中南大學
CENTRAL SOUTH UNIVERSITY

Unit 3 Pyrometallurgy

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School of Metallurgy and Environment

New words and expressions

- chromite['kroʊmaɪt]铬铁矿，亚铬酸盐
- lead [liːd]铅
- calcination [ˌkælsɪ'neɪʃən]煅烧
- roasting['roʊstɪŋ]焙烧
- calcine ['kælsaɪn]焙砂
- sintering ['sɪntərɪŋ]烧结
- agglomeration [əˌglɑːmə'reɪʃn]结块，成团
- sulfide ore ['sʌlfaɪd]硫化矿
- carbonate ore ['kɑːrbənət]碳酸盐矿物
- matte smelting造硫熔炼
- reduction smelting 还原熔炼
- fossil fuel['fɑːsl]矿物燃料

- fugitive ['fju:dʒitiv] 易挥发的
- intrinsic [in'trinsik]本质的
- equilibrium [ˌi:kwɪ'lɪbriəm] 平衡
- thermodynamics [ˌθɜ:rmoʊdaɪ'næmɪks] 热力学
- kinetics [kaɪ'netɪks]动力学
- mass-transfer rates 传质速率
- diffusion [dɪ'fju:ʒn] 扩散
- convection **[kən'vekʃn]** 对流
- reaction equilibrium反应平衡
- Prominence['prɔminəns]突出
- stringent regulations **['strɪndʒənt]** 严厉的规则

A

New words and expressions

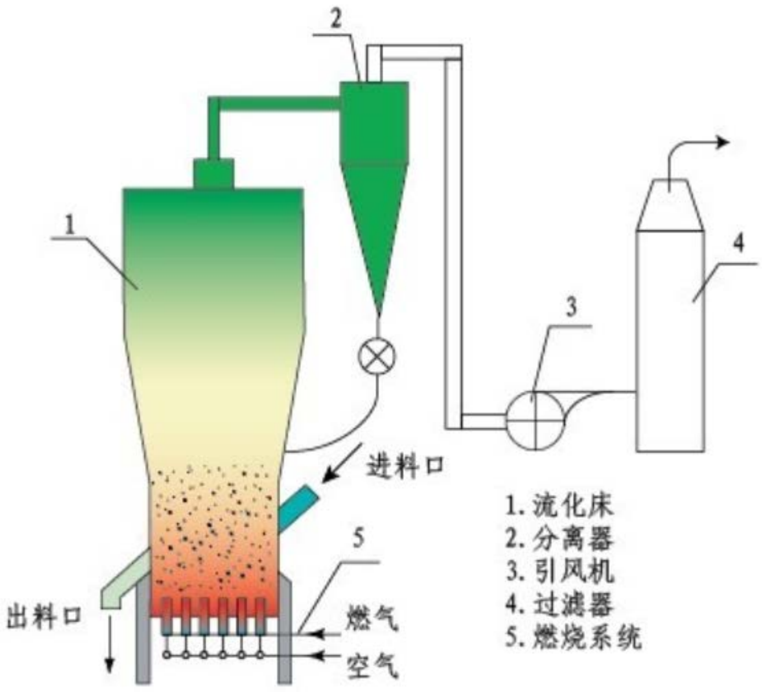
- phase equilibria 相平衡
- molten base-metal 熔融贱金属
- vapor pressure 蒸汽压
- silico-thermic reduction 硅热还原[sɪ'lɪkəʊ]
- Imperial Smelting [im'piəriəl] Process ['prəʊses] 帝国熔炼工艺
- fume and dust 烟尘
- noxious elements ['nɑːkʃəs] 有毒的元素
- stable Slags 渣
- interface 界面
- fluid bed roasting流态化床焙烧 ['fluːɪd]
- flash smelting闪速熔炼
- Coke焦炭
- Sinter烧结

New words and expressions

- continuous smelting [kən'tinjʊəs] 连续熔炼
- Mitsubishi [mi'tsubiʃi]continuous copper smelting and converting process三菱连续铜熔炼和吹炼过程
- shaft furnace smelting 竖炉熔炼
- zinc-lead blast furnace process锌铅鼓风炉
- copper cathodes ['kæθoʊd] 阴极铜
- process streams工艺物料流
- sulfuric acid [sʌl'fjʊrɪk] 硫酸
- limestone **['laɪmstoʊn]** 石灰
- chalcopyrite [ˌkælkə'paɪraɪt] 黄铜矿
- Account for 占…比列
- condenser [kən'densə] 冷凝器
- blister copper 粗铜

