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Secondary Non-ferrous Metals Industry in China: Present Situation and Development Tread

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Abstract: The production of Secondary Non-ferrous Metals (SNM) is characterized by low investment, energy consumption and cost, less pollution as well as rather simple technology. In the past years, the SNM industry has seen relevantly rapid progress in China. Especially in the field of clean hydrometallurgical treatment certain novel technologies for recovery and separation have successfully been elaborated, and a number of medium and small commercial plants established. On the basis of four common metals Cu, Al, Pb, Zn, and Ni, Co, this paper describes the status quo and progress of SNM industry in China, indicating that a lot of work should still be done in salvage of waste metals. It is recommended that measures for collecting and classifying SNM resource should be strengthened and the research on new technologies for scavenging such metals should be supported.
Keywords: Secondary Non-ferrous Metals; Copper; Aluminum; Lead; Zinc

Introduction

As an important part of Non-ferrous metals (NM) industry, the production of SNM has increasingly been attached importance to in view of its lower investment, lower energy consumption and cost, less pollution as well as rather simple technology. In the past 20 years, with the rapid economic growth in China, the consumption of NM has swift gone up, resulting in large a mounts of recoverable NM resources. In the meantime the production of SNM has scored considerable expansion. According to incomplete statistics in 1999, the output of SNM in China amounted to 670 thousands t, or 9.7% of the total NM production. Among them, the output of reclaimed copper accounted for 340 thousands t, that of reclaimed aluminum for 210 thousands t, reclaimed lead 100 thousands t, and reclaimed zinc 20 thousands t[1]. Based on four common metals Cu, Al, Pb, Zn, and Ni, Co, this paper gives an overview of the present situation and progress of SNM production in China.

1. Secondary Copper

The salvage of copper scrap is the best sector of re-utilizing NM wastes in China. In 1999 the output of secondary copper reclaimed from copper scrap amounted to 340 thousands t, or 29% of the total production of electrorefined copper that year. In recent years remarkable progress has been recorded in the scavenging technology, especially in hydrometallurgical treatment. At the same time the work on classifying scraps copper resources has also been consolidated during recycling.

1.1 Resource

Waste materials for making secondary copper in China are mainly rejected copper parts, scraps from copper alloy production or mechanical working, copper slag and dust, spent electric wires cables, and circuit boards. Scraps of brass and red copper are dominant, accounting for 90% of the total resource. In recent years the output of secondary copper has been increased by salvaging spent circuit boards to a certain extent.

1.2 Status quo and technology

Dependent on different resources, the processes for making secondary copper are mainly as fellows:
a) Production of wire-bar copper from pure and clean red copper scraps. For smelting is usually used reverberatory or shaft furnace, and the process involves four stages, i.e. melting, oxidation, reduction and costing, with a recovery over 99.5% Cu.
b) Production various brands of copper alloy from pure and clean copper scraps. The scraps are blended with pure metal or intermediate alloy in proper proportion, and the process is composed of blending, melting, degassing, deoxidization, composition regulation, refining and casting. The recovery is in the range from 93% to 95% Cu.
c) Production of secondary copper from copper scraps. Domestic process usually involves two stages. In the first stage scraps undergo reduction smelting in a blast furnace or converter smelting, and in the second one anode copper is produced by refining in a reverberatory furnace. The process recovery reaches 99% and higher.
d) Production of copper sulfate from oxide copper slag. This process includes oxidizing roasting, leaching in a bubble column and stirring crystallization, yielding copper sulfate of first grade. In the bubble column oxide copper powder and acid leach liquor flow in countercurrent with air, and the copper sulfate resulted is crystallized.

1.3 Recent progress in production of secondary copper[2]

Apart from the conventional pyrometallurgical methods employed presently, a number of domestic institutions have made more or less progress in hydrometallurgical treatment of copper scraps of different composition. For example, the Iron and Steel Research Institute in Chongqing city has developed an ammonia leaching process for treating copper-coated steel scrap, direct electrolysis process for making electro-refined copper from copper alloy scrap, and a method of high current density for making red copper tubes from copper scrap. Again, the Northwest Research Institute of Mining & Metallurgy has worked out an acetonitrile process to produce pure copper powder from copper scrap. Further, Beijing General Research Institute of Mining & Metallurgy (BGRIMM) has elaborated a slurry electrolysis process (SEP) to produce copper powder and zinc sulfate from copper slag, and a process of direct electrolysis to yield electro-refined copper and copper powder from copper scrap. The principle of SEP flow sheet to produce copper powder from copper slag is shown in Figure 1.

