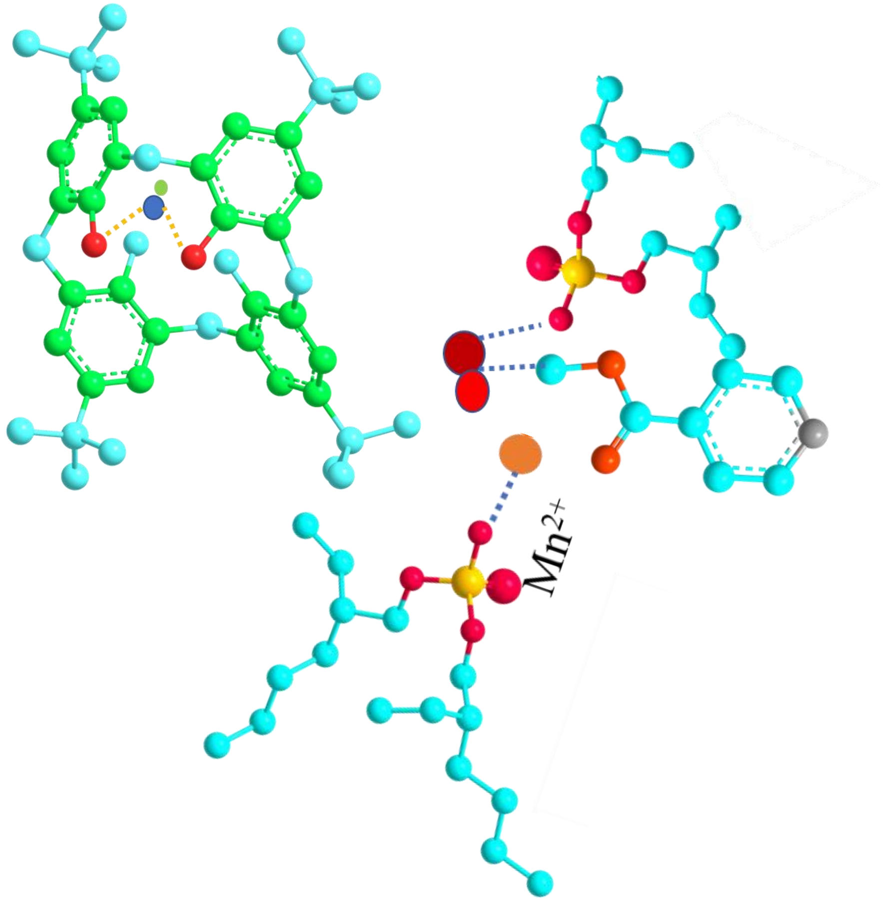


Extraction efficiency of Ni/Co/Mg vs. pH by HEHEHP

Extraction of small amount of Ni/Co from massive Mg is an ideal method.

However, the existing extractants can not achieve this goal.

3.4 Selectively extraction of Ni/Co from $MgSO_4$ solutions



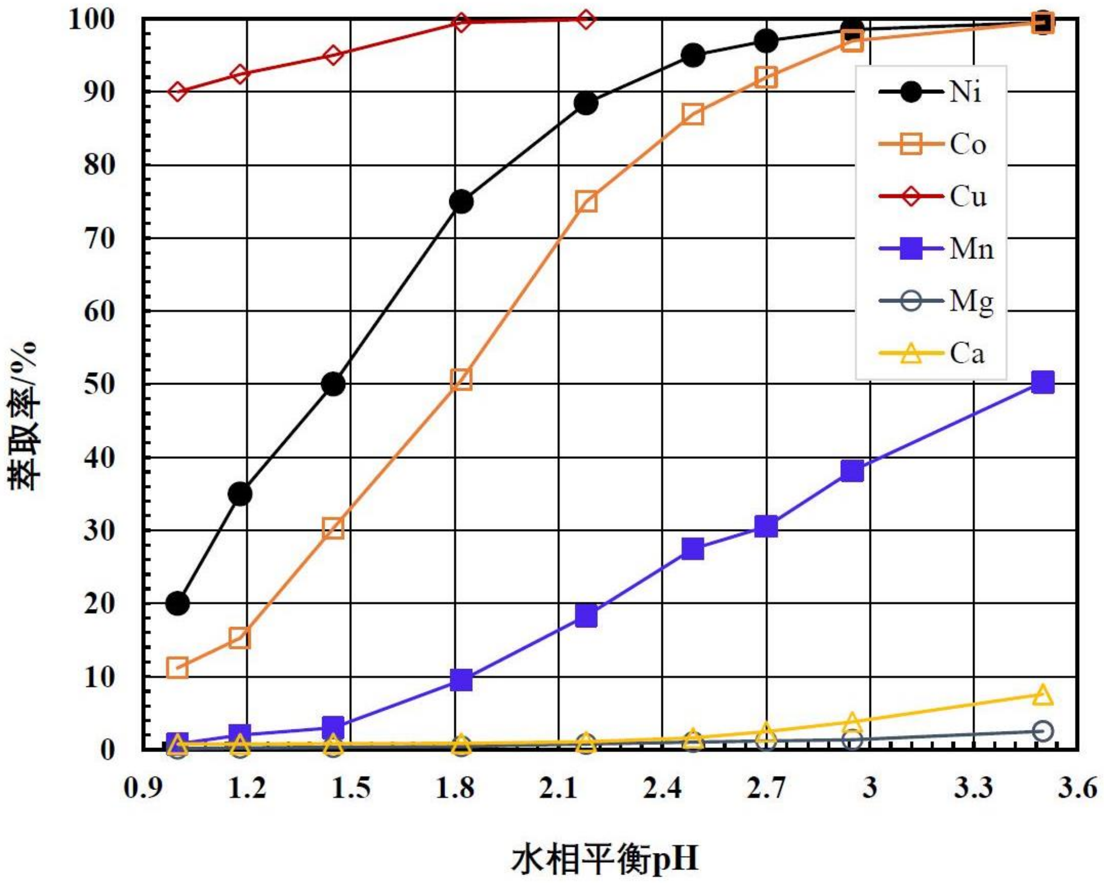
Synergistic extractants

- A represents an acidic organic binder for cation exchange.
- B is a neutral extraction agent，providing coordination atom for target ions

HBL-120/HLB-221/ 222/ 116…

HT-040、HT-19-R/D、59、7…

3.4 Selectively extraction of Ni/Co from $MgSO_4$ solutions

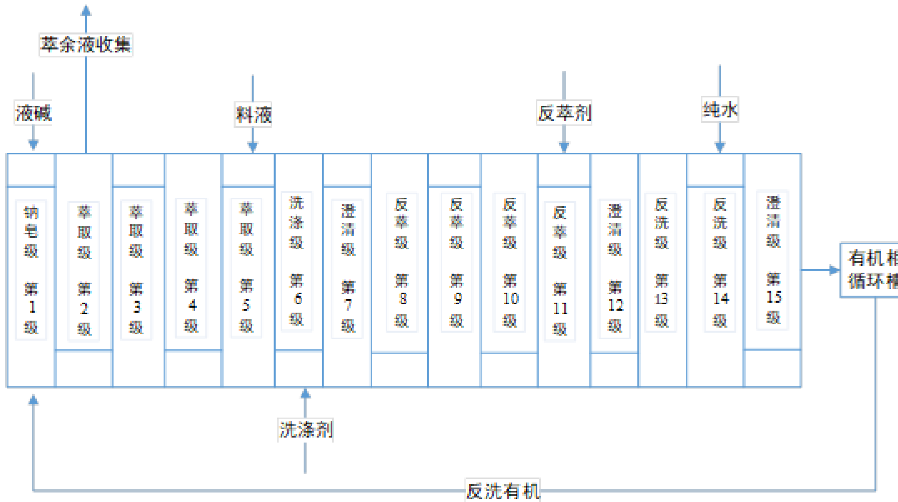


Extraction isothermal of metal cations by HT-059

Excellent separation coefficient between Ni/Co to Mg was achieved by HBL-116（HT-059）