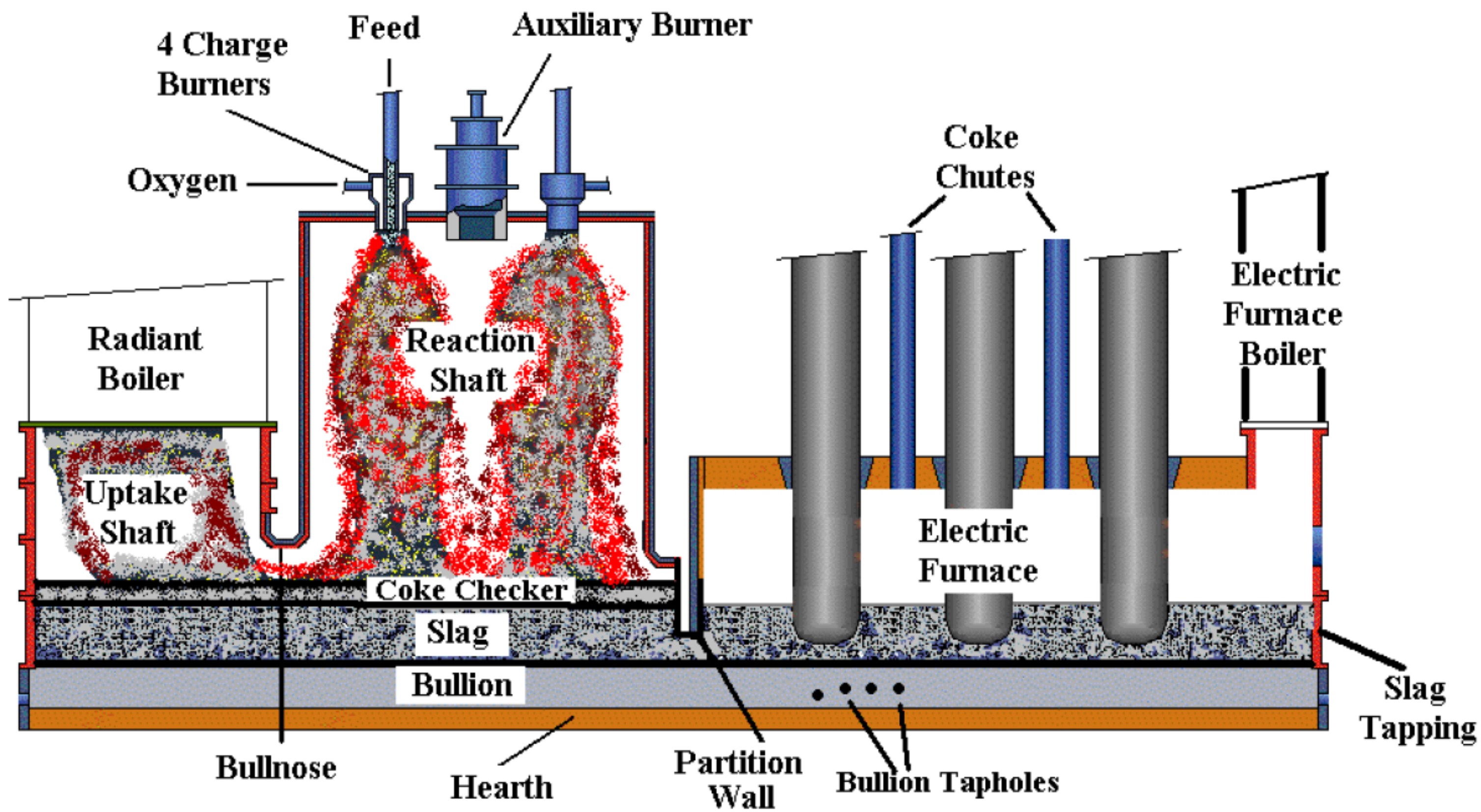
- Describe an operation
- Describe some advantages and disadvantages of some processes
- Familiar with some sentence types
  - Due to
  - Be contrasted with
  - Lead to/result in