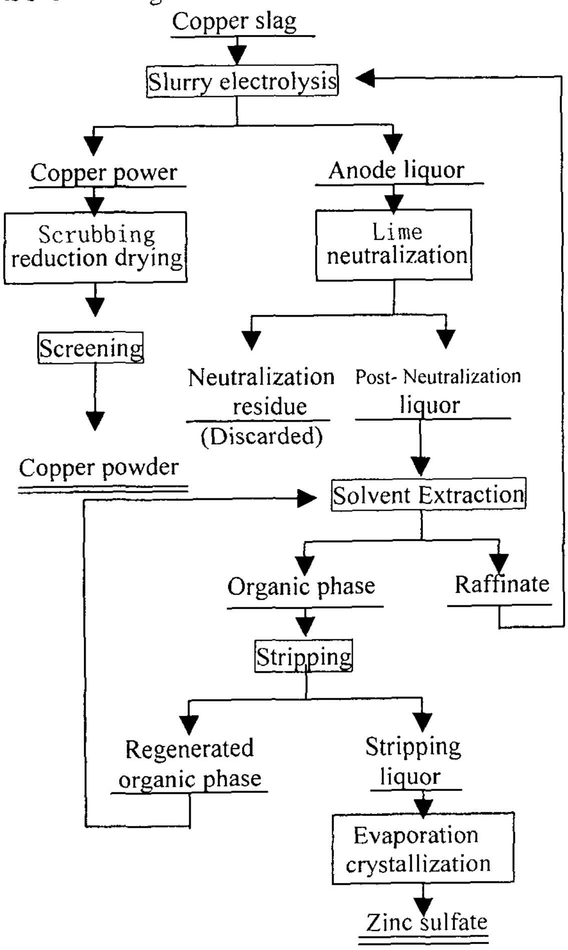

Fig.1 Principle SEP flow sheet for making copper powder from copper slag

2.Secondary Aluminum

The output of secondary aluminum in China is relatively low, amounting to 210 thousands t in 1999, only 7.5% of the total aluminum production that year. Plants of this kind are small in scale, low in productivity and thermal efficiency, operating with outmoded equipment, and the recovery of aluminum is mediocre. Smelting technology with induction electric and/or single hearth reverberatory furnaces dominates in most of such plants, except Foshan plant in Guangdong province, where in 1989 a production line of secondary aluminum was introduced with converting furnace for smelting.

2.1 Resource

According to the physical configuration, the resources of secondary aluminum can be classified into three groups. a) Al-containing rejected parts and leftover plates, including those from processing, forging or casting sheet, wire or figured materials for making aluminum articles, such as rejected parts of aircraft and ship, used cans, spent tubes of toothpaste, waste wire and cable. b) Aluminum scraps from machining of aluminum metal and alloy. c) Dross and flue ash from smelting of aluminum and its alloy.

2.2 Status quo and technology[2,3]

Production process of secondary aluminum is relatively simple. Usually, based on the composition of aluminum scraps pyrometallurgical technology is employed to make aluminum alloy of various brands. Plants of this kind in China are moderate in scale, where mostly are still used induction electroic and/or single hearth reverberatory furnaces. For example, at Changsha Aluminum works, Hunan province, a crucible induction electric furnace is used for smelting, showing 91~95% Al recovery, 65% thermal efficiency and energy consumption 600~700kwh/t alloy. But at Shanghai Baohua smelter, a single hearth reverberatory furnaces is employed for smelting, followed by casting of aluminum alloy, which demonstrates a recovery of 90% Al and thermal efficiency 25~30%.

2.3 Recent progress in production of secondary aluminum

a) Salvage of aluminum wastes. In China several billions of toothpaste tubes are turned out, consuming nearly 20 thousands t of aluminum a year. Moreover, in recent years with the development of metal packaging of food, the consumption of aluminum for this purpose also reaches over 10 thousands t of aluminum per year. For salvaging spent tubes and package scraps a new clean technology has been developed by Tianjin Non-ferrous Metal alloy Works. It embraces such operation as crushing, scrubbing, drying, screening and smelting, and turns out aluminum ingot of 99.7%purity at a recovery over 90% Al.

b) Salvage of aluminum scraps. The technology for this purpose has been developed and commercialized. It consists of crushing such scraps as leftover bits and pieces, spent foils and filings followed by radial extension to manufacture ready-to-reuse aluminum material.

