



REVIEW ON THE PROCESSING RESEARCH OF OCEAN MINERAL RESOURCES IN CHINA

COMRA

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1 Introduction

- **Development of the processing research of PMNs in world (Proposed many metallurgical processes, expanded test was carried out in part)**
 - **America** , Kennecott Cuprous ion ammonia leaching, High temperature and high pressure sulphuric acid leaching
 - **France**, Smelting sulfur-leaching, reduction roasting ammonia leaching, high temperature and high pressure sulphuric acid leaching
 - **Russia**, Smelting sulfur-leaching, reduction roasting ammonia leaching, atmospheric pressure sulfuric acid leaching
 - **IOM**, Reduction roasting ammonia leaching, high temperature and high pressure sulphuric acid leaching , Smelting sulfur-leaching,



1 Introduction

- **Development of the processing research of PMNs in world(Proposed many metallurgical method,expanded test was carried out in part)**
 - **India**,Smelting sulfur-leaching, Reduction roasting ammonia leaching, Sulfur dioxide reduction ammonia leaching
 - **Japan**,Smelting sulfur-leaching, Reduction ammonia leaching, Sulfur acid leaching
 - **Korea**,Smelting leaching



1 Introduction

□ Development of the processing research of ocean mineral resources in China

– Started in 1982

– Mainly research institutions:

- **BGRIMM** – Beijing General Research Institute of Mining and Metallurgy Technology Group;

Mainly study on hydrometallurgical processes

(Direct leaching)

- **CRIMM** – Changsha Research Institute of Mining and Metallurgy

Mainly study on pyro-metallurgical processes

(Reduction smelting)



1 Introduction

- **Development of the processing research of ocean mineral resources in China**
 - **ocean mineral resources**
 - PMNs, Cobalt-rich crusts, Polymetallic sulphides
 - **Main research**
 - Processing mineralogy;
 - Ore dressing;
 - Extractive metallurgy



1 Introduction

Extractive metallurgy :

- Ammonia leaching with CO reduction
- Sulfuric acid leaching
- Hydrochloric acid leaching
- Reductive smelting
- Manganese-enriched slag preparation
- Manganese-silicon alloy preparation
 - Directly used as catalyst or adsorbent;
 - Leaching residues used as functional materials (coating, etc) and additives



1 Introduction

□ Characteristics of PMNs

- Complex mixture of the oxides,
- No significant separated minerals of nickel, cobalt and copper, which disperse in iron and manganese oxides;
- Difficult to be enriched with mineral processing;
- High moisture, 40~50% chloride;
- Value metals, $Ni + Co + Cu \leq 3\%$;
- Key factors to extract the metal values: the reduction of manganese oxides.



1 Introduction

□ Characteristics of Cobalt-rich crusts

- Complex mixture of the oxides,
- No significant separated minerals of nickel, cobalt and copper, which disperse in iron and manganese oxides;
- Mining is difficult and bedrock need to be removed by ore dressing;
- High moisture, 40~50% chloride;
- Value metals, $Ni + Co + Cu \approx 1\%$ and $Co \approx 0.5\%$;
- Key factors to extract the metal values: the reduction of manganese oxides.



1 Introduction

□ Extraction processes

– Ammonia leaching

- ☑ Selective leaching
- ☑ Recyclable lixiviants
- ☑ Disadvantage: low extraction of cobalt

– Smelting

- ☑ Manganese → slag
- ☑ Drying and smelting: intensive energy consumption

– Acid leaching

- ☑ Higher recovery of metals
- ☑ No selectivity
- ☑ Complicated treatment of the leaching solution