Fluidized bed roasting

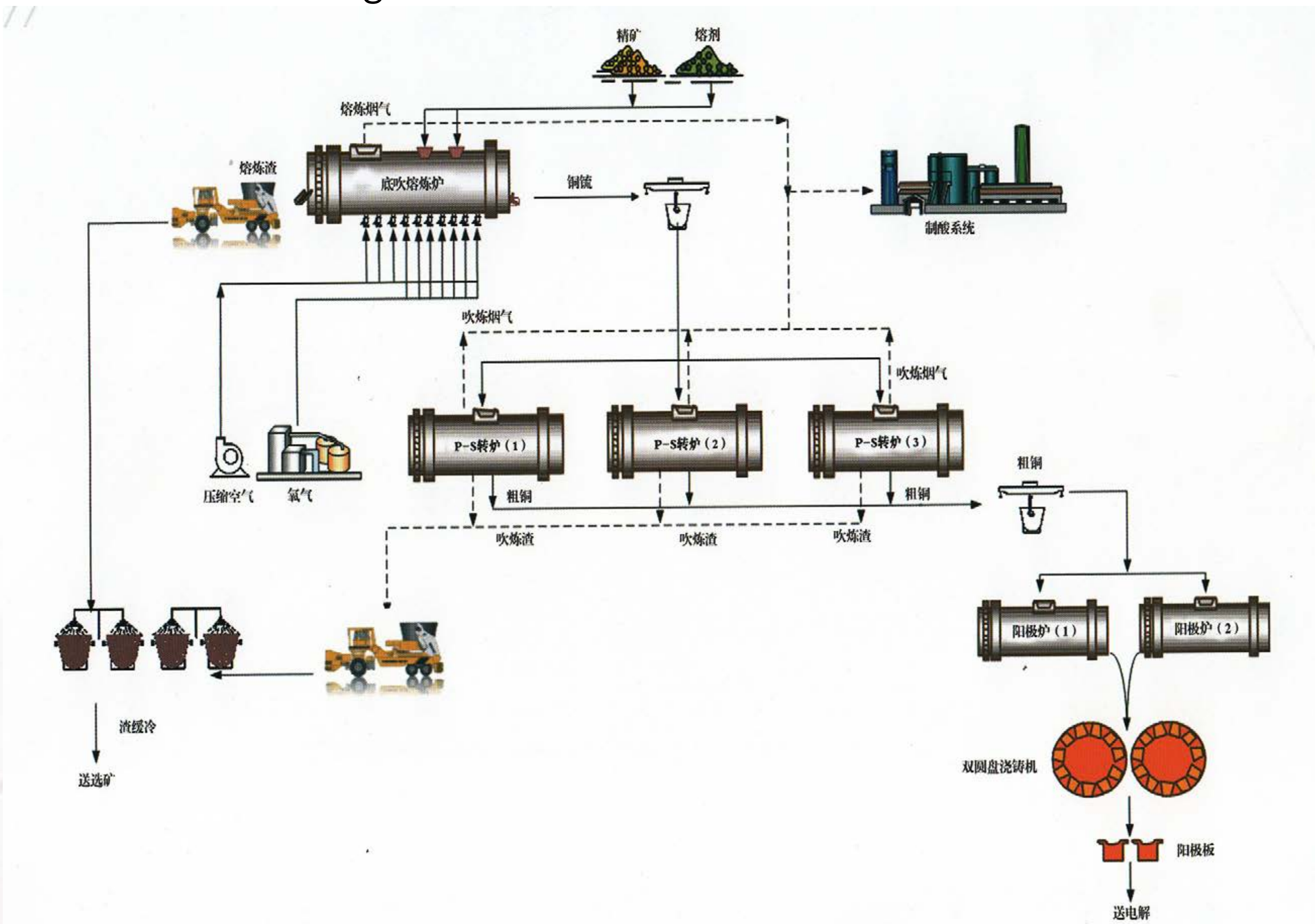


流态化焙烧炉系统示意图

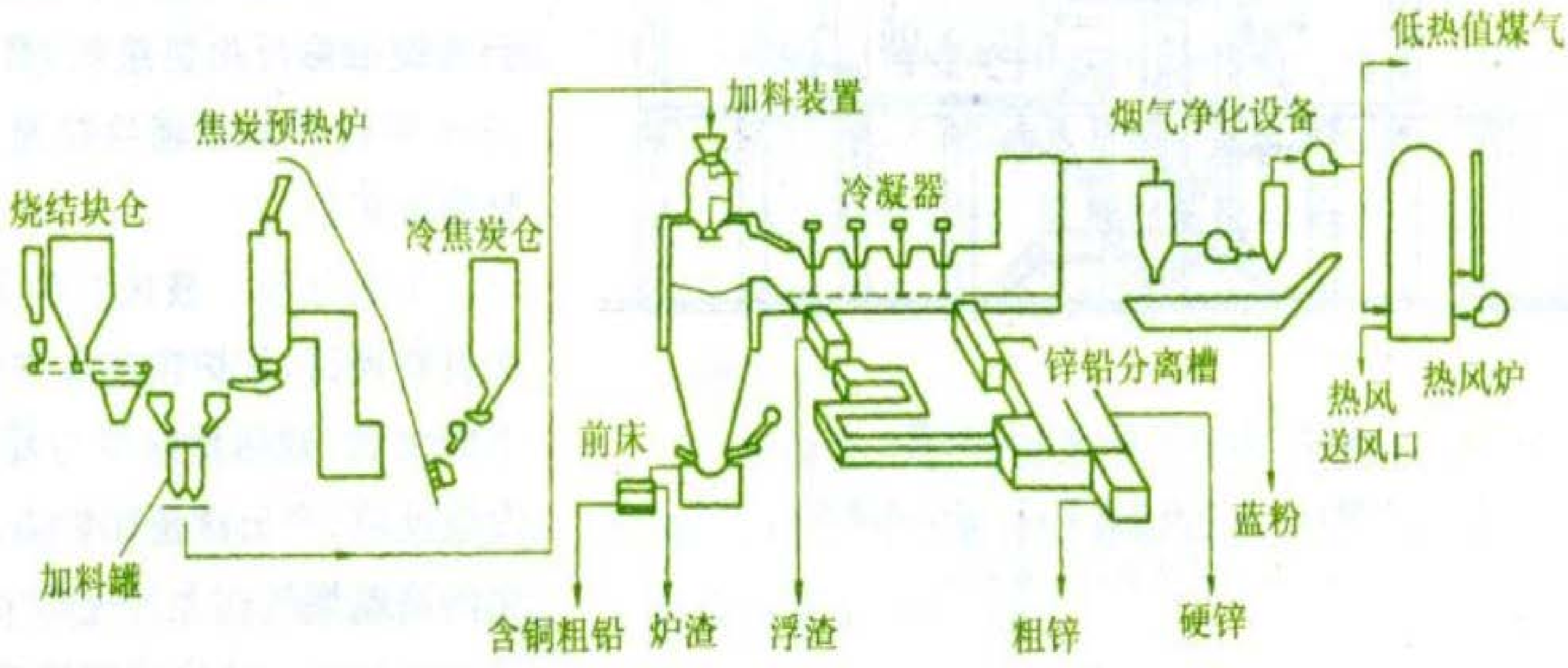
Flash smelting



Continuous smelting



帝国熔炼法


低热值煤气
加料装置
焦炭预热炉
烟气净化设备
冷凝器
烧结块仓
冷焦炭仓
锌铅分离槽
热风炉
热风
送风口
前床
蓝粉
加料罐
硬锌
含铜粗铅
炉渣
浮渣
粗锌