排数	萃余液含 Ni (g/L)	萃余液含 Co (g/L)	萃余液含 Mg (g/L)	萃余液 pH
1	1.523	2.543	60.22	2.39
2	0.003	0.013	--	3.61
3	0.002	0.013	--	3.63
4	0.003	0.007	--	3.71
5	0.0005	0.003	--	3.80
6	0.0007	0.003	--	3.61
7	0.0008	0.003	--	3.58
8	0.0008	0.007	60.41	3.50
9	0.0006	0.002	60.82	3.53

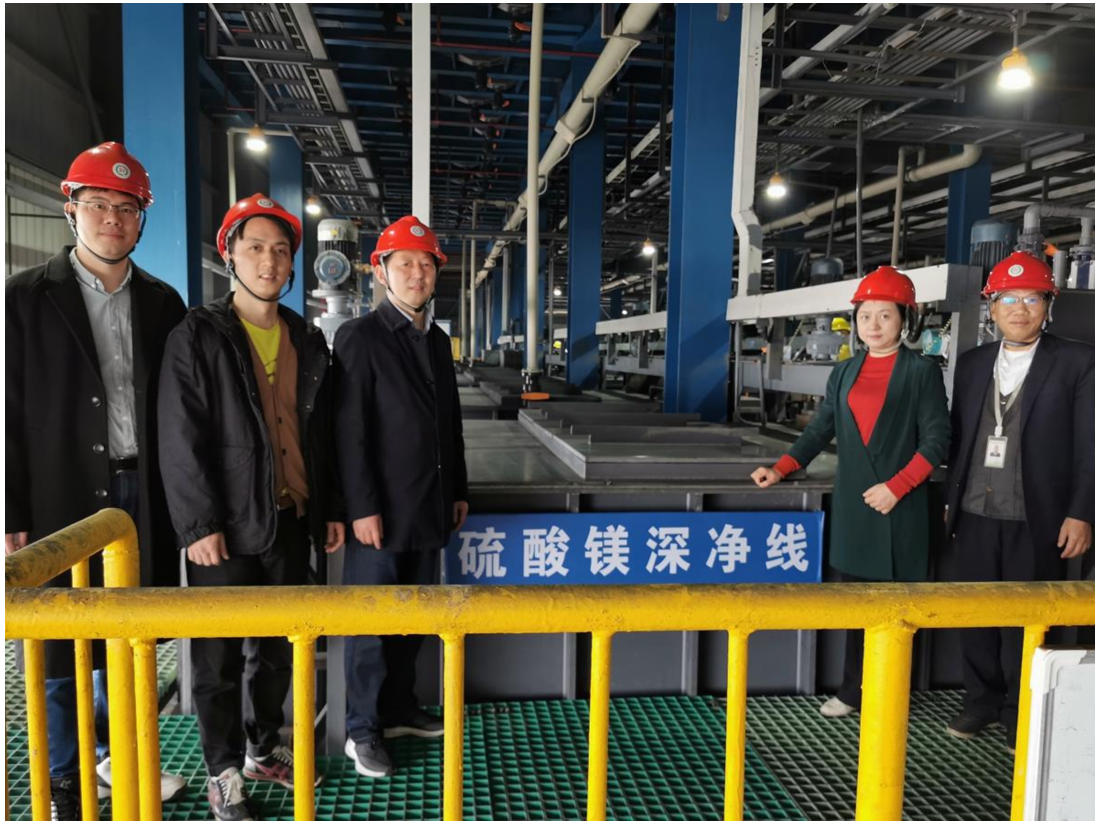
3.4 Selectively extraction of Ni/Co from $MgSO_4$ solutions



	水相					有机相			水相
	Co	Mg	Ni	pH	NH3-N	Co	Mg	Ni	Fe
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	/

Pilot Scale Line 4： Selectively extraction of Ni/Co from $MgSO_4$ solutions by HBL-116(HT-059) for Huayou Cobalt Quzhou, Zhejiang.（conducted during June. 2021 ）

3.4 Selectively extraction of Ni/Co from $MgSO_4$ solutions



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

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

（launched in June 2020 ）

Raffinate TOC：8.14-16.06ppm，COD：59.43-96.68ppm

Stripping TOC: 4.19-10.97ppm，COD：28.04-40.67ppm

3.4 Selectively extraction of Ni/Co from $MgSO_4$ solutions

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 (1462m^3/d)

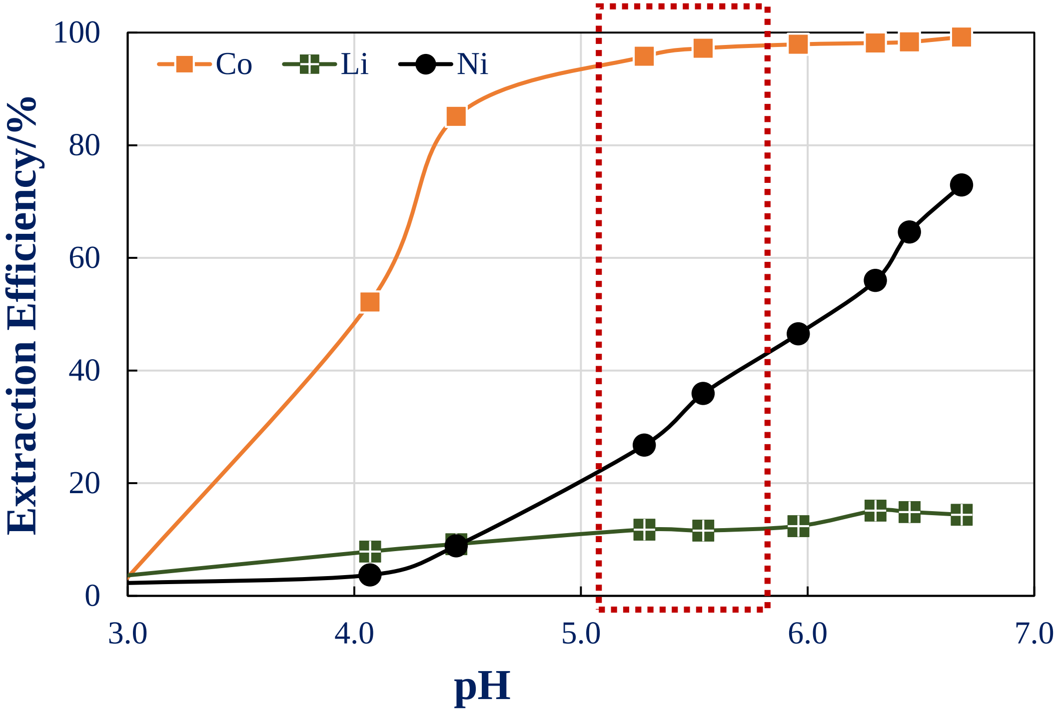
原液成分							
Ni(g/L)	Co(g/L)	Mg(g/L)	NH_4^+(g/L)	SO_4^{2-}(g/L)	油分(mg/L)	Cod(g/L)	pH
1.12	0.10	3.38	27.48	93.04	40-60	1.2	5.0-5.5

