

# Unit 16 aluminum metallurgy



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School of Metallurgy and Environment

- radiant energy 辐射能
- electrical conductivity 电导
- electrical transmission line 电线
- vegetation [,vedʒi'teɪʃən] 植被
- gibbsite ['gɪbzait] 三水铝矿
- Hydrargillite [hai'drɑ:dʒələit] 水铝矿
- aluminum [ə'luminəm] 铝
- boehmite ['bə:mait] 勃姆石，一水软铝石
- diaspore ['daɪəspɔ:] 一水硬铝石
- anatase ['ænəteɪs] 锐钛矿
- kaolinite ['keɪlənaɪt] 高岭石
- rutile ['rʊtɪl] 金红石
- brookite ['bru:kait] 板钛矿
- ilmenite ['ilmənait] 钛铁矿  
 $\text{FeTiO}_3$
- corundum [kə'rʌndəm] 刚玉；  
金刚砂
- supersaturate [su:pə'sætʃəreɪt] 超饱和
- decantation [di:kæn'teɪʃən] 倾析
- paper filler 纸张填料
- paper coating 纸上涂胶，纸上涂布

- zirconium [zə:'kəʊniəm] 锆
- vanadium [və'neidiəm] 钒
- gallium ['gæliəm] 镓
- chromium ['krəʊmiəm] 铬
- manganese [mæŋgə'ni:z] 锰
- Alumina monohydrate  
[ə'lu:miənə] [,mɒno'hai,dret]
- fused cryolite ['kraɪələɪt] 冰晶石
- anorthosite [ə'nɔ:θəsait] 斜长石
- syenite ['saɪənait] 正长石，黑花岗岩
- alunite ['æljunait] 明矾石
- bayer process
- digest 溶出
- caustic soda ['səʊdə] 苛性碱
- red mud 赤泥
- sodium aluminate 铝酸钠
- desilication [di:sili'keɪʃən] 脱硅作用
- counter current 逆流
- nepheline ['nefəlin] 霞石

- spent liquor 废液
- desiccant ['desikənt] 干燥剂
- catalyst ['kætəlist] 催化剂
- limestone ['laɪmstəʊn] 石灰石
- pedersen process 佩德森法
- stub [stʌb] 树桩
- cavity ['kævɪti] 洞
- prebaked anode 预焙阳极
- carbonaceous [kɑ:bə'neɪʃəs] 碳质的
- soderberg anode 自焙阳极（索德伯格阳极）
- crust 外壳
- sidewall 侧壁
- siphon ['saɪfən] 虹吸
- rectifier losses 整流器
- potline ['pɒtlain] 电解槽系列
- carbon block 碳块
- pitch coke 焦炭
- coal tar 焦油
- ground coke
- bus bar 母线