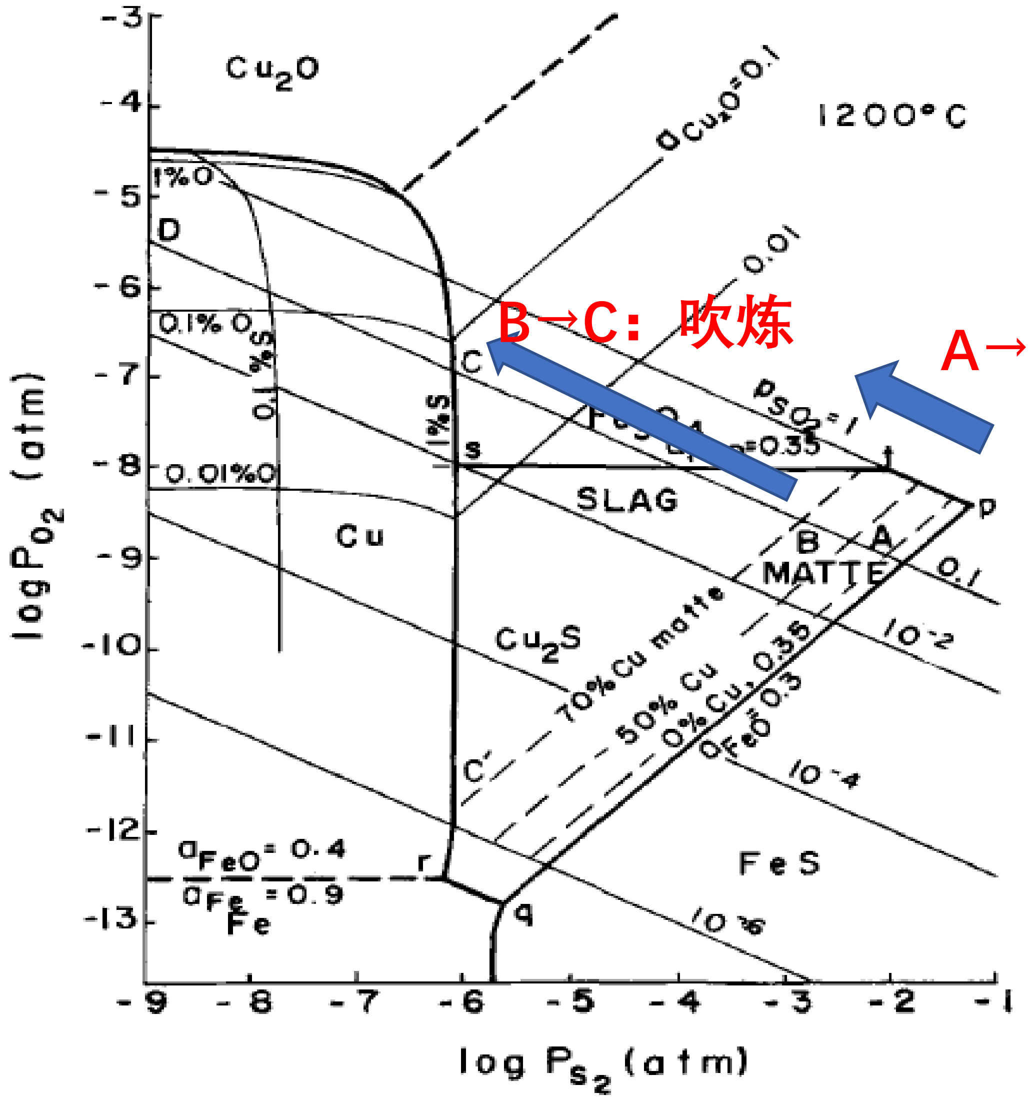


Fig. 10—Sulfur-oxygen potential diagram for Cu-Fe-S-O-SiO$_2$ system at 1200°C.