3. Secondary Lead

According to the statistics in 1999, the output of Secondary lead in China amounted to 100 thousands t, or 10.9% of the total lead production that year, ranking the third, next to those of secondary copper and aluminum. Although there are nearly 100 secondary lead smelters of various sizes, they are all rather small. The Largest has a capacity of 10 thousands t/a. or less, and the smaller only 100 t/a. The dominant production processes are primary smelting by liquation followed by electrolysis and alkaline refining, and the conventional reverberatory and/or blast furnace smelting. Still there are smelting operation of lead ores blended with lead scraps for production of secondary lead metal, and regeneration operation of secondary lead alloy from lead-base alloy scraps.

3.1 Resource

The composition of lead metal and alloy wastes is closely related to their consuming proportions in various sectors. At present such proportions are roughly 40% for battery industry, 30% for lead alloy and sheet, 15% for communication cable, 10% for welding electrode, and 5% for inorganic paint. Therefore, resources for salvaging are mainly rejected lead battery, lead cable and process wastes of lead metal and alloy, with the first accounting for 80～90% of the total.

3.2 Status quo and technology

a) Process of primary smelting by liquation at Shanghai Smelting. The scrap is firstly subjected to primary smelting by liquation to remove part of copper and antimony followed by casting into lead anode plates. Such plates then undergo direct electrolysis under the condition of the stable chemical composition of electrolytic solution to yield electro-refined lead grading 99.64～99.68% Pb. Finally, this product is refined in a reaction bath of alkaline media to produce No.1 refined grading 99.995% Pb.
The major technico-economic date are reported: rate of first grade refined lead –100%, recovery rate of primary smelting –97% Pb, overall recovery of electrolysis – 99.5% Pb, recovery of alkaline refined – 99.7% Pb, overall recovery of smelting –98% Pb; current efficiency – 95.2%, average coal consumption – 120kg/t Pb, consumption of fluosilicic acid – 7.5kg/t Pb, and direct current consumption – 140 kwh/t Pb.
b) Process of smelting lead ore blended with lead scraps at Zhuzhou Smelter, Hunan province. The output of secondary lead at this plant accounts for only 1～5% of its total lead production. Such product is therefor used only for blending lead ore in smelting process, and No.1 refined lead is finally produced.
c) Process of smelting with blast furnace at Tonghua Smelter, Jilin province. At this plant electro-refined lead is produced in a chain of operations, comprising agglomeration, smelting in blast furnace, liquation for removing impurities and electrolytic refining.
The composition of blast furnace slag is as follow: 27～35% SiO_2, 25～35%FeO, 10～15%CaO, and≤20 Al_2O_3. The blast furnace has a capacity of 65～80t /m^2·d, showing a recovery of 95% Pb and coke factor 16～20%, and its slag contains 0.6～3.5% Pb.
d) Process of making secondary Pb-Sb alloy with reveberatory smelting at Guangzhou Xingxing Smelting. This smelting produces secondary Pb-Sb alloy for lead batteries using rejected ones as its major feed. The technological flow sheet involves reveberatory smelting and liquation by use of mixed flux of iron filings plus coke dust and lime for slagging. Two stage smelting is practiced, comprising melting at low temperature followed by calcination and reduction, slagging. This process is proved economically efficient because of metal recovery raised, and slag formation and its content of lead reduced.

3.3 Recent progress in production of secondary lead[4]

Research on recovering lead from spent lead batteries started quite late in China. However, remarkable progress has been scored in recent years. For instance, the technology of electric reduction of solid phase has first been commercialized in small scale in China, and that for recovering lead through wet desulphurization and reduction at low temperature developed by North-east University and BGRIMM is being realized in production. The principle flow sheet of the second is shown in figure 2.
The second technology features are: a) mechanized pretreatment with high separation performance; b) conversion of lead paste by ammonia carbonate, leading to SO_2 pollution eliminated during lead smelting, beneficial to the environment; c) smelting in short kiln, resulting in higher metal recovery and pollution due to lead evaporation rooted away, realizing direct recycling of batteries and thus better utilization; and d) low equipment investment but high economic return.

4. Secondary Zinc

The output of secondary zinc in China is minor, only 20 thousands t in 1999, accounting for 1.2% of the total zinc production that year. Resources for making secondary zinc are mainly dust and slag from thermic zinc plating, rejected parts from zinc article manufacture, zinc hypo-oxide and zinc bearing industrial garbage. Pyrometallurgy dominates for this purpose, such as horizontal retorting, distillation and electrothermic method, and yielding secondary zinc ingot and zinc chemicals such as zinc powder and zinc oxide. As for the hydrometallurgical means for salvaging zinc wastes, an ammonia process for making active oxide developed by BGRIMM has been commercialized, and production technology for active electrolytic zinc powder has been granted a patent license and also industrialized. On the other hand, the technology for fully salvaging Zn-Mn dry batteries has also been seen in commercial production at the recovery of 81.3% Zn and 85.5% Cu.