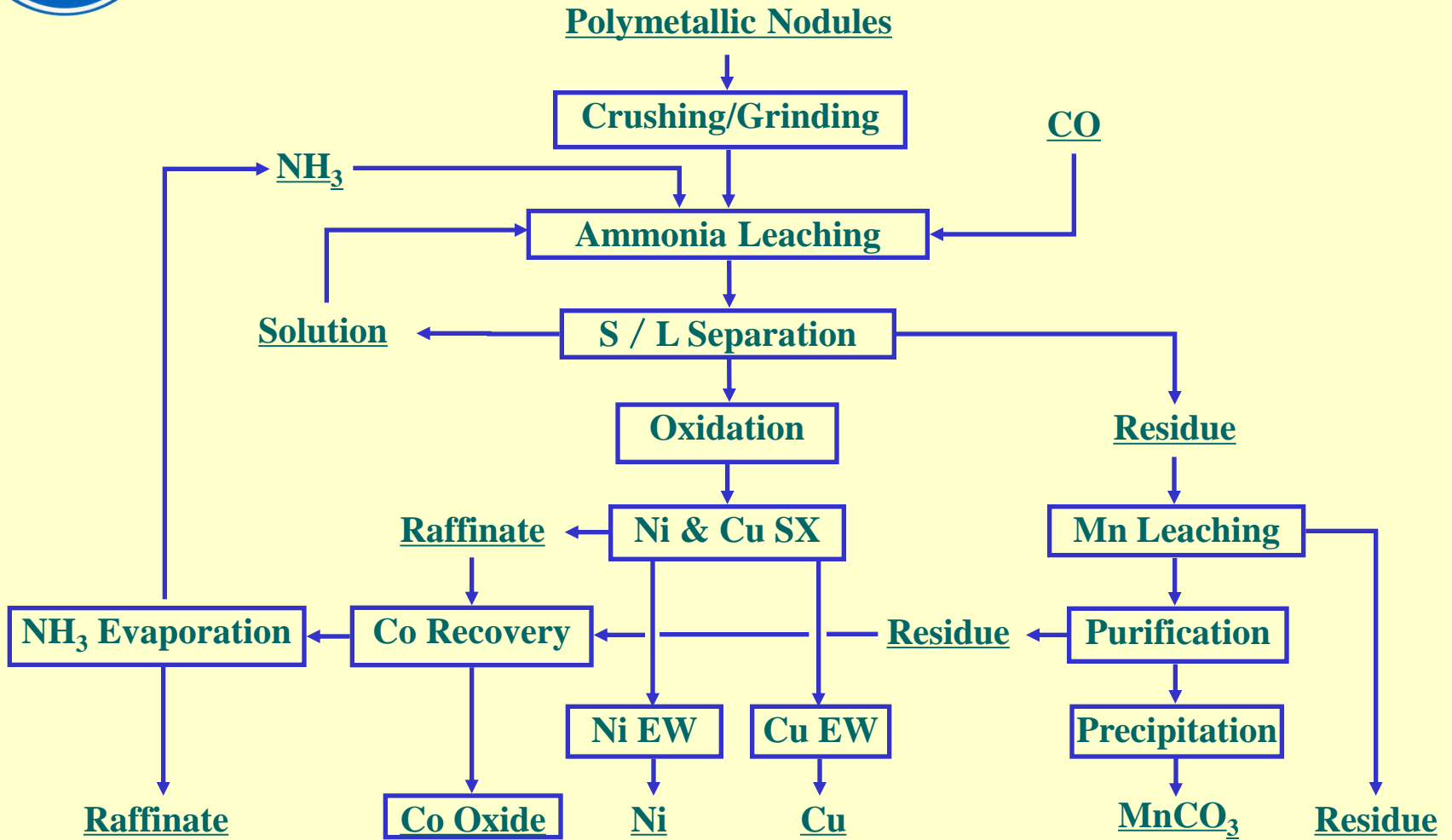


2 Research on Metallurgy in China

2.1 Reductive Ammonia Leaching

Researches before 1990

- Kennecott Copper Corporation (Agarwal, JC, 1979); Mn (IV) in the nodules is reduced with CO with Cu(I) acting as the catalyst.
- Advantages of ammonia leaching with carbon monoxide are: the reducing agent is clean and cheap, and the leaching conditions are mild (room temperatures).
- Disadvantage: the cobalt extraction is low.

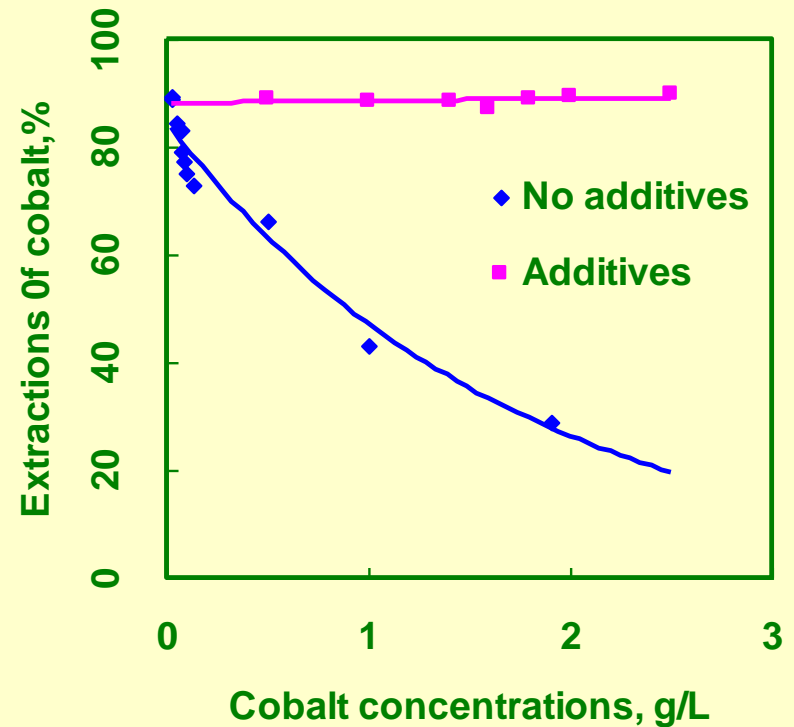


— Reductive Ammonia Leaching process of BGRIMM



2 Research on Metallurgy in China

- Cobalt extraction ratio decreases as its concentration goes up, without additives.
- The effects of cobalt concentrations is quite limited in the presence of additives.





2 Research on Metallurgy in China

- Certain additives is good for the leaching of cobalt.
- The self-catalysis reductive reaction is achieved in the tests.
- 1000 kg/d expansion test was completed
- The extractions for nickel, copper and cobalt are above 98%, 98% and 90% respectively.
- 84% Zinc and 96% Mo are leached at the same time.
- The total metal ion (Cu + Ni + Co) concentration is 25-30 g/L:
Ni 13-15 g/L, Cu 10-12 g/L, Co 2-3 g/L.