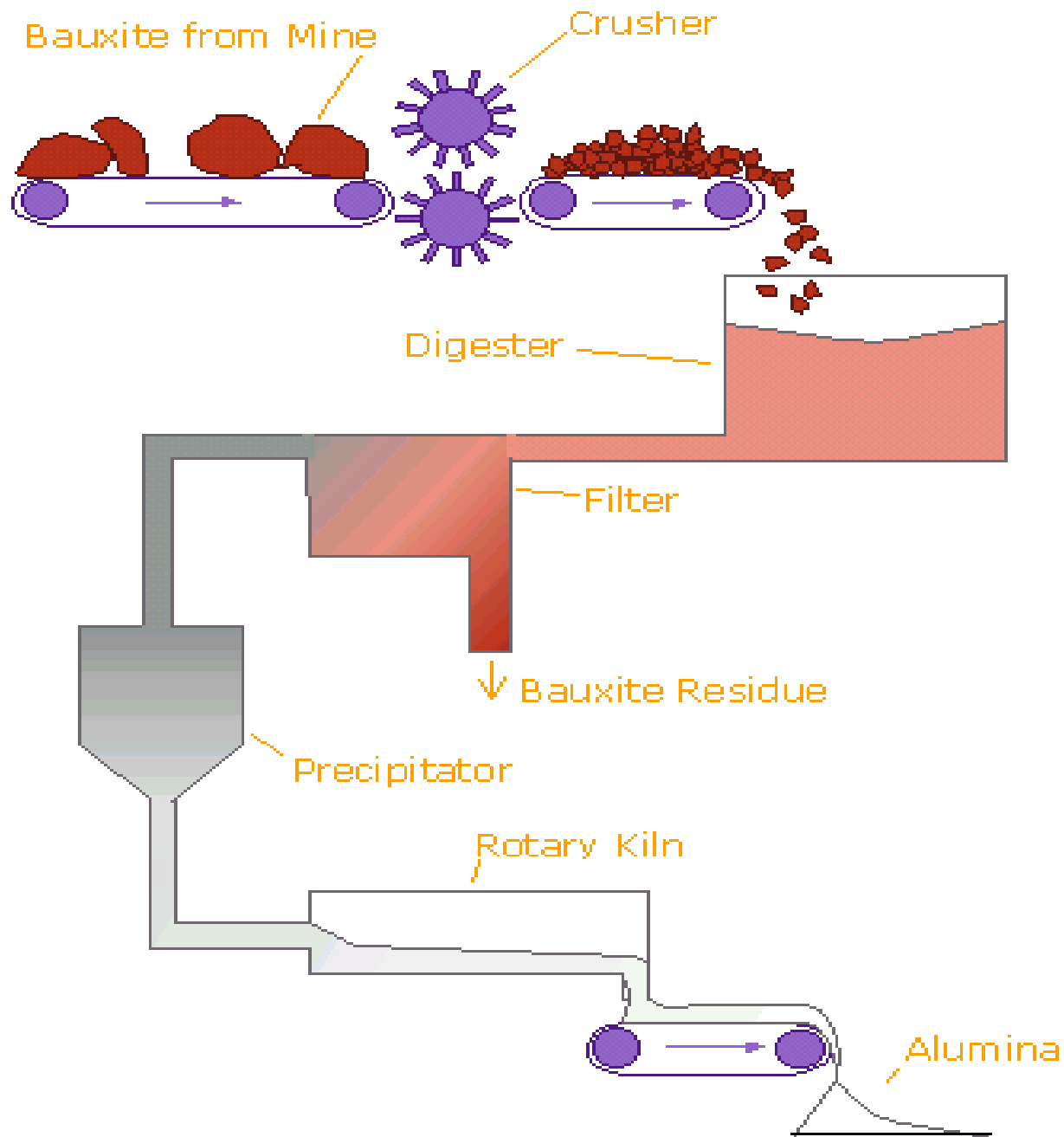
- Introduction
- Natural occurrence of aluminum ore
- Production process
  - Alumina extraction: Bayer process
    - Ore processing
    - digestion:
      - dilution
      - decomposition
      - evaporation
  - calcination
  - Electrolysis
    - Cell and electrolyte
    - Current efficiency and energy consumption
    - anode