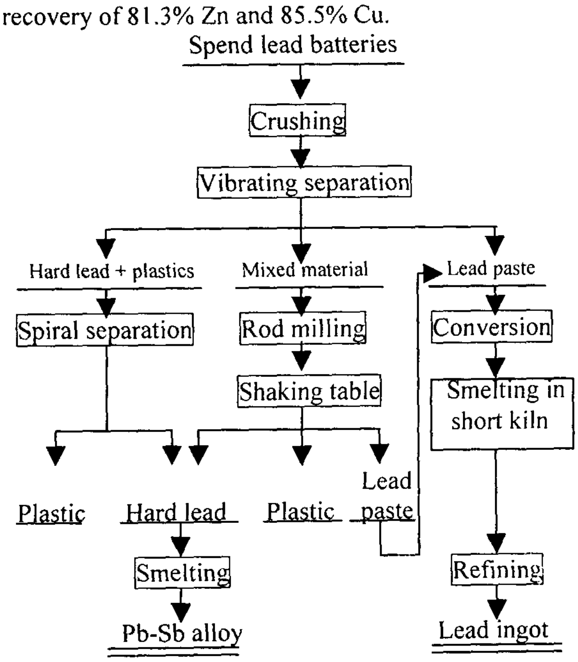

Fig. 2. Principle flow sheet of lead recovering through wet desulphurization and reduction at low temperature

5. Secondary Nickel and Cobalt

The domestic production of nickel, especially cobalt is far from meeting the need of national economic development. Moreover, the price of cobalt metal has recently risen by a large margin on the world market. As a result the industry of salvaging nickel and cobalt wastes in China has remarkably been developed. Now there are 20 and more plants working at recovering and regenerating nickel and cobalt chemicals from the wastes. Their production capacity is in the range of 50~200 t Co/a, amounting to 2500 t equivalent cobalt metal per year.

5.1 Resource

Domestic wastes for recycling scrap nickel and cobalt is mainly scrap of high temperature alloy steel and chrome-nickel alloy steel, spent hard alloy, magnet steel and Ni-Co catalysts. However, in recent years nickel and cobalt scraps imported from Russia, USA, Canada and Africa have accounted for a significant part of such resources.

5.2 Status quo and technology

a) Process of melting & casting -- liquidation by electrolysis – purification – electrolysis. Earlier Ni -- Co scavengers, for example, the cobalt workshop at Nanjing Steel Works, were designed to treat domestic Ni – Co scraps. There the scrap alloy steel is firstly subjected to converting to remove impurities followed by casting, then the product undergoes such operations as liquidation by electrolysis, neutralization to remove iron, tri-iso-octylamine solvent extraction for removing copper and cobalt, and deep purification with chlorine. Finally, the purified solution returns to electrolysis with electro-refined nickel resulted. On the other hand, the cobalt raffinate reports to stripping followed by tri-iso-octylamine solvent extraction for separation, and ion exchange for removing lead and copper. And the anode is subjected to electrowinning with electro-refined cobalt yielded.

b) Process of acid dissolving scraps – D_2EHPA solvent extraction for removing impurities – PC-88A solvent extraction for separating nickel from cobalt – deposition by oxalic acid. This process is widely used presently for treating nickel and cobalt scraps, including those imported abroad. It consists of a chain of operations, such as dissolving scrap nickel and cobalt by hydrochloric or sulfuric acid, D_2EHPA solvent extraction for removing Fe, Cu, and Zn, PC-88A or Cyanex 272 solvent extraction of cobalt, stripping by hydrochloric acid, and deposition of $CoCl_2$ by oxalic acid. The cobalt oxalate resulted is finally subjected to calcination to make cobalt oxide. On the other hand, PC-88A raffinate undergoes deposition with ammonia carbonate to make nickel carbonate or reports to thickening and crystallization to yield crystalline nickel sulfate. This technology has been realized by BGRIMM at six domestic plants, where recovery rate of both cobalt and nickel is reported over 90%. It principle technological flow sheet is shown in figure 3.