2 Research on Metallurgy in China

- In 2011, COMRA organized and conducted studies on the possibility of recovering REES in metallurgical processing of polymetallic nodules.
- The studies were made mainly on the distribution of REES in ammonia leaching residues of polymetallic nodules, exploring the possibility of recovering REES from ammonia leaching residues.
- The REES concentration was 889.2ppm measured in the experimental residues, of which LREES and HREES accounted for 75% and 25% respectively.
- about 80% of REES in the residues could be recovered



2 Research on Metallurgy in China

The measure to reduced investment and decreased cost:

- Reduced Liquid/solid ratio
- Continuous operation
- Self-catalysis reductive
- Comprehensive recovery of molybdenum and REES
- Merging processing of polymetalluric nodules and cobalt rich crusts



2 Research on Metallurgy in China



**Leaching sub-system of polymetallic nodules
with the scale of 1 t/d**



cathode copper



cathode nickel



2 Research on Metallurgy in China

2.2 Smelting – Oxidative Leaching – Solvent Extraction of PMN (CRIMM)

- The technology of atomization powder is used to obtain alloy powder and solve the problem that the alloy is hard to break.
- Rust leaching technology was used with alloy powder in dilute acid solution under blowing air condition, copper, nickel, cobalt in smelting alloy enter into the solution.



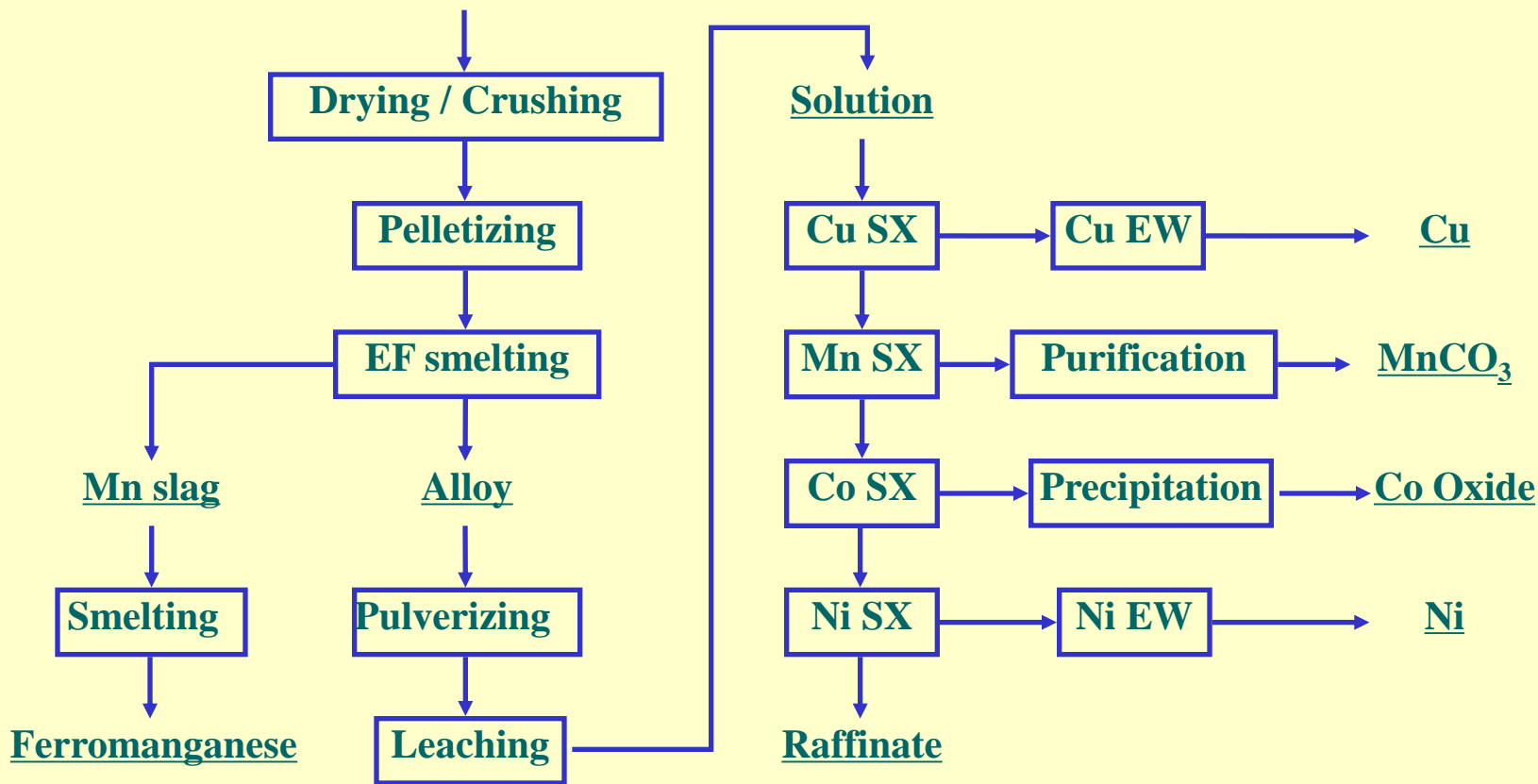
2 Research on Metallurgy in China

2.2 Smelting – Oxidative Leaching – Solvent Extraction of PMN (CRIMM)

- 100 kg/d expansion test was completed
- About 90~95% Ni, Cu, Co and Fe are enriched in the molten alloy, which is only 15~20 % by weight of the nodules.
- 90~95% manganese enters the smelting slag, which can reduce the content in the Si-Mn alloy.