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	/

3.5 Selectively extraction of Ni from Li by HT-059

Extraction of Ni by HEHEHP (PC-88A/P507) leads to ~8% of Li loss

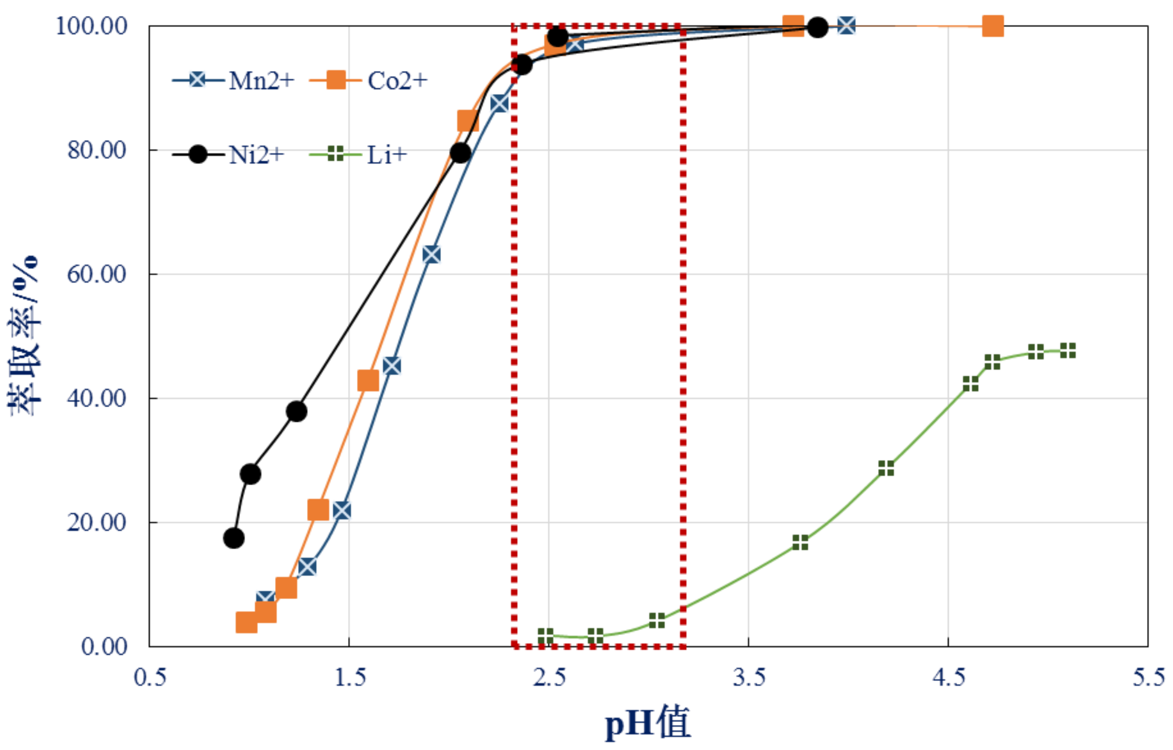


Extraction isothermal of metal cations by P507

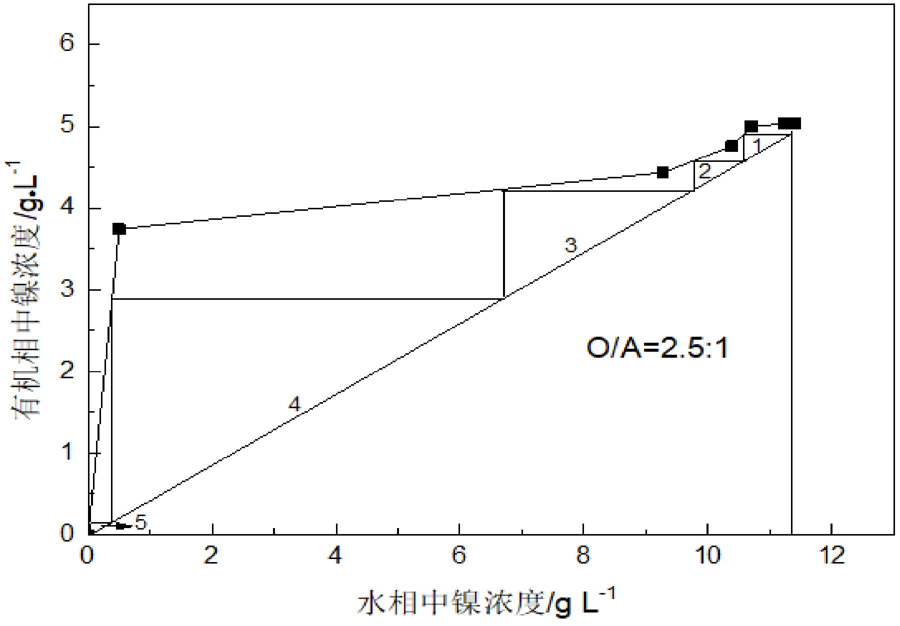
Separation coefficient for Ni to Li by P507 is 10~20

1. Dozens of scrubbing stages, low production efficiency
2. Massive of Ni was co-scrubbed, increasing H^+/ OH^- consumption significantly
3. Uncompleted separation of Li from Ni ($NiSO_4$ contains about 2g/L Li)
4. Huge amount of scrubbing water dilutes the Li in the raffinate

3.5 Selectively extraction of Ni from Li by HT-059



Extraction isothermal of metal cations by HT-059

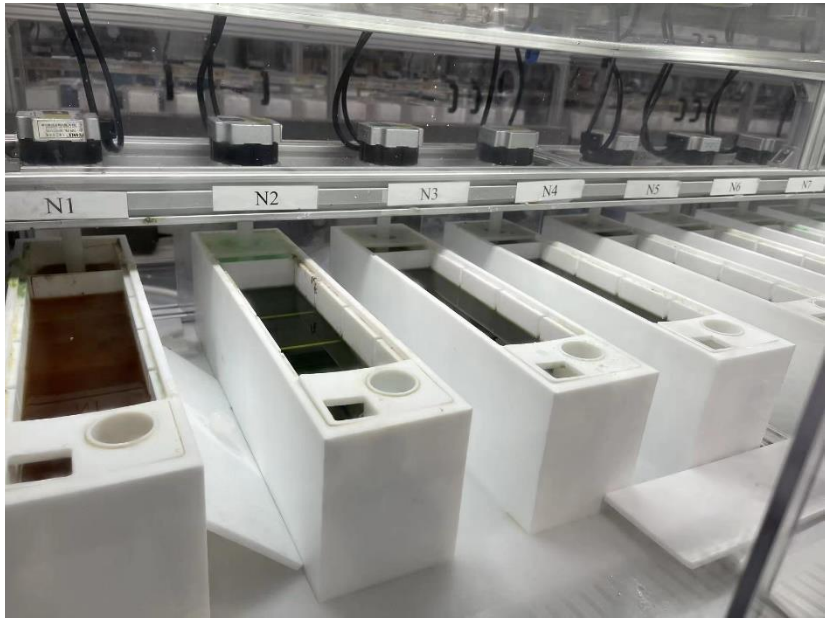


Elements	Concentration/g L^{-1}			Efficiency/%
	Feed	Raffinate	Organic	
Ni	10.96	0.0010	4.083	99.98
Li	2.862	2.855	0.0015	<0.1

Using (HBL-116)HT-059 with 5 stages count current extraction could selectively extract Ni from Li

3.5 Selectively extraction of Ni from Li by HT-059

Lanzhou Jintong Energy Storage New Materials Co., LTD., Austin Elements, USA, adopted HT-59 for Ni&Co co-extraction to prepare high-purity sulfate mixed liquor pilot line, Guizhou Dalong Huicheng heavy metal slag acid leaching solution HT-59-1 Ni, Co&Mn co-extraction to prepare battery grade Ni, Co&Mn sulfate mixed aqueous solution production line (2021~2023)