Yazawa A.. Metall Trans B 1979;10:307-321

传统烧结-还原熔炼工艺

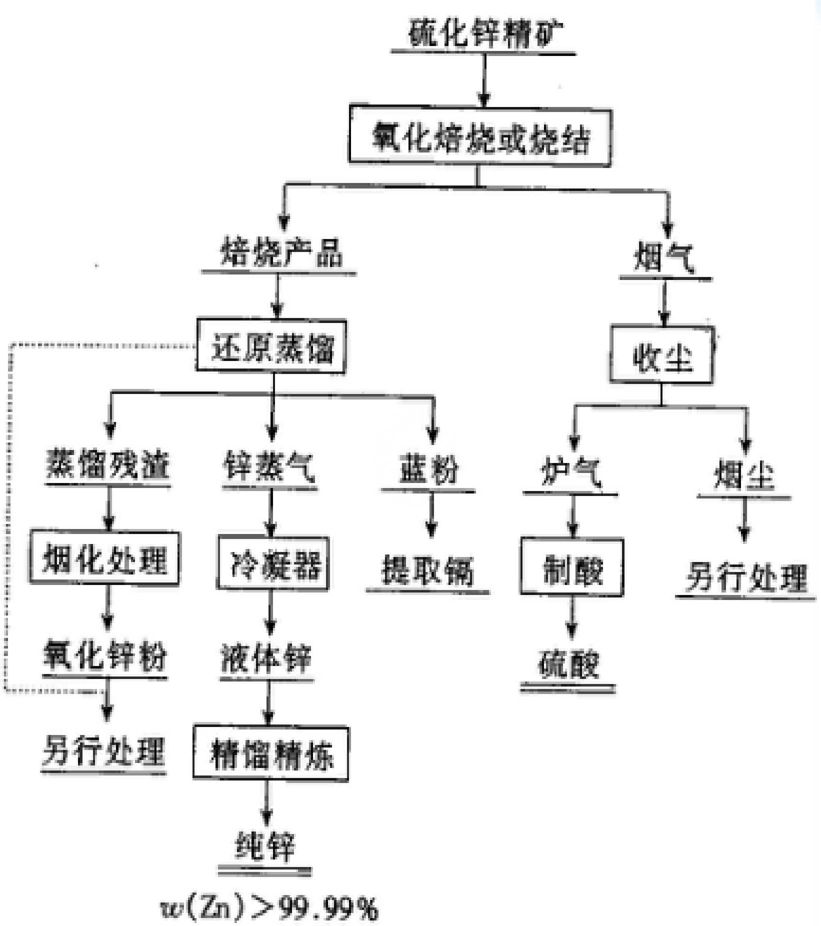
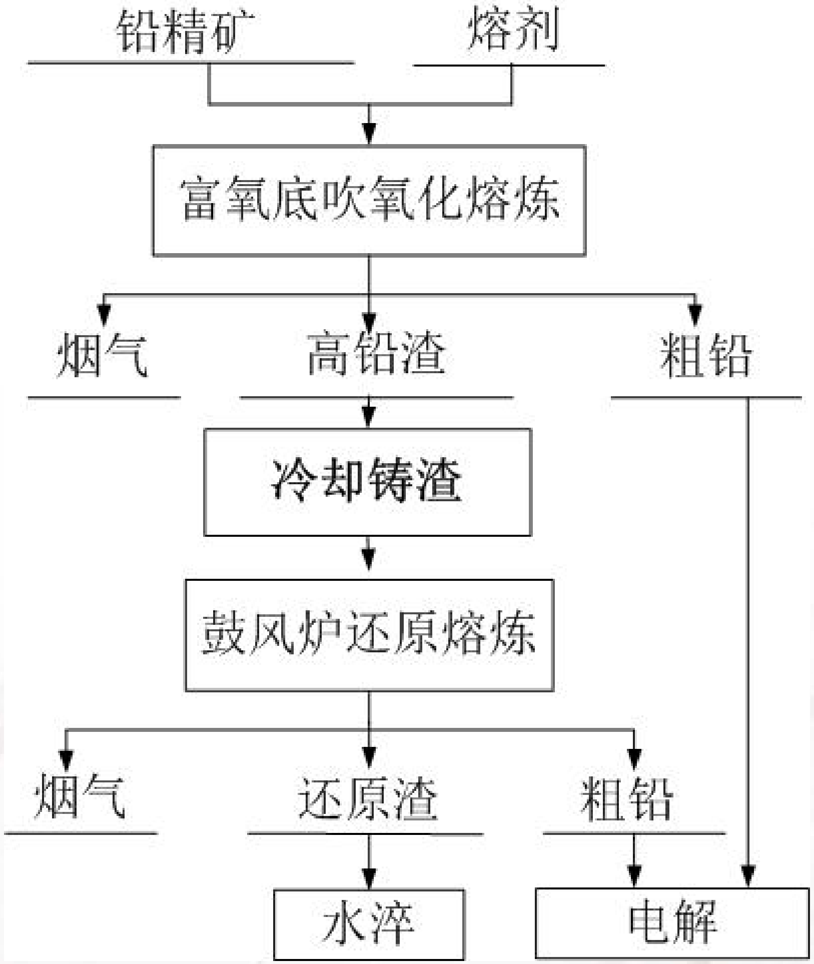


图3-1 火法炼锌原则工艺流程图

富氧熔炼-还原熔炼工艺



Imperial smelting

- The process starts by charging solid sinter and heated coke into the top of the blast furnace. Preheated air at 190 to 1050 °C is blown into the bottom of the furnace. Zinc vapor and sulfides leave through the top and enter the condenser. Slag and lead collect at the bottom of the furnace and are tapped off regularly. The zinc is scrubbed from the vapor in the condenser via liquid lead. The liquid zinc is separated from the lead in the cooling circuit.

C

outline

- Definition of pyrometallurgy
- History of pyrometallurgy
- Development
- Position
- intrinsic properties

Text A Characteristics of pyrometallurgy

1 Definition of pyrometallurgy

Pyrometallurgy works on the thermal treatment of ores or concentrates resulting in physical and chemical transformations in parent minerals and enables the recovery of valuable metals. The treatment produces saleable products (metals) or intermediate compounds/alloys (impure metals) for further processing (refining). The pyrometallurgical process is suitable for iron ore, chromite, lead, zinc, copper, tin, tungsten, etc. Pyrometallurgy follows one or more of the following processes:

(1) Calcination, which is the thermal decomposition of a sulfide/carbonate ore.

(2) Roasting, which drives out unwanted sulfur and carbon from sulfide/carbonate ore in the oxidizing environment, leaving an oxide.