Polymetallic Nodules



— Reductive smelting of CRIMM



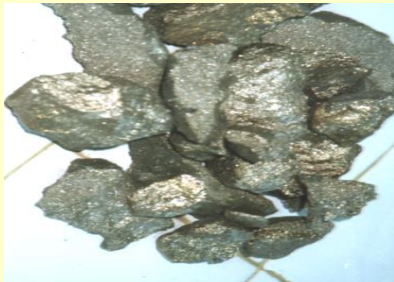
2 Research on Metallurgy in China



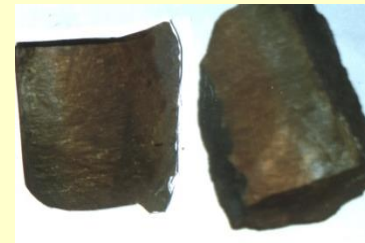
200KVA DC arc Furnace



Smelting alloy pulverizing



Mn-Si alloy

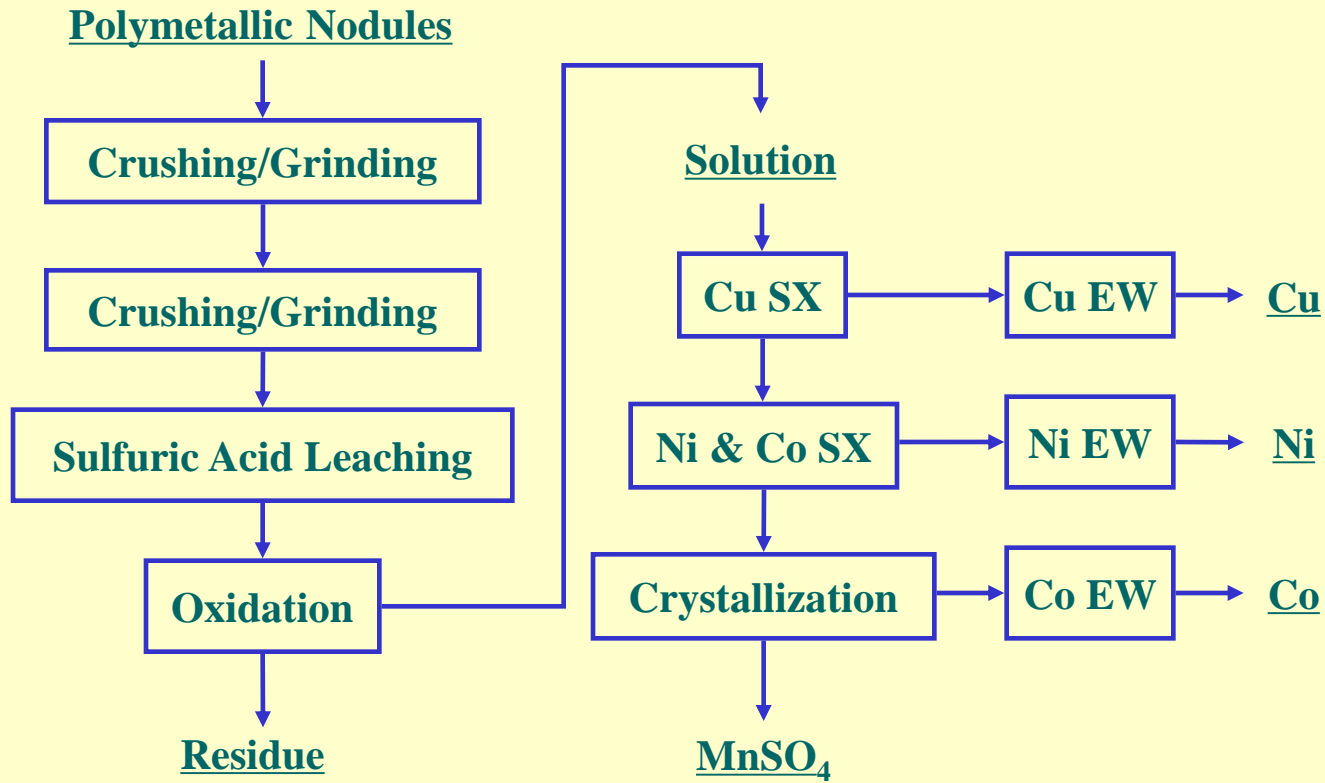


Mn-rich slag



2 Research on Metallurgy in China

2.3 Sulfuric Acid Leaching of PMN (BGRIMM)

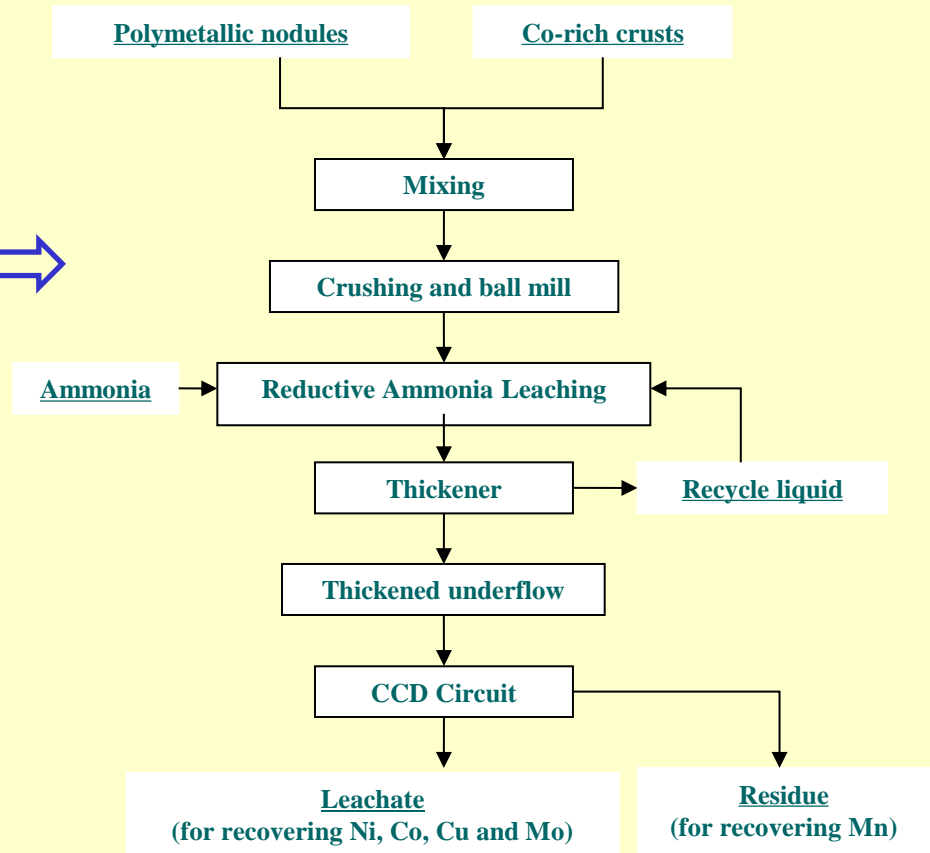
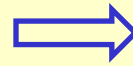




2 Research on Metallurgy in China

2.4 Research on the Metallurgical Tests with Feed Containing both Polymetallic Nodules and Cobalt-rich crusts

- Reductive ammonia leaching on mixture of polymetallic nodules and cobalt-rich crusts with ammonia