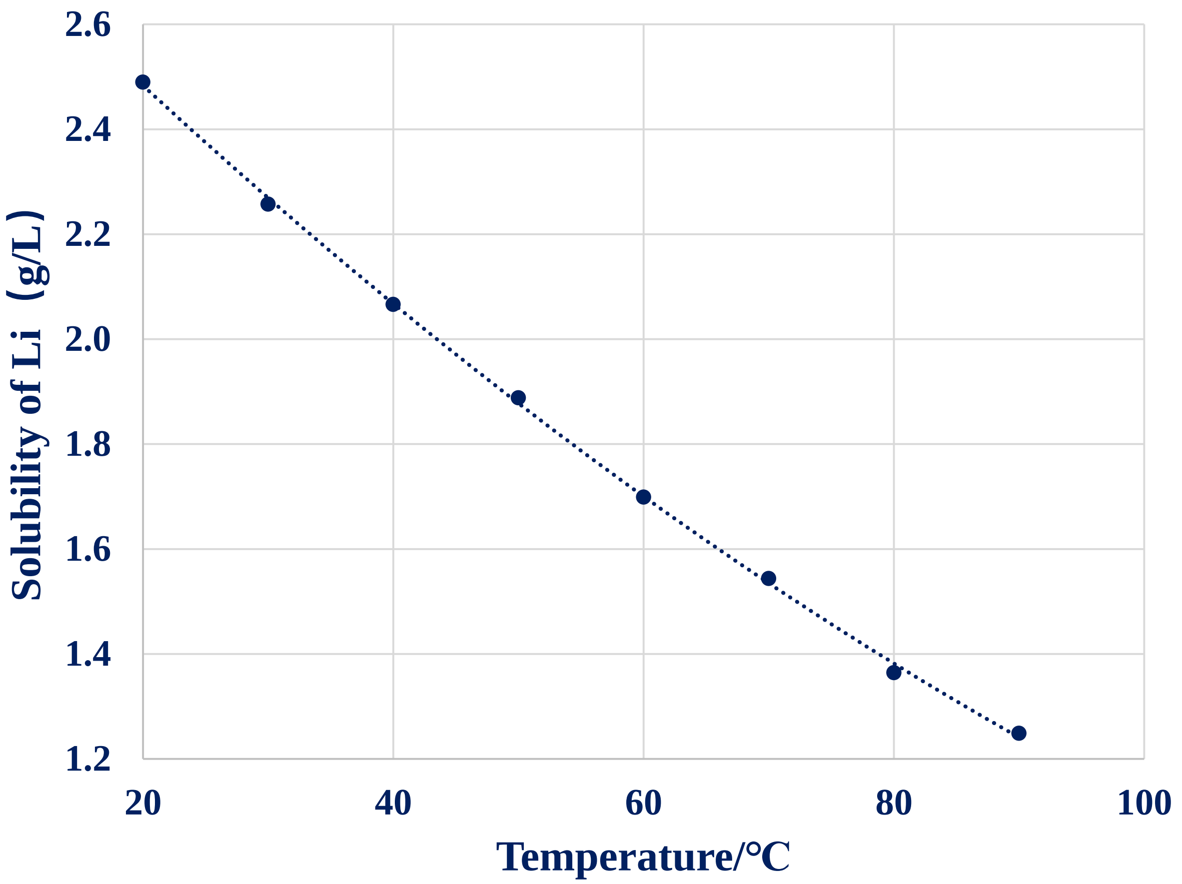


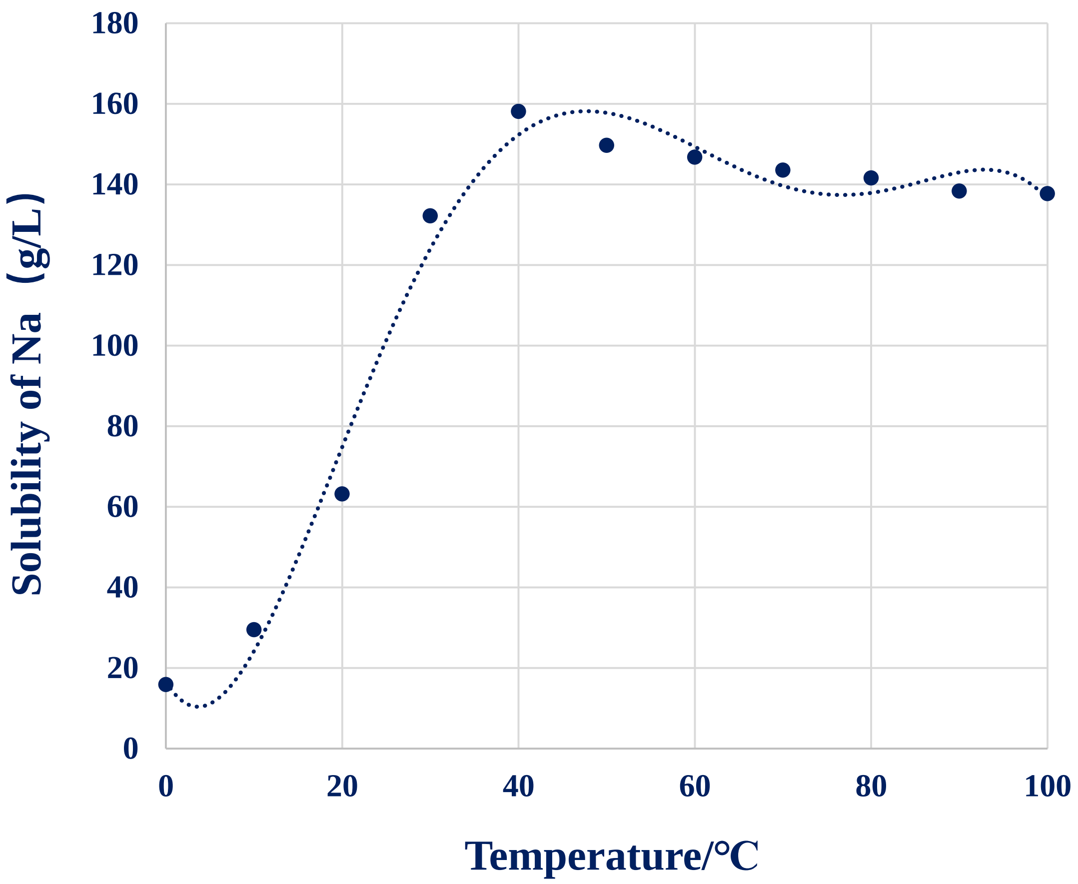
2.6 Separation of Li from the spent LIBs

Traditional processes recovery Li at the last step, loss massive Li in front operations, high energy consumption, high recovery cost

1. Large amount of scrubbing water from extraction operations of Ni、Co、Mg、Ni, Li concentration in aqueous solution was diluted from 10g/L to 2~3g/L;
2. ~5% Li was entrained (isomorphous substitution) in Na_2SO_4 crystals during the evaporation concentration of Li from 2~3g/L to 10g/L;
3. Lower limit of Li is 2g/L for carbonate precipitation, indicating a direct recovery ~80%, the mother liquor needed a second evaporation and re-precipitation!

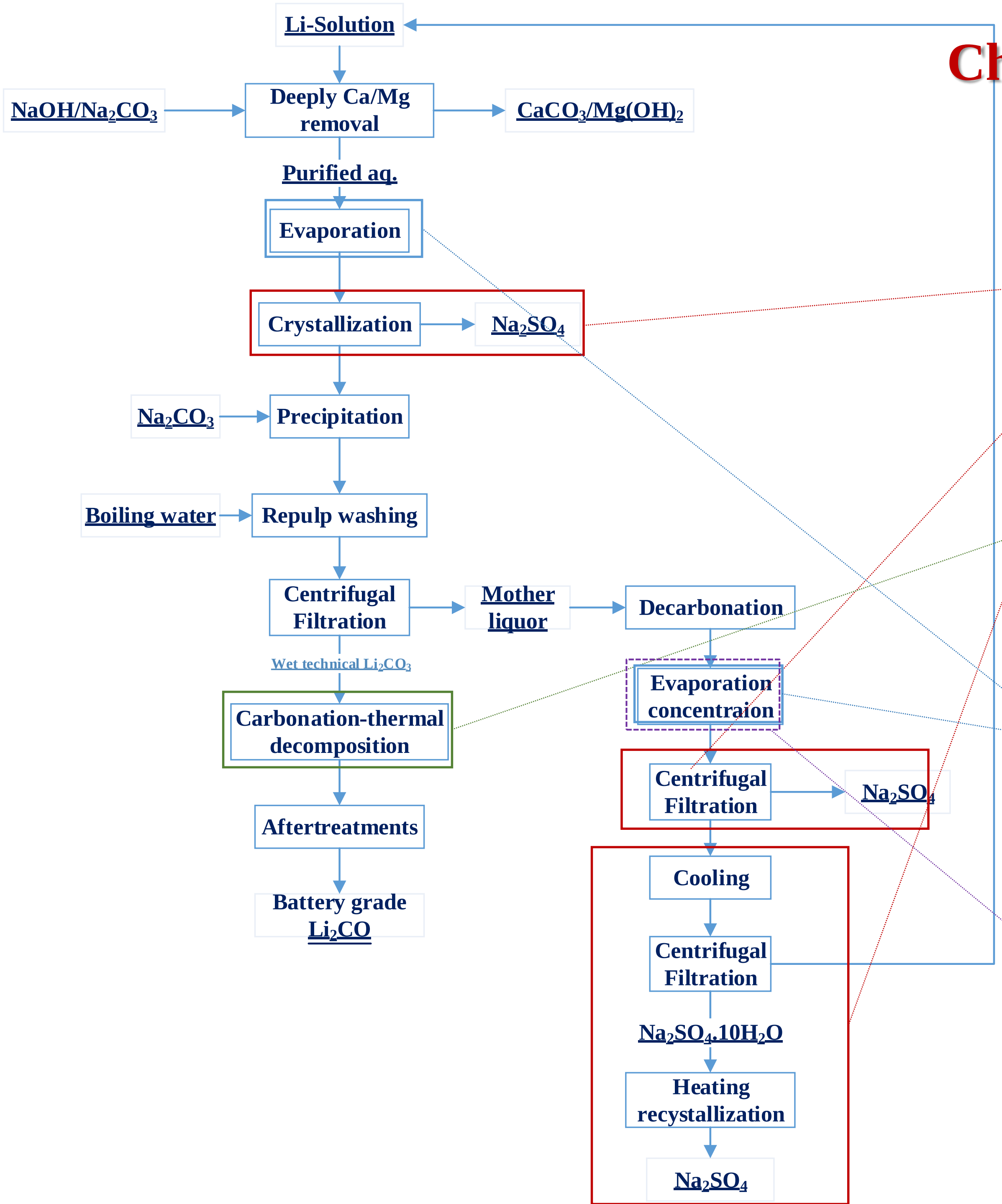
2.6 Separation and recovery of Li from the spent LIBs