(3) Sintering, which is the agglomeration process to cause the powdery ore or oxide to become coherent particles by heating without melting.

(4) Smelting, which is mainly a process of melting and separation of the charge into two immiscible liquid layers, i. e. liquid slag and liquid matte or liquid metal. There are two major types of smelting process: matte smelting and reduction smelting. Matte smelting processes are carried out in two stages: matte making step and converting.

(5) Refining, which removes impurities in the crude metal through fire refining or distillation.

Commercially, the production of iron, zinc, lead, and tin adopts the roasting/sintering-reduction smelting-refining process, whereas copper and nickel are preferable to matte making-converting-refining process.

2 History and development of pyrometallurgy

Pyrometallurgy for many years was the only method available for the recovery of metals from their ores, and dates back to as early as 3000 B. C. It was not until the late nineteenth century that hydrometallurgy and electrometallurgy were introduced. Although hydrometallurgy has come to play an increasingly important role in the production of nonferrous metals, numerous improvements in nonferrous pyrometallurgy have enabled it to retain its prominence in spite of stringent regulations regarding sulfur dioxide emissions and rising energy costs.

Although the basic chemistry of pyrometallurgical processes has remained the same, the practice of pyrometallurgy has undergone major improvements due to a better understanding of the high-temperature chemistry, the introduction of improved refractories and other materials of construction, the availability and use of low-cost oxygen, the development of flash smelting and continuous smelting processes, the application of control devices, including computer process control, and the reduction in gaseous emission to the atmosphere. The processes of nonferrous pyrometallurgy which have come into practice include fluidized bed roasting, flash smelting, and continuous smelting of copper concentrates using oxygen, shaft furnace melting of copper cathodes, and continuous casting of copper rod, cakes, and billets, and the zinc-lead blast furnace process.

Pyrometallurgy accounts for more than half of nonferrous metal production, and is likely to retain this position because of its many inherent advantages. Large volumes of waste gas and fugitive gas released to the work-place are now recognized as serious disadvantages of most conventional smelting processes. Modern process designs, however, can significantly reduce the volume of waste gas that must be cleaned and processed, reduce the escape of fugitives, and, at the same time, further exploit the inherent ability of pyrometallurgy to yield energy-efficient processes of high specific capacity.

3 Characteristics of pyrometallurgy

Table 1 lists nine properties of the high-temperature systems of pyrometallurgy that help to explain both the advantages and disadvantages of this means of metal processing. These are intrinsic properties—they remain true regardless of development of new technology.

Table 1 Some intrinsic properties of high-temperature processes

(1) High chemical reaction rates at high temperature.
(2) Temperature variation can be used to alter reaction equilibrium.
(3) Metal sulfides are also fuels.
(4) Process streams have high concentration of metal.
(5) Many molten metals are immiscible with molten oxides (slags).
(6) Precious metals are soluble in molten lead, copper or nickel.
(7) Vapor pressures are often large at high temperature.
(8) Processes, almost invariable, produce a waste gas stream.
(9) Metallurgical slags are relatively stable in the natural environment.

(1) **High reaction rate**: Typical pyrometallurgical processes operate at temperatures between 800℃ and 1600℃ and at these temperatures most chemical reaction rates are so high that overall process kinetics are controlled by mass-transfer rates (diffusion and convection) to the reaction site. This must be contrasted with leaching reactions of hydrometallurgy near ambient temperature

(25−150℃), where slow chemical kinetics frequently control the process rate, and lead to the need for long residence time in the reactor.

(2) **Reaction equilibrium**: The freedom in high temperature processing of selecting the process temperature makes possible the adjustment of the equilibrium state of a given reaction to favor a desired result. Thus, conversion of white metal to blister copper by blowing with air depends upon the equilibrium state of the Reaction (3−1).

$$Cu_2S + 2Cu_2O = 6Cu + SO_2 \qquad (3-1)$$

This reaction equilibrium is favorable for copper production at 1200℃, and unfavorable at 800℃. Similar examples are legion in pyrometallurgy. The severely restricted range of temperature in hydrometallurgy precludes the use of temperature variation to significantly alter reaction equilibrium except in a few cases.

(3) **Sulfide fuel**: That raw material sources of many nonferrous metals are sulfides ($CuFeS_2$, ZnFeS, PbS, FeNiS, etc.) is a fact of nature. That oxidation of the sulfur and iron in these minerals releases considerable heat is both a fact of nature and a big advantage to pyrometallurgy processes that can use this heat to replace that from fossil fuels.

(4) **Metal concentration**: The process stream in pyrometallurgy—be it the concentrate and flux mixture, or metal and slag mixture—is highly concentrated with respect to metal, typical values range from 500−2000 grams of metal per liter. This contrasts with hydrometallurgical system, where metal concentration usually ranges from 10−100 grams of metal per liter. The absence of the large volume of dilute water in pyrometallurgical practice accounts for this difference.

(5) **Phase equilibria**: The immiscibility that exists between molten metal and oxide slag, and between sulfide matte and slag, for many nonferrous systems is a fact of nature that leads itself to simple, inexpensive phase separations in pyrometallurgy. Likewise, the preferential solubility of the precious metals in molten base-metal (Pb, Cu or Ni) compared with their solubility in slag or matte is an inherent property of high-temperature systems that has few counterparts in hydrometallurgical processing.