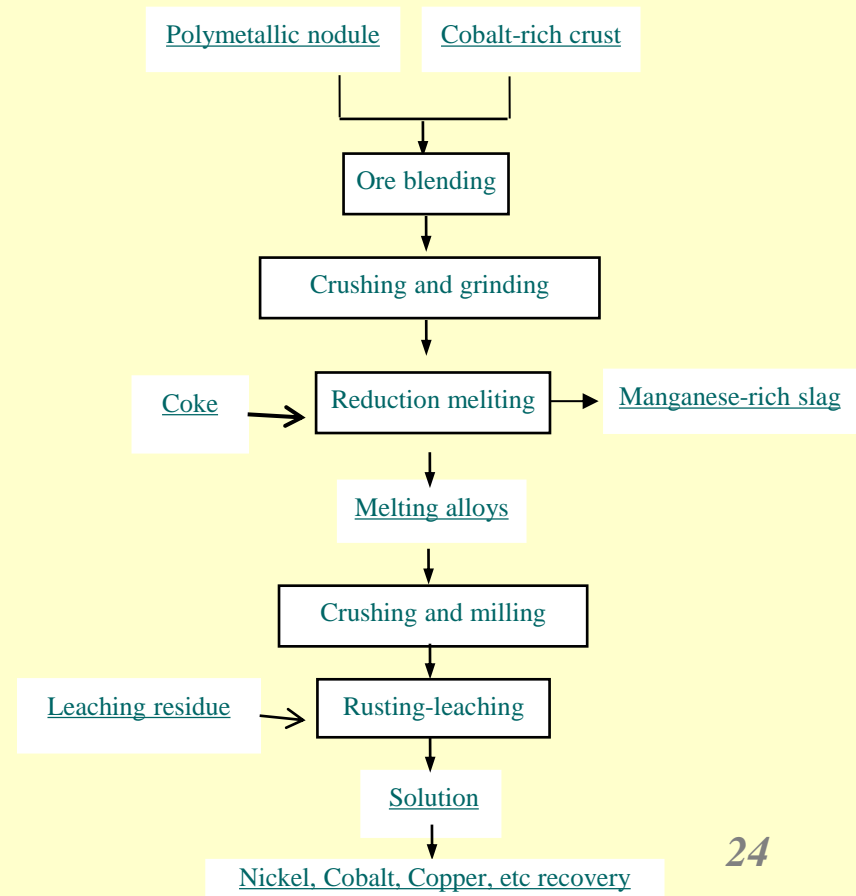




2 Research on Metallurgy in China

2.4 Research on the Metallurgical Tests with Feed Containing both Polymetallic Nodules and Cobalt-rich crusts

- Smelting process on mixture of polymetallic nodules and cobalt-rich crusts with coke





2 Research on Metallurgy in China

2.5 Research on the Metallurgical Tests with Cobalt-rich Crusts

- In view of the problem of dilution rate because of bedrock entrainment in commercial exploitation in the future, COMRA **adopt combination process of ore dressing and metallurgy** to treat cobalt-rich crusts, namely first remove the bedrock entrapped in cobalt-rich crusts by ore dressing and then recovery of nickel, cobalt, copper and manganese by metallurgy process.