## ■ 非限制性定语

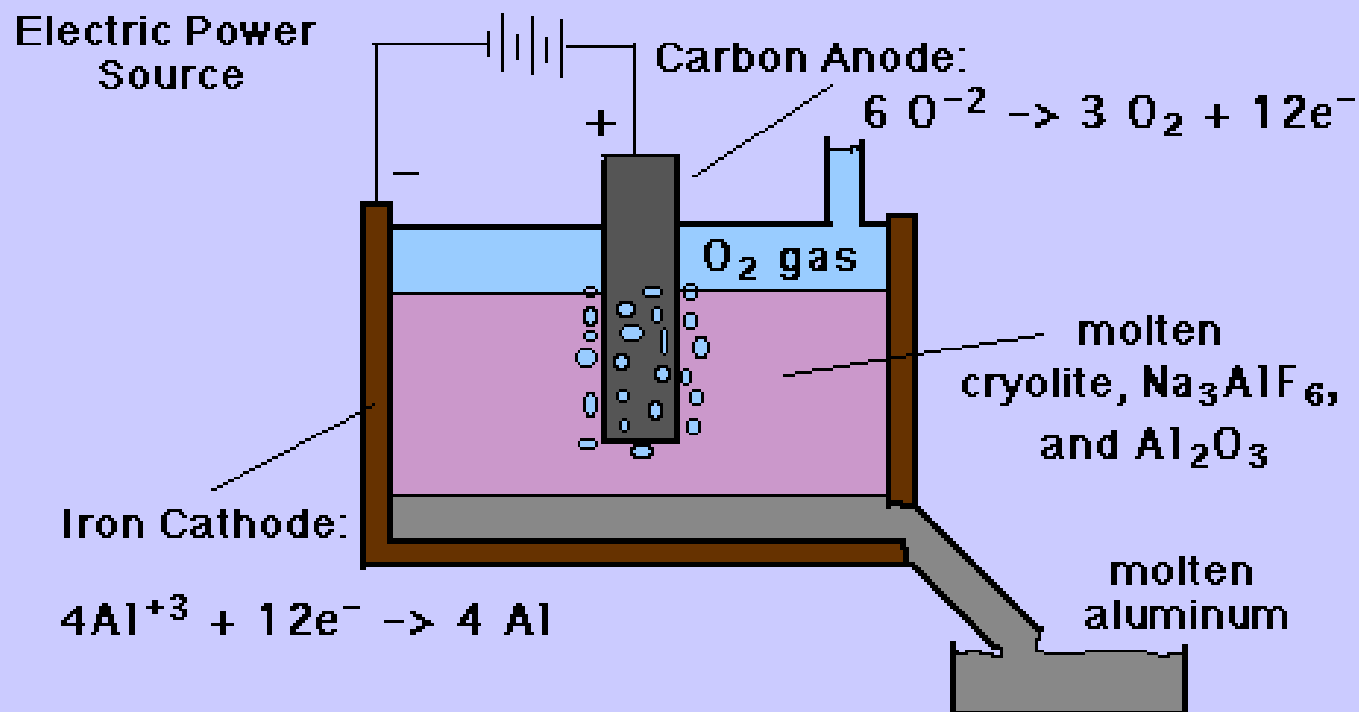
➤ 形容词短语，过去分词短语，现在分词短语，介词短语

- Your parents, looking greatly worried, walk up and down on the street.
- The story, written by a young girl, became popular with the young.
- Our earth, in traveling around the sun, may meet many unidentified objects in space.
- The student, ashamed of his bad temper, became kind now.

## ■ 一个工艺或工序连续动作的描写



# Electrolysis of Aluminum



Bauxite ore is purified to  $\text{Al}_2\text{O}_3$ , which is mixed with cryolite, a mixture of  $\text{NaF}$  and  $\text{AlF}_3$ , which melts at 1000 C.



- The density of aluminum is small, only  $2.7 \text{ g/cm}^3$ , pure aluminum is soft, but can be made into all kinds of hard aluminum alloy;
- the electrical conductivity of the aluminum is only inferior to silver and copper;
- Aluminum is a good conductor of heat.
- Aluminum has good ductility. In  $100^\circ\text{C} \sim 150^\circ\text{C}$ , Aluminum can be made into thin  $0.01 \text{ mm}$  aluminum foil.

Because of its many desirable physical, chemical and metallurgical properties, aluminum has become the most widely used non-ferrous metal.



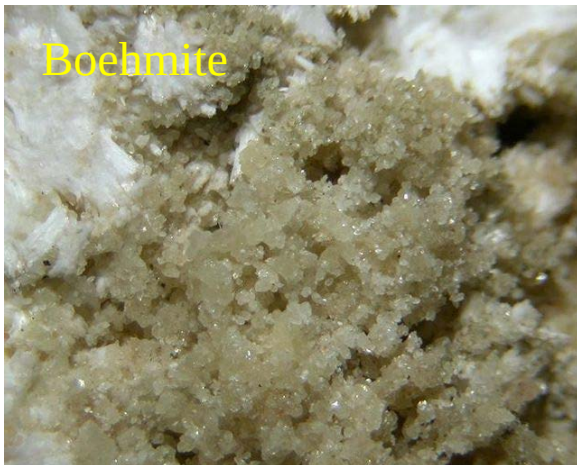
- Aluminum is the most abundant metallic element on the Earth and Moon, but is never found free in nature.
- It makes up more than 8% of the solid portion of the Earth's surface, seawater contains an average of only 0.5 ppm aluminum.
- The element is widely distributed in plant where it may be present in significant concentrations, particularly in vegetation in marshy place and acid soils.



- Bauxite is often thought of as a mineral but is really a rock composed of aluminum oxide and hydroxide minerals such as gibbsite, boehmite,  $\text{AlO}(\text{OH})$  and diaspore,  $\text{HAlO}_2$ , as well as clays, silt and iron oxides and hydroxides.
- **Gibbsite, diaspore and boehmite** are 3 major minerals of bauxite.
  - Gibbsite is aluminum hydroxide minerals in bauxite deposit. It is often designated as  $\gamma\text{-Al}(\text{OH})_3$  (but sometimes as  $\alpha\text{-Al}(\text{OH})_3$ ). It is also sometimes called hydrargillite



- Boehmite, structural formula  $\text{AlO}(\text{OH})$ , molecular formula  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . It is white with tints of yellow, green, brown or red due to impurities.
- Diaspore has a molecular formula  $\text{HAlO}_2$ , Often containing trace iron and manganese. It occurs sometimes as flattened crystals, but usually as lamellar or scaly masses有鳞的, It is colorless or greyish-white, yellowish, sometimes violet in color, and varies from translucent半透明 to transparent .