(6) **Vapor pressure**: Pyrometallurgical processes often operate at temperatures where the vapor pressure of metals and metal compounds is appreciable (1.0×10^2 Pa to 1.0×10^5 Pa). This can lead to a desired result, such as selective vaporization of magnesium in the Silico-thermic Reduction Process, or vaporization of the zinc in the Imperial Smelting Process. It can, and frequently does, lead to unwanted vaporization with the production of fume and dust that must be collected and returned to the process (e. g. vaporization of PbS, PbO and Pb in lead smelting).

(7) **Waste gases**: The ubiquity of waste gas streams in pyrometallurgy resembles the ever-present aqueous phase in hydrometallurgy. High temperature is achieved and maintained by combination of fuel—either intentionally added or present in the raw material treated and combustion gases are the result. Only when expensive electric heating is employed are combustion gases absent, and even in such cases a significant volume of waste gas is usually generated by the smelting reactions themselves. By the very nature of things, pyrometallurgy will always be faced

- Pyrometallurgy works on the thermal treatment of ores and concentrates resulting in physical and chemical transformations in parent minerals and enables the recovery of valuable metals. The treatment produces saleable products（metals）or intermediate compounds/alloys（impure metals）for further processing（refining）. The pyrometallurgical process is suitable for iron ore, chromite, lead, zinc, copper, tin, and tungsten.
  - parent minerals 母矿　valuable metals有价金属
  - 本句翻译：火法冶金就是热处理矿物和精矿，使得他们发生物理和化学的转变，从而可以回收有价金属。热处理可以生产可出售的金属产品，也可生产需要进一步处理的中间化合物或者合金。火法冶金适合于铁矿，铬铁矿，铅，锌，铜，锡和钨矿。

- Pyrometallurgy follows one or more of the following processes:
  - Calcination: which is the thermal decomposition of a sulfide / carbonate ore.
  - Roasting: which drives out unwanted sulfur and carbon from sulfide / carbonate ore in the oxidizing environment, leaving an oxide.
  - Sintering: which is the agglomeration process to cause the powdery ore or oxide to become coherent particles by heating without melting.
  - Smelting: which is mainly a process of melting and separation of the charge into two immiscible liquid layers, i. e. liquid slag and liquid matte or liquid metal. There are two major types of smelting process: reduction smelting and matte smelting. Matte smelting processes are carried out in two stages: mattemaking step and converting.
  - refining: which removes impurities in the crude metal through fire refining or distillation.

■thermal decomposition:热分解

■Immiscible混熔的

- The extraction of nonferrous metals from ores and concentrates is based on chemical reactions carried out at high temperatures. Pyrometallurgy for many years was the only method available for the recovery of metals from their ores, and dates back to as early as 3000 B.C.
- 句 型 ： reaction or experiment was carried out/performed at ….temperature.

- It was not until the late nineteenth century that hydrometallurgy and electrometallurgy were introduced.
- Although hydrometallurgy has come to play an increasingly important role in the production of nonferrous metals, numerous improvements in nonferrous pyrometallurgy have enabled it to retain its prominence in spite of stringent regulations regarding sulfur dioxide emissions and rising energy costs.
- 句型： … plays an increasingly important role in sth

- Although the basic chemistry of pyrometallurgical processes has remained the same, the practice of pyrometallurgy has undergone major improvements due to a better understanding of the high-temperature chemistry, the introduction of improved refractories and other materials of construction, the availability and use of low cost oxygen, the development of flash smelting and continuous smelting processes, the application of control devices, including computer process control, and the reduction in gaseous emission to the atmosphere.

- The processes of nonferrous pyrometallurgy which have come into prominence include fluid bed roasting, flash smelting, and continuous smelting of copper concentrates using oxygen, shaft furnace melting of copper cathodes, and continuous casting of copper rod, cakes and billets and zinc-lead blast furnace process.

- The pyrometallurgical process is suitable for iron ore, chromite, lead, zinc, copper, tin, and tungsten.
- Pyrometallurgy follows one or more of the following processes:
  - (1) Calcination, which is the thermal decomposition of a sulfide/carbonate ore.
  - (2) Roasting, which drives out unwanted sulfur and carbon from sulfide/carbonate ore in the oxidizing environment, leaving an oxide.
  - (3) Reduction, which is a type of thermal application at temperatures above melting point of the metal, with at least one product in the molten phase. The metal oxide is heated with coke/ charcoal, a reducing agent that liberates oxygen as carbon dioxide leaving a refined metal.

- Pyrometallurgy accounts for more than half of nonferrous metal production, and is likely to retain this position because of its many inherent advantages. Large volumes of waste gas and fugitive gas released to the work-place are now recognized as serious disadvantages of most conventional smelting processes. Modern process designs, however, can significantly reduce the volume of waste gas that must be cleaned and processed, reduce the escape of fugitives, and, at the same time, further exploit the inherent ability of pyrometallurgy to yield energy-efficient processes of high specific capacity.高产能

Table 1 lists nine properties of the high-temperature systems of pyrometallurgy that help to explain both the advantages and disadvantages of this means of metal processing. These are intrinsic properties-they remain true regardless of development
of new technology.