Traditional separation Na/Li based on the solubility variation between Na/Li at high/low temperature

Challenges faced by traditional Li recovery method



Issue 1
Difficulty in Li separation from High Na/K
Long process, Low recovery, High cost

Issue 2
Extra Carbonation purification process
High CaPEX & Opex, extra ion exchange

Issue 3
Repeatedly evaporation-cooling, low [Li]
Energy intensity, expansion of mother liquor

Issue 4
Circulation of mother liquor for Li recovery
Accumulation of anion impurities, COD

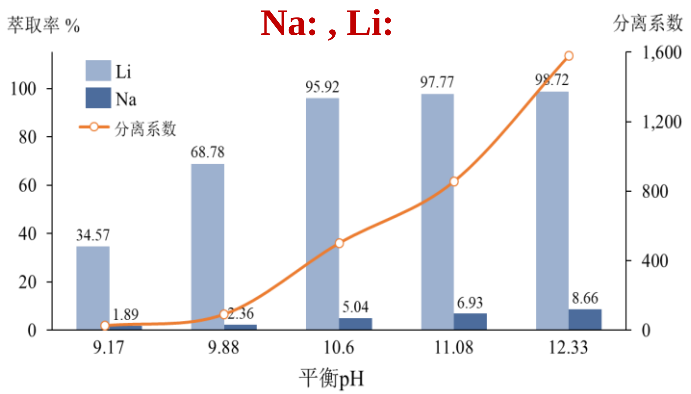
2.6 Separation of Li from the spent LIBs

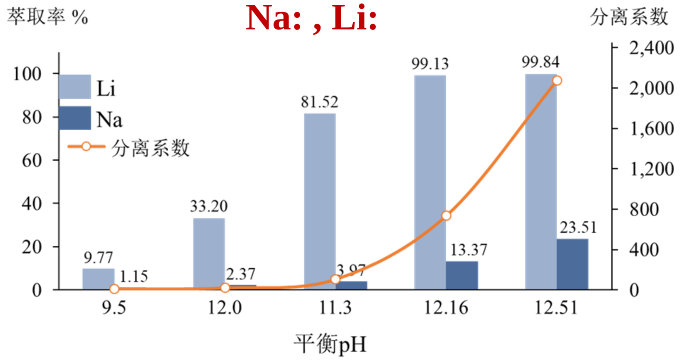
Li extracted species obtained by different authors.

β-diketone	ligand	Extracted species	Reference
LIX 54	Cyanex 923	$\overline{Li(A)(Cyanex\ 923)}$	Current study
LIX 54	TOPO	$\overline{Li(A)(TOPO)_{1.3}}$	Kunugita et al. (1989)
HTTA	TOPO	$\overline{Li(TTA)(TOPO)_2}$	Healy (1968)
HTTA	TOPO	$\overline{Li(TTA)(TOPO)_2}$	Kim et al. (2003)
HTTA	PHEN	$\overline{Li(TTA)(PHEN)}$	Ishimori et al. (2002)
HTTA	DMP	$\overline{Li(TTA)(DMP)}$	Ishimori and Imura (2002)

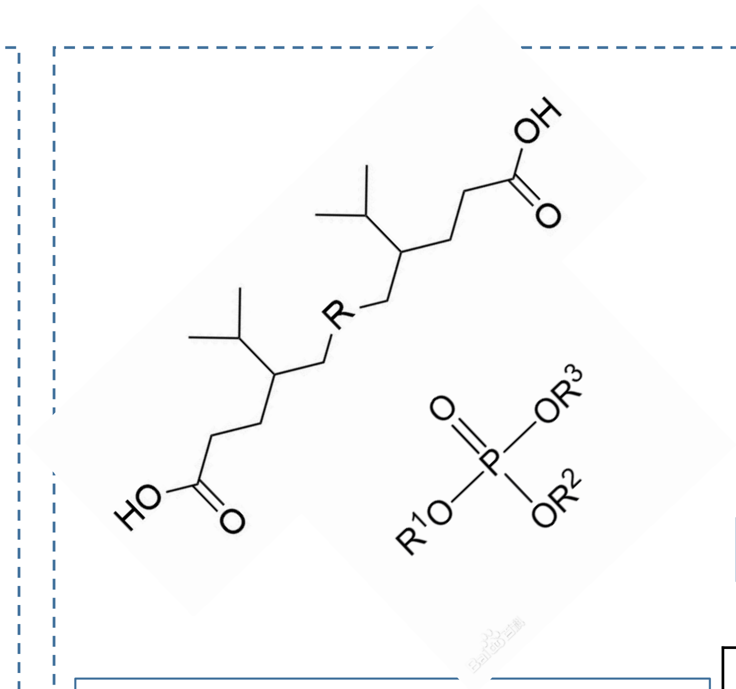
- **Low loading capacity, <2g/L Li^+ with >40 vol% of mixed Lix54+Cyanex923/TOPO**
- **Poor phase segregation performance, >10min of phase separation time**
- **Easily emulsification generation once pH variation >1.0 or >2.0g/L Li^+ loaded in organic**

2.6 Selectively extraction of Li from Na_2SO_4 by HT-007





- **Excellent Li extraction efficiency and Li to Na separation coefficient（1600-2000）；**



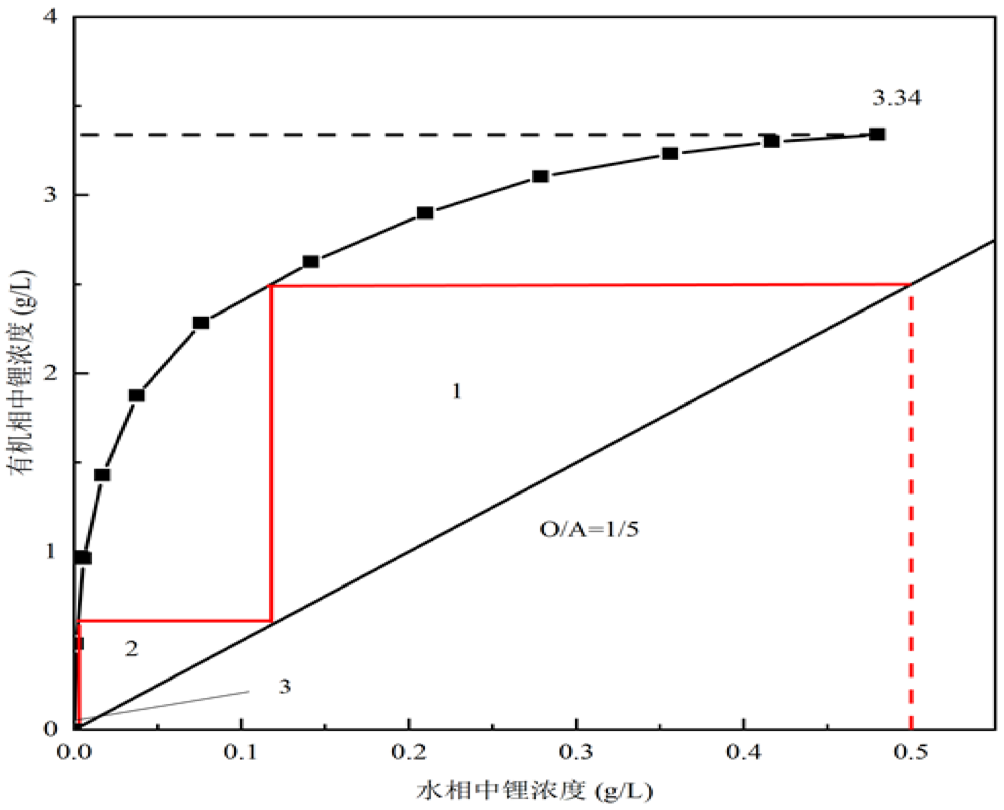
- Selectively extraction of Li from concentrated Na/K salt，
- **Li remained in raffinate <5mg/L, Li in stripping aqueous >30g/L**