- Clay minerals such as kaolinite  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ , quartz  $\text{SiO}_2$ , and anatase, rutile, and brookite  $\text{TiO}_2$ , small amounts of magnetite  $\text{Fe}_3\text{O}_4$ , ilmenite  $\text{FeTiO}_3$  and corundum  $\text{Al}_2\text{O}_3$  are sometimes present.
- In addition to the foregoing minerals, bauxites usually contain traces of other insoluble oxides such as those of zirconium, gallium, chromium, and manganese.
- The term alumina trihydrate is often applied to the mineral gibbsite, and alumina monohydrate to the minerals boehmite and diaspora.

In addition to 除。。。之外，还有

- Bauxites are often classified as trihydrate bauxites and monohydrate bauxites, depending upon their content of the principal mineral or minerals containing the extractable alumina.

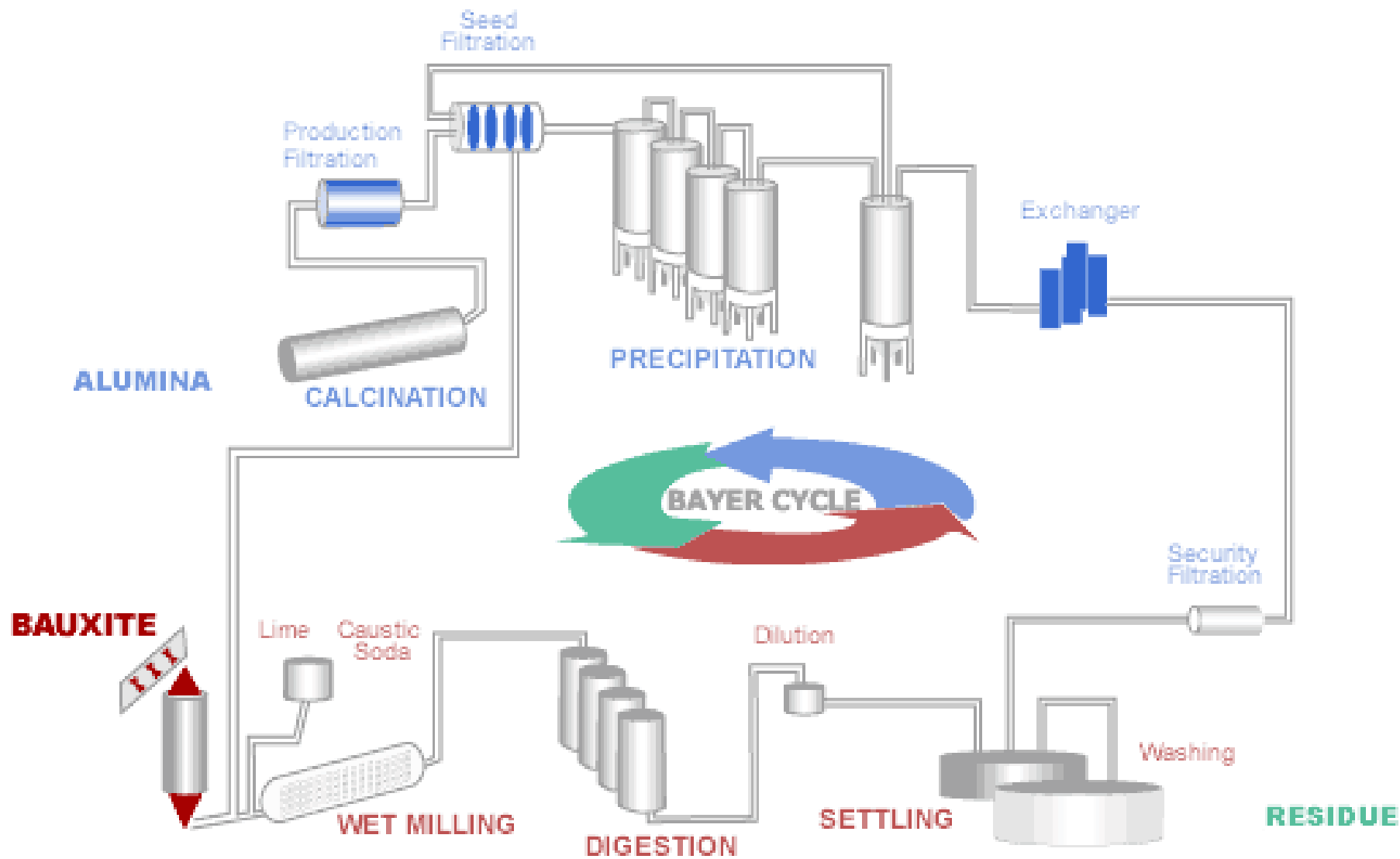
非限制性定语

- The suitability of bauxite as a raw material for aluminum production depends not only on its alumina content but also on its content of combined silica, which is usually in the form of the mineral kaolinite.
- Kaolinite not only contains aluminum which cannot be extracted in the Bayer process, but it also reacts with the caustic-aluminates solution to cause a loss of caustic soda.

Attention: their content or the content ? 提问能否替换

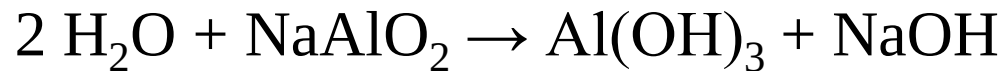
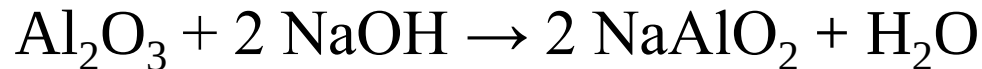
- Production. The most widely used technology (Fig. 16-1) for producing aluminum involves two steps; **extraction and purification of alumina** from ores, and **electrolysis** of the oxide after it has been dissolved in fused cryolite.
- Bauxite is by far the most used raw material at the present time. Technically feasible processes exist for the extraction of alumina from other raw materials such as clays, anorthosite, nepheline, syenite, and alunite.
- However, these processes have not been competitive with the Bayer process in the Western world.