2 Research on Metallurgy in China

2.5 Research on the Metallurgical Tests with Cobalt-rich Crusts

- Carried out the research **gravity separation, flotation, strong magnetic separation, the combination process of gravity separation and magnetic separation technology** on cobalt-rich crust. The results show magnetic separation is better than other methods.
- Carried out lab test for Sulfuric Acid Leaching of Cobalt-rich Crusts. The extractions for, cobalt, nickel, copper and manganese are above **98%, 98%, 80% and 95% respectively.**



2 Research on Metallurgy in China

2.6 Research on the Metallurgical Tests with Polymetallic Sulphides

- Put forward process mineralogy plan of polymetallic sulphide.
- Carried out the pre-trial research of polymetallic sulphide.



3 Direct Utilization of PMN

3.1 Catalysis Effect of PMN

- Catalysis effect of PMN on the hydrogenation-methanation reaction of CO

T (°C)	O ₂ (%)	CO (%)	CH ₄ (%)
250	/	96.3	2.0
300	0.4	75.6	10.4
350	0.3	59.3	40.4
400	0.3	/	99.7



3 Direct Utilization of PMN

3.1 Catalysis Effect of PMN

- Catalysis effect of PMN on the hydrogenation-methanation reaction of CO₂

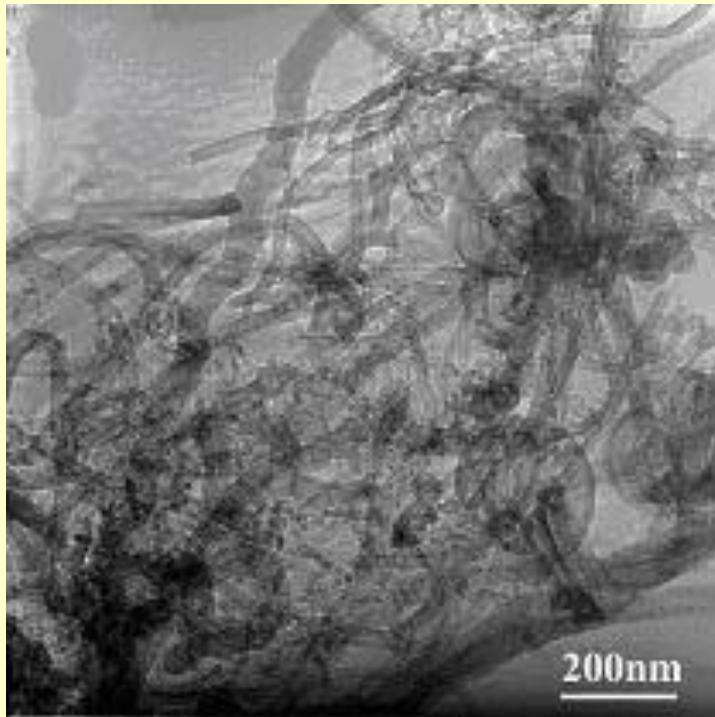
T (°C)	O ₂ (%)	CO (%)	CH ₄ (%)	CO ₂ (%)
250	11.5	4.7	/	83.8
275	1.5	10.21	/	88.3
300	3.1	4.9	82.0	/
375	0.5	2.2	97.3	/
420	0.3	/	99.7	/



3 Direct Utilization of PMN

3.1 Catalysis Effect of PMN

- PMN as a catalyst for making carbon nano-tubes



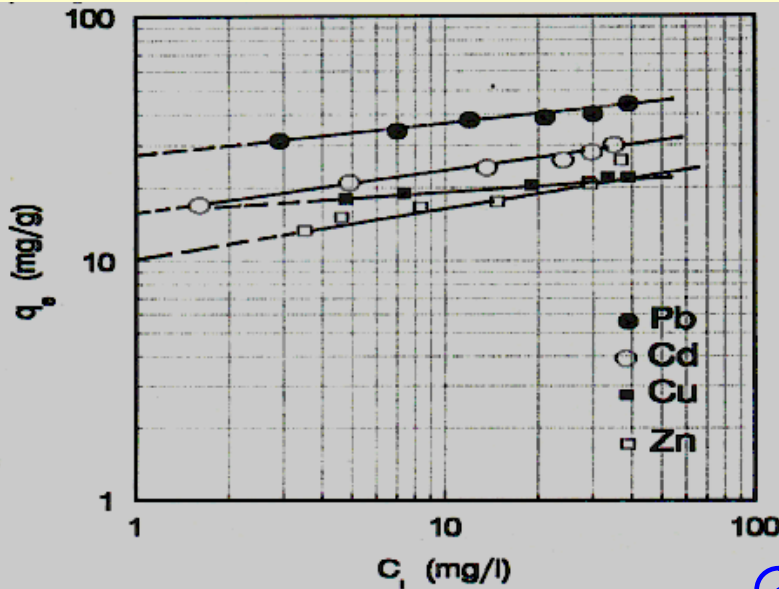
TEM image of the carbon nano-tubes prepared with manganese nodules