- **Good segregation performance**

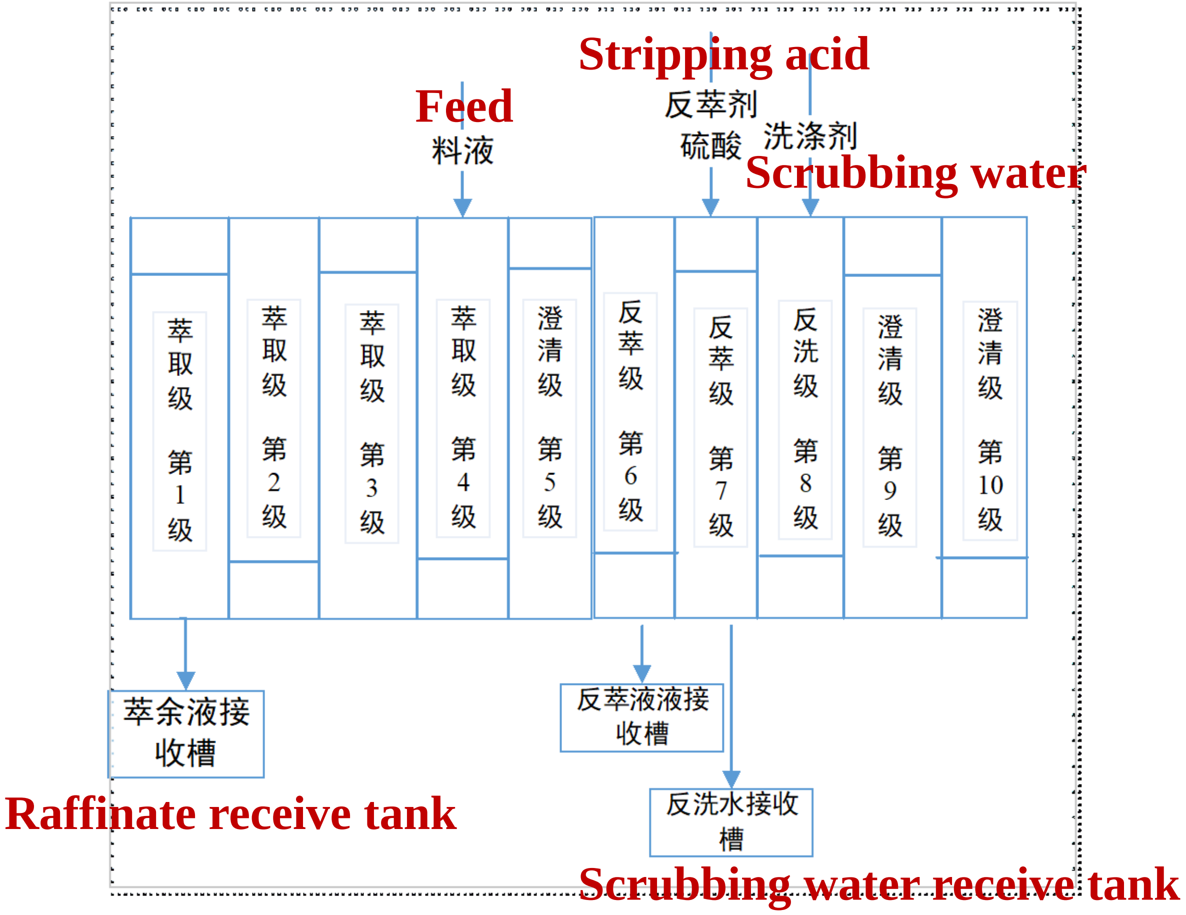
Element	Concentration/g·L^{-1}			Extraction /%
	Feed	Raffinate	Stripping	
Li	1.5	0.0010	51.2	98.5
Na	52.76	49.48	0.22	<0.1

*Countercurrent extraction, Extraction section 3 stages, Scrubbing 3 stages

2.6 Selectively extraction of Li from Na_2SO_4 by (HBL-121)HT-007



McCabe-Thiele of Li extraction with HT-007



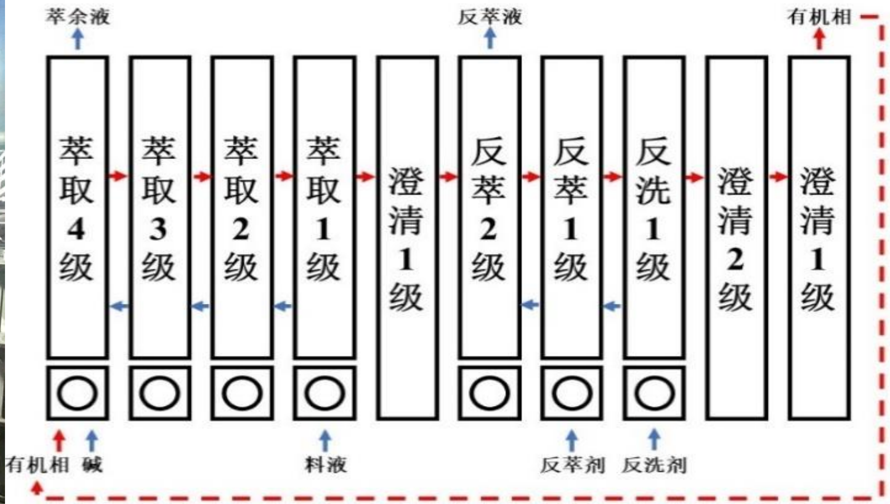
Solvent of HBL-121 (HT-007) achieved selective extraction of Li from Na in sulfate solutions, $\beta_{Li/Na}$ is over 1000, Li left in raffinate <5mg/L, Li in stripping solution was over 30g/L.

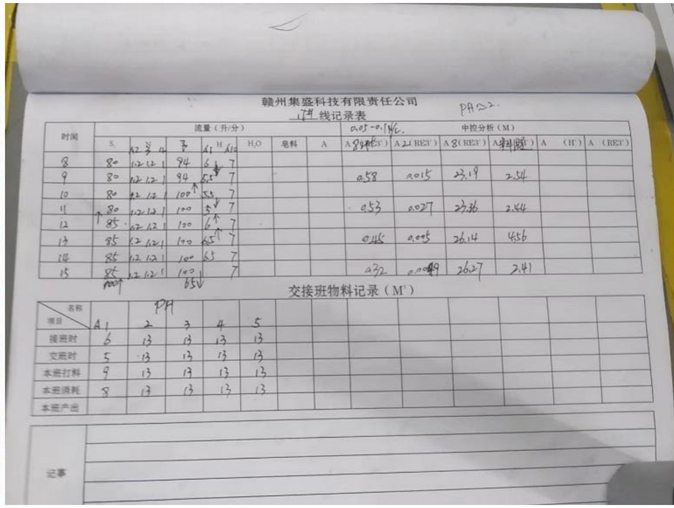
2.6 Selectively extraction of Li from Na_2SO_4 by HT-007

Experimental line and Production Line: Selectively extraction of Li from Na_2SO_4 solutions by HT-007.

（ launched in Aug. 2023 ）

2.6 Selectively extraction of Li from Na_2SO_4 by HT-007

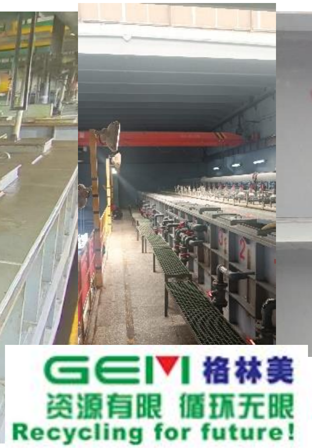




Ganzhou Jisheng Co., LTD, Production Line: Selectively extraction of Li from Na_2SO_4 solutions by HT-007.