- With the present rapidly changing economics of bauxite production, some of the processes may well become competitive in the near future. A few of these alternate raw materials are used as a source for alumina in Europe and Asia.





# Bayer Process

- Bauxite is converted to aluminum oxide ( $\text{Al}_2\text{O}_3$ ) via the Bayer process. Relevant chemical equations are:



- Bayer Process include 4 main processes: **dissolution of bauxite, digestion slurry dilution, seed decomposition and the mother liquor evaporation.**

补充拜耳法的4个工序

## Dissolution of Bauxite Reaction

- Bauxite is digested by washing with a hot solution of sodium hydroxide, NaOH, at 175 °C, under pressure.



- For **monohydrate type bauxite**, the reaction must be under high temperatures (300°C), high pressures, and high alkali concentration.



- The intermediate sodium aluminate, 非限制性定语 given the simplified formula  $\text{NaAlO}_2$ , is soluble in strongly alkaline water, and the other components of the ore are not. This treatment also dissolves silica, but the other components of bauxite do not dissolve.

## Digestion Slurry Dilution

- In order to promote the decomposition of sodium aluminate solution
- To reduce the viscosity of sodium aluminate solution
- To facilitate the settlement and separation of red mud
- Further desilication of sodium aluminate solution
- The red mud was washed in order to reduce the loss of  $\text{Al}_2\text{O}_3$  and sodium hydroxide.

## Digestion Slurry Dilution

- Sometimes lime is added here, to precipitate the silica as calcium silicate. The solution is clarified by filtering off the solid impurities, commonly with a rotary sand trap, and a flocculant such as starch, to get rid of the fine particles. The mixture of solid impurities is called red mud.

## Seed Decomposition

- After cooling, the solution is supersaturated with respect to aluminum. It is seeded with recycled synthetic gibbsite (alumina trihydrate) and agitated.
- A large part of the alumina in solution thus crystallizes out as gibbsite. This gibbsite is classified into product and seed, the seed being recycled and the product washed.