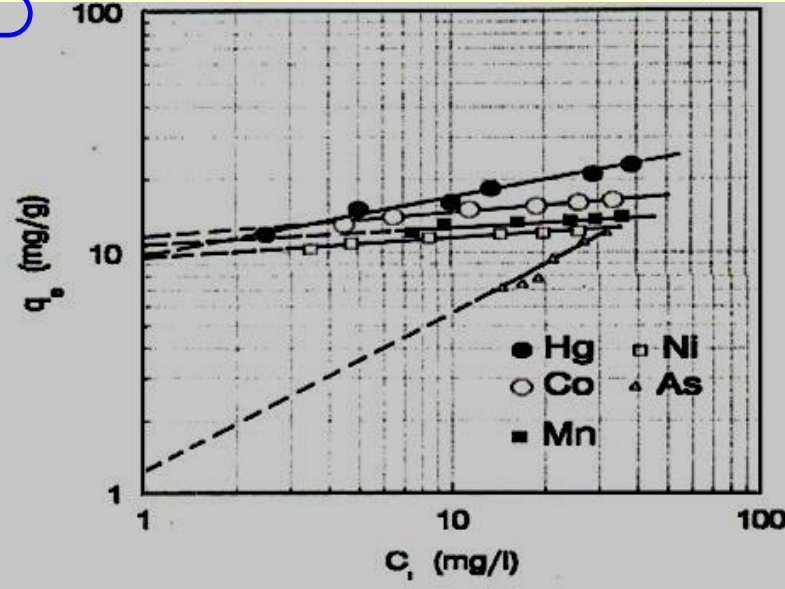
3. Direct Utilization of PMN

3.2 Adsorption of Harm Elements Using PMN

– Adsorption of Heavy Metal ions in Waste Water



Good adsorption to Pb, Cd, Hg, Zn, Ni, Co, Cu, Mn, As





3 Direct Utilization of PMN

3.2 Adsorption of Harm Elements Using PMN – Adsorption of SO₂ in Waste Gases

Effect of temperature on fix sulfur

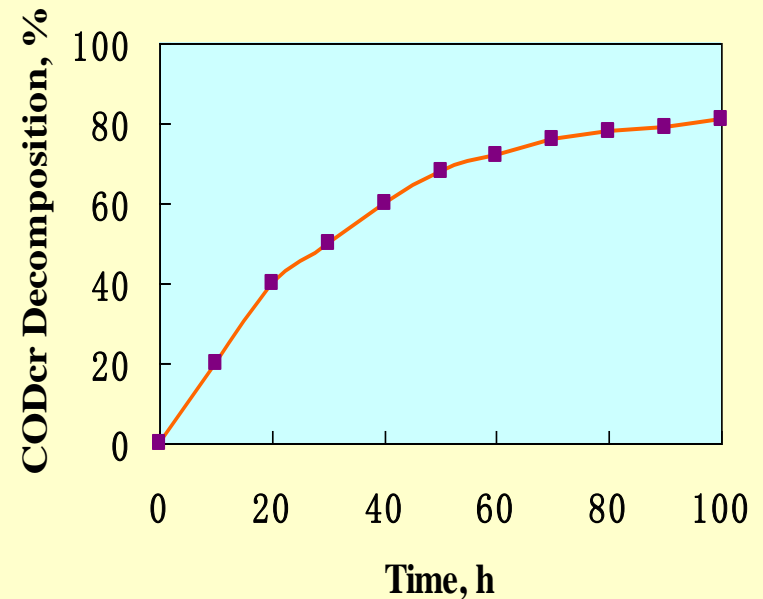
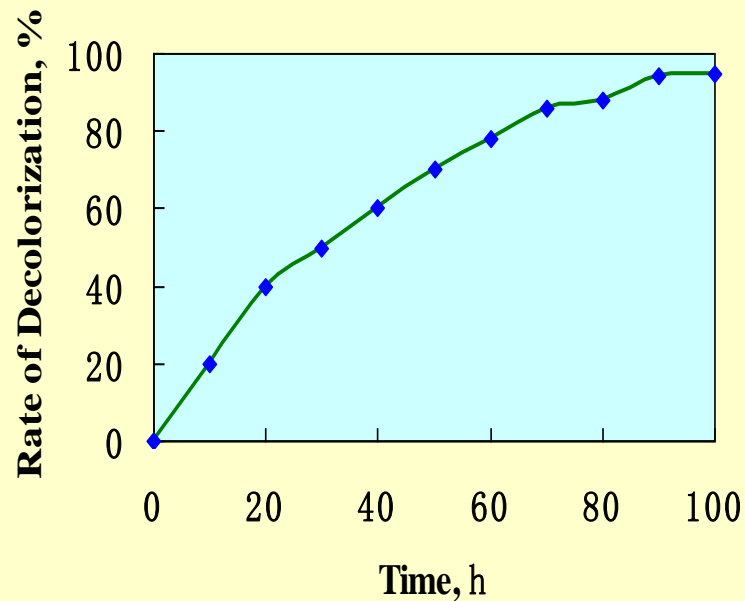
Temperature (°C)	Sulfur in PMN adsorbent (%)
250	8.84
350	10.79
450	12.04