Table 1. Some Intrinsic Properties of High-Temperature Processes

No.	Properties
1	High chemical reaction rates at high temperature.
2	Temperature variation can be used to alter reaction equilibrium.
3	Metal sulfides are also fuels
4	Process streams have high concentration of metal.
5	Many molten metals are immiscible with molten oxides slags)
6	Precious metals are soluble in molten lead, copper or nickel.
7	Vapor pressures are often large at high temperature
8	Processes, almost invariable, produce a waste gas stream
9	Metallurgical slags are relatively stable in the natural environment

High Reaction Rate:

- Typical pyrometallurgical processes operate at temperature between 800 °C and 1600 °C and at these temperatures most chemical reaction rates are so high that overall process kinetics are controlled by mass-transfer rates (diffusion and convection) to the reaction site.
- This must be contrasted with leaching reactions of hydrometallurgy near ambient temperature (25-150°C), where slow chemical-kinetics frequently control the process rate, and lead to the need for long residence time in the reactor.

residence time停留时间
Contact time接触时间
Reaction time反应时间

- 获得的结果与....相反
  - The results obtained contrast with
- 获得的结果与。。。相一致
  - The result obtained agrees with
  - is in agreement with
  - is in line with
  - is consistent with
  - fits into

Reaction equilibrium:

- The freedom in high temperature processing of selecting the process temperature makes possible the adjustment of the equilibrium state of a given reaction to favor a desired result.
- Thus conversion of white metal to blister copper by blowing with air depends upon the equilibrium state of the reaction.

$$Cu_2S + 2Cu_2O = 6Cu + SO_2$$

- This reaction equilibrium is favorable for copper production at 1200°C, and unfavorable at 800°C. Similar examples are legion in pyrometallurgy.
- The severely restricted range of temperature in hydrometallurgy precludes the use of temperature variation to significantly alter reaction equilibrium except in a few cases.

将白冰铜转化为粗铜取决于下列反应的平衡状态

Sulfide fuel:

- That raw material sources of many non-ferrous metals are sulfides (CuFeS2, ZnFeS, PbS, FeNiS, etc.) is a fact of nature. That oxidation of the sulfur and iron in these minerals releases considerable heat is both a fact of nature and a big advantage to pyrometallurgy processes that can use this heat to replace that from fossil fuels.

注意4个that的用法

Metal concentration:

- The process stream in pyrometallurgy----be the concentrate and flux mixture, or metal and slag mixture----- is highly concentrated with respect to metal, typical values range from 500-2000 grams of metal per liter.
- This contrasts with hydrometallurgical system, where metal concentration usually ranges from 10-100 grams of metal per liter. The absence of the large volume of dilute water in pyrometallurgical practice accounts for this difference.

这个反应对于铜离子是一级反应，对于氢离子是二级反应。

Phase equilibria:

- The immisicibility that exists between molten metal and oxide slag, and between sulfide matte and slag, for many non-ferrous systems is a fact of nature that leads itself to simple, inexpensive phase separations in pyrometallurgy.
- Likewise, the preferential solubility of the precious metals in molten base-metal (Pb,Cu or Ni) compared to their solubility in slag or matte is an inherent property of high-temperature systems that has few counterparts in hydrometallurgical processing.

Vapor pressure:

- Pyrometallurgical processes often operate at temperatures where the vapor pressure of metals and metal compound is appreciable (0.001 to 1.0atm).
- This can lead to a desired result, such as selective vaporization of magnesium in the silico-thermic reduction process, or vaporization of the zinc in the Imperial smelting Process. It can, and frequently does, lead to unwanted vaporization with the production of fume and dust that must be collected and returned to the process (e.g. vaporization of PbS, PbO and Pb in lead smelting).

Waste gases:

- The ubiquity of waste gas streams in pyrometallurgy resembles the ever-present aqueous phase in hydrometallurgy. High temperature are achieved and maintained by combination of fuel---either intentionally added or present in the raw material treated and combustion gases are the result. 普遍存在
- Only when expensive electric heating is employed are combustion gases absent, and even in such cases a significant volume of waste gas is usually generated by the smelting reactions themselves.
- By the very nature of things, pyrometallurgy will always be faced with waste gases containing dust, fume and noxious elements, the volume and composition of the waste gas produced, however, will vary significantly with the specific design of the process.

Stable slags:

- Slags, the solid waste from many pyrometallurgical processes, are close relative of natural rocks, and are relatively resistant to leaching and weathering in the natural environment.

➢Homework

Please describe an example that how is a conventional pyrometallurgical process improved to reduce waste gas emission and energy consumption.

➢**translation**

- 将30g黄铜矿和20克石灰lime、10克石英quartz混合均匀后，放入坩埚中，将坩埚放入炉膛加温区中，升温，升温速度为10℃/min。当温度达到1200 ℃，通入空气，空气流速air flow rate为0.2L/min，在1200 ℃下煅烧3h后roast，然后冷却，当温度降到100 ℃，取出坩埚crucible，分离冰铜和渣。

➢ translation

- The melting experiments were carried out by mixing 30 g chalcopyrite ,20 g lime with 10 g quartz(30 g chalcopyrite, 20 g lime were mixed with 10 g quartz). After the mixture was filled into a crucible, it was placed into the hot zone of the furnace and heated at a rate of 10℃/min to a temperature of 1200 ℃. Then, air was blown at a flowrate of 0.2L/min. After roasting for 3 h, the furnace was cooled to 100 ℃ in order to separate the matte and slag phases each other and from the crucible.

THANKS

The End

lecturer:

School of Metallurgy and Environment