6. Gap between SNM Industry in China and Its Advanced Level Abroad

It can be seen from the overview above that in recent years the SNM industry in China has recorded relatively speedy development, but still there exists a large gap between it and the advanced level overseas. Such gap can be expressed mainly as follows:

6.1 Small production scale, outmoded equipment and severe pollution.

There are only five SNM plants in China operating with the capacity ranging from 5000 to 10000 t/a, others are all small in size. Small plates are technically outmoded, showing low recoveries of metals and poor comprehensive utilization of resources, and posing severe pollution.

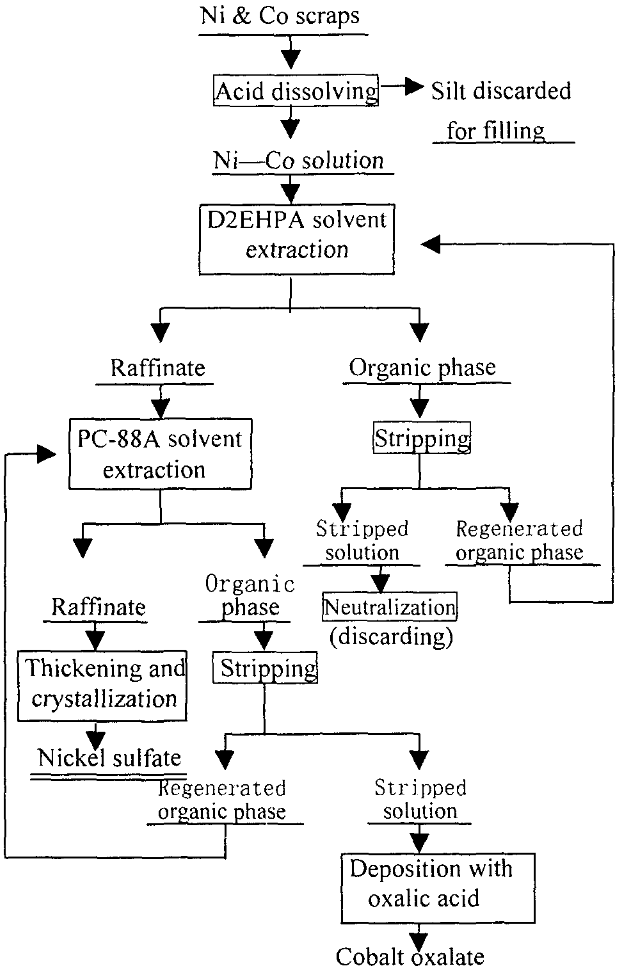

Fig.3 Principle technological flow sheet for making Ni & Co chemicals from their scrap

6.2 Crude classification and pretreatment of scrap metals.

The unified National Standards on Classification of Scrap Metals were promulgated in 1992, but they are being implemented not so strictly by a number of regional authorities. So crude classification is still seen somewhere. And the pretreatment is mostly resorted to handcraft, resulting in mediocre productivity.

6.3 Difficulty in collecting scrap metal.

Domestic consumption of Zinc metal for making dry batteries in a volume about ten billion pieces a year, amounts to about 200 thousands t/a, and that of aluminum for toothpaste tubes accounts for about 20 thousands t/a. However, the rejected batteries and spent tubes are not fully collected and salvaged due to trouble, which not only poses environmental pollution, but also waste valuable resources.

7. Conclusion

In recent years, the SNM industry in China has been quite speedy development. Especially in the area of clean hydrometallurgical technology, a lot of research work has been done, and a number of such plants showing less pollution and higher performances have been set up. The proportion of SNM reclaimed to the overall production of non-ferrous metals is gradually going up, and more attention is paid to the collection, classification and scavenges of scrap metals. Nevertheless, for the time being the SNM enterprise in China are mostly small in scale, causing more or less severe pollution to the surroundings somewhere. And the SNM resources are difficult to collect due to their dispensed distribution. With the national economy growing further as a whole, the consumption of non-ferrous metals surely goes up, bringing about expanding SNM resources. In view of this it is necessary for the government authority to elaborate more detailed polices to encourage the reutilization of such resources, and more advanced technologies concerned should be developed by relevant research institutions. All this will be targeted for better protection of the environment and sounder utilization of the resources.

References

[1] The 2000 Yearbook of Nonferrous Metals Industry of China, 2000.09(in Chinese)
[2] Ding Chaomo, Progress in Non-ferrous Metals Production, Central South University of Technology Publishing House, 1995(in Chinese)
[3] Yue Songguang, Metallurgy of Secondary Non-ferrous Metals, Central South University of Technology Publishing House, 1995(in Chinese)
[4] Chen Jiayong et al., Research and Development of Hydrometallurgy, Metallurgical Industry Press,1998(in Chinese)