（ launched in July. 2023 ）

2.6 Selectively extraction of Li from Na_2SO_4 by HT-007



Guangdong Weima new materials, Esokai cycle, Hunan Ruisai， Hunan Lisheng New materials, Jiangxi Ruihong...

More than ten plants have launched industrial application of HT-007 for Li extraction

2、试验萃取槽级数划分

萃取段：第 1-3 级；

洗涤段：第 4-5 级，洗液至萃取段第 3 级混合室；

反萃段：第 6-8 级；

水洗段：第 9 级，洗有机水外排。

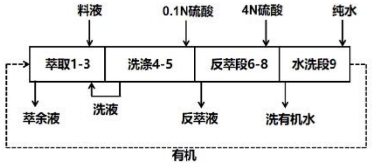
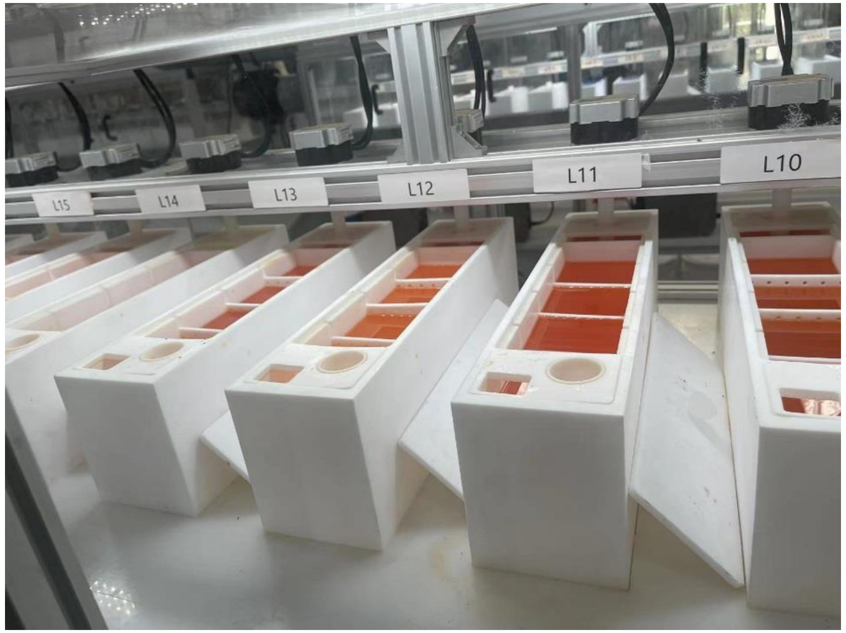


图 1 试验萃取槽级数划分

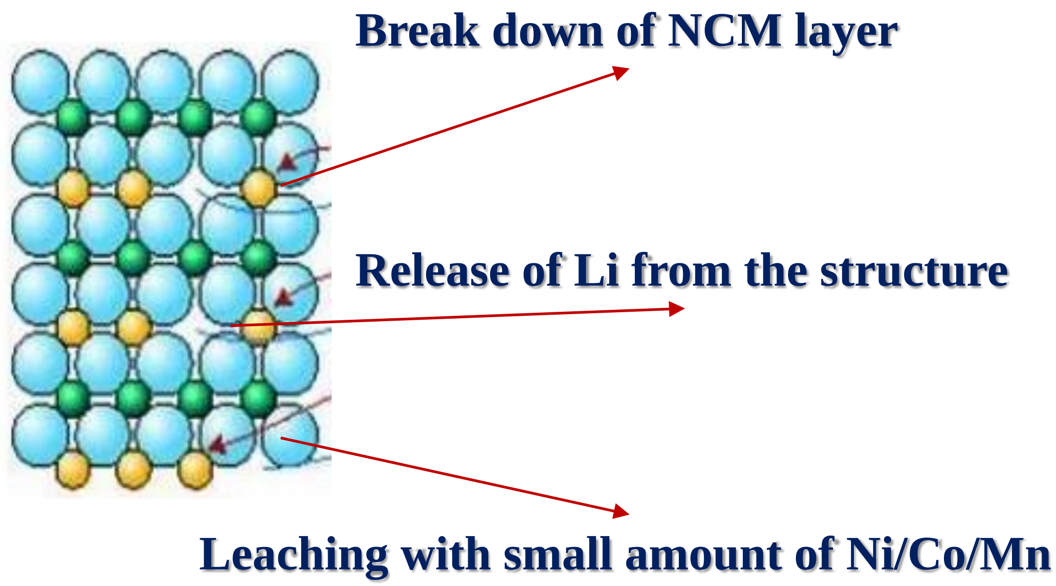
Guangxi Huayou Cobalt, Jiangxi Guoxuan, Pingxiang Tuoyuan, Hubei Libao... 12 enterprises have completed the pilot test and are running the process design

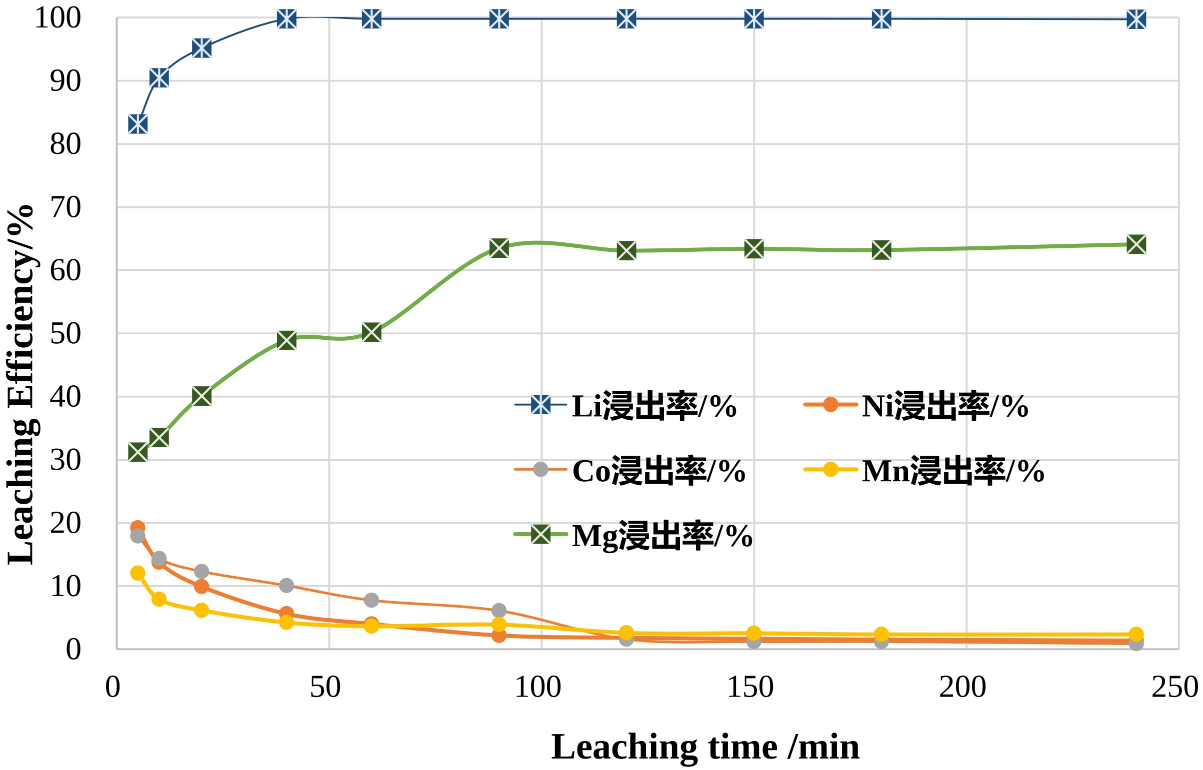
2.6 Selectively extraction of Li from Na_2SO_4 by HT-007



Austin Element from United States, BASF from Germany have completed lab-extraction test, and recognized that the extraction process is significantly better than the traditional evaporation crystallization