3 Direct Utilization of PMN

3.2 Adsorption of Harm Elements Using PMN

- Adsorption and degradation of organics in waste water

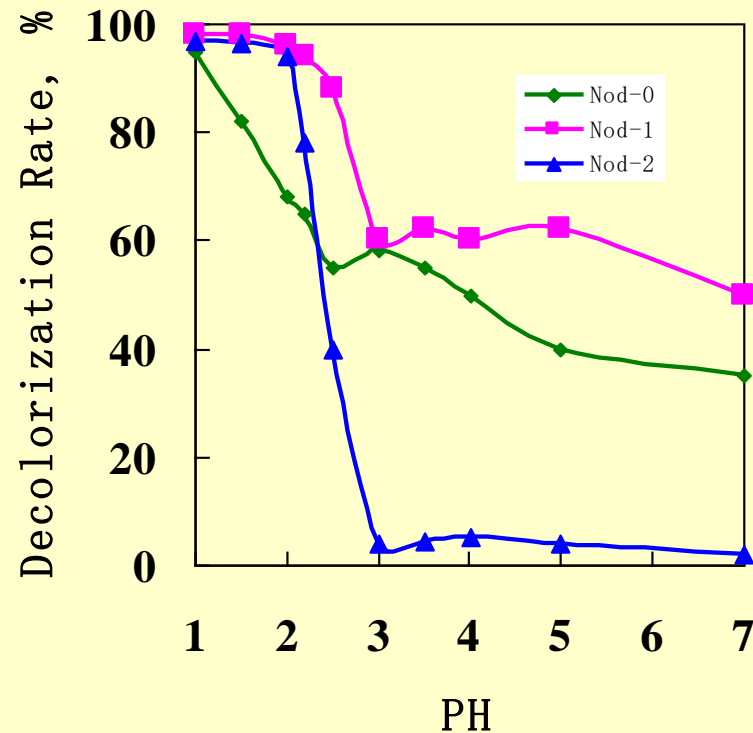




4 Comprehensive Utilization of the Leaching Residue

4.1 Treatment of printing and dyeing waste water using residues

The ammonia leaching residues have the abilities of adsorption and degradation of dyes in printing and dyeing waste water



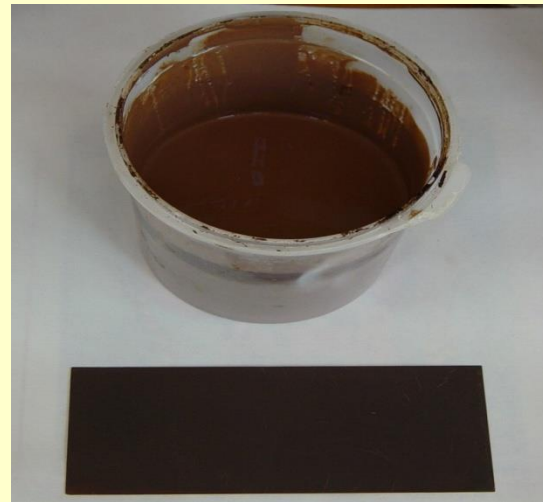


4 Comprehensive Utilization of the Leaching Residue

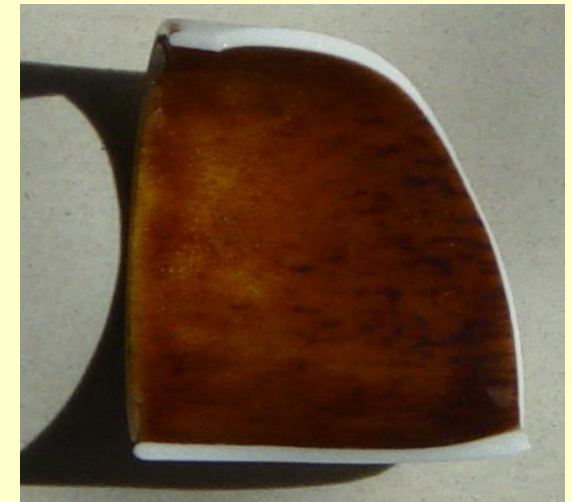
4.2 Making antirust dope and ceramic glaze with leaching residues



Antirust dope made from acid leaching residues and its pain-coat



Antirust dope made from acid leaching residues and its pain-coat



Rufous ceramic glaze coatings prepared with leaching residues



5 Conclusions

- There are many smelting processes for ocean mineral resources, which need to be selected according to actual conditions, such as energy, resources, investment, etc.
- Multiple metal product programs, including three metal methods(Ni,Co,Cu), four metal methods(Ni,Co,Cu,Mn), five metal methods(Ni,Co,Cu,Mn,Mo)among which manganese has a variety of product options, such as manganese carbonate, manganese silicon alloy, manganese-rich slag, etc.



5 Conclusions

- Different metal product programs will lead to big changes in the value of ton ore

element	Ni	Co	Cu	Mn	
Products	Cathode nickel	Cathode cobalt	Cathode copper	MnCO ₃ (Mn47.8%)	Mn-Si alloy(Mn 65%)
Content(%)	1.25	0.25	1	25	
Recovery(%)	94	85	94	94	
Unit price(\$/t)	13310	64000	6000	1150	1330
Value(\$)	156.4	136	56.4	565.4	480.8
Three metals(\$)	348.8			/	/
Four metals(\$)	914.2				829.6



5 Conclusions

- Smelting scale is closely related to benefit, but it will also lead to dramatic changes in the metal market. For example Cobalt and manganese market
- The construction of the smelter will lead to an increase in environmental costs

Thank you for attentions!