2.7 Firstly separation of Li from the spent LIB cathodes

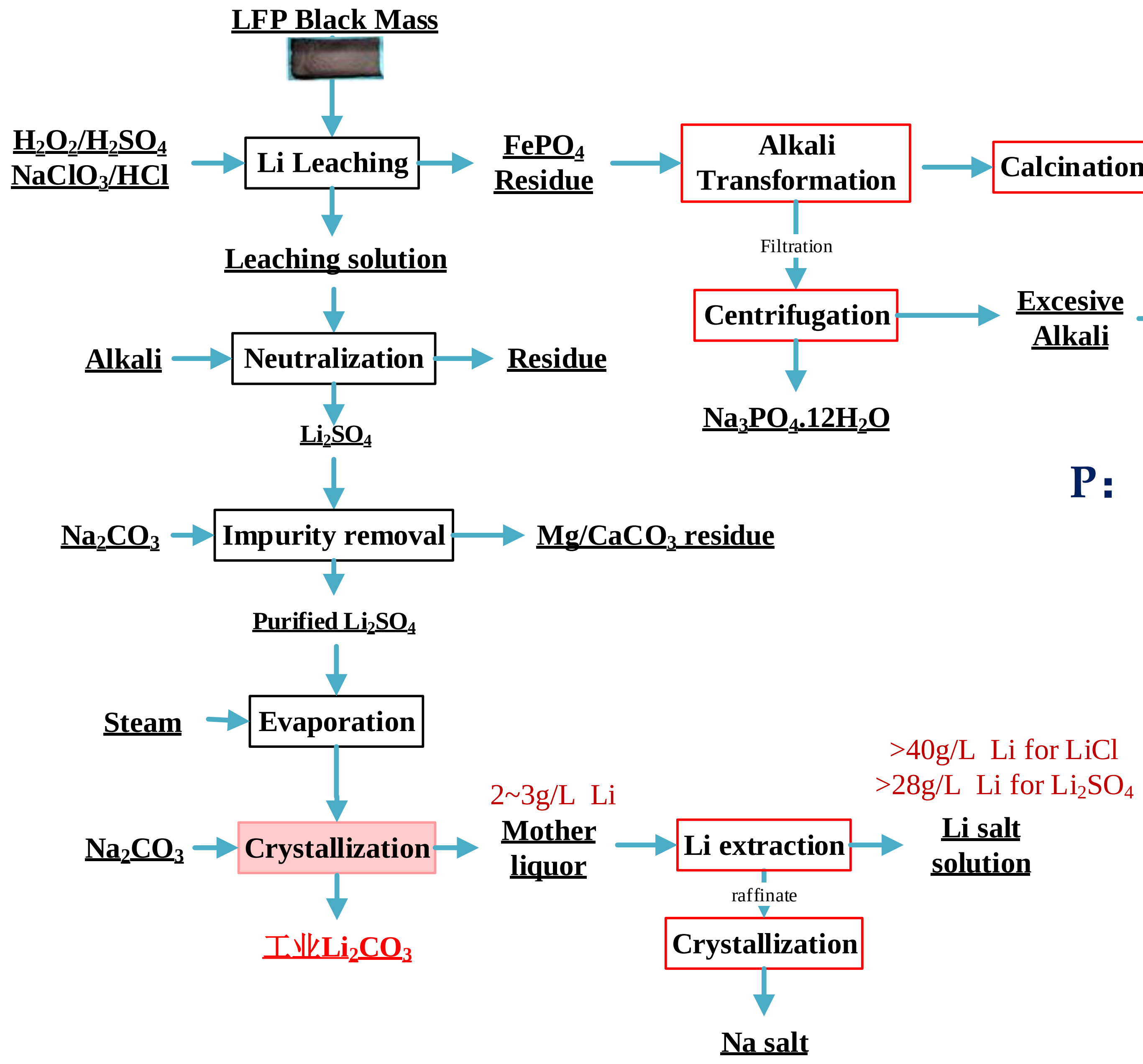




Reinforced Li selective leaching technology

Li leaching efficiency>98%, Li concentration>20g/L，Ni+Co+Mn leaching efficiency <5%，Mg remained in the NCM solid phase <0.005wt%（no need of Mg removal operation for purification）；

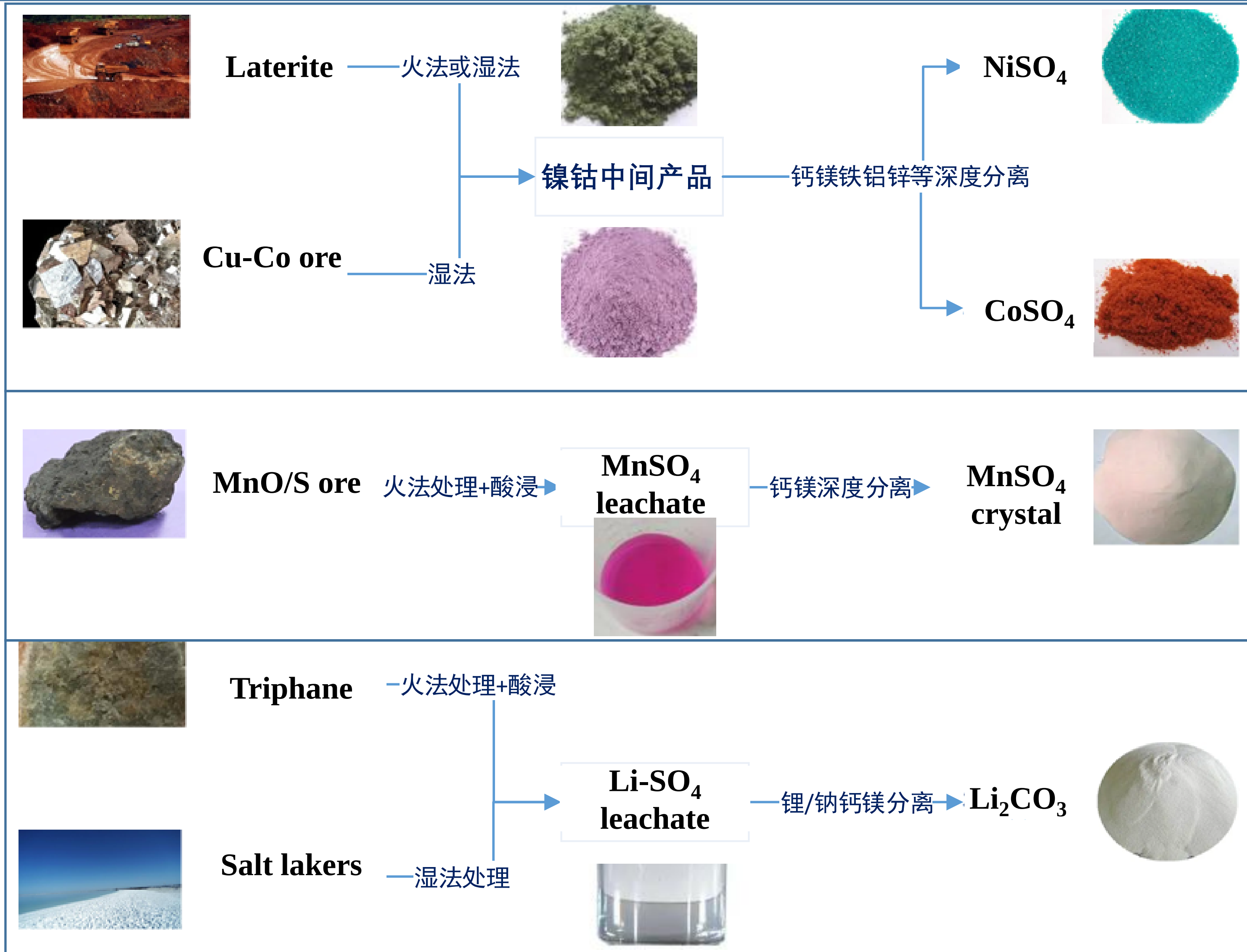
3、 Perspectives for metal recovery from the spent LFP



P: $NaPO_4.12H_2O$, Fe: Crude iron ore, Li: Li_2CO_3

- Completely recovery of valuable elements
- Eliminate P and iron slag stacking
- High Li recovery
- Li&Na completely separation

3、 Perspectives for the recovery of metals from the spent LIBs



Long process、low recovery、high reagent and energy consumption, high cost

Hazardous heavy metal residue

Recrystallization method to remove Ca/Mg

Challenged by low recovery and high cost

Difficulty in Li/Na separation

Long process and huge wastes