## Evaporation

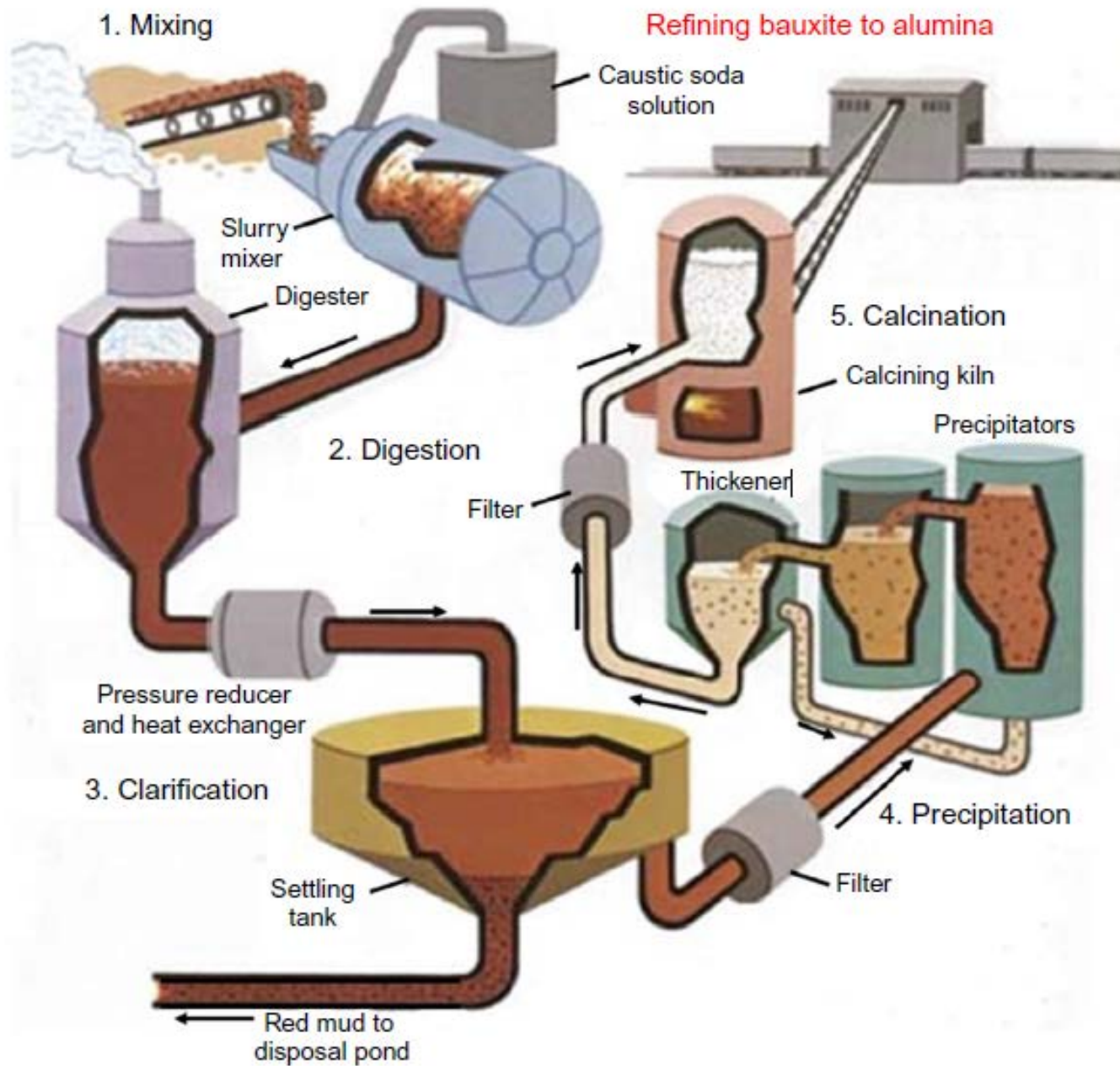
- The main aim is to remove excess moisture in the process and keep the water balance in the circulatory system, making the mother liquor concentration reach the requirements of digestion of bauxite.



- Alumina extraction. In the Bayer process, (Fig. 31-1) bauxite is **crushed and ground, then digested** at elevated temperature (140-230°C) and pressure in a strong solution of caustic soda (80-110g Na<sub>2</sub>O/litre).
- For monohydrate type bauxites. in which the alumina occurs in forms which are more difficult to dissolve than in trihydrate type bauxites, **stronger** solutions (up to 220g Na<sub>2</sub>O/litre), **higher** temperatures (up to 300°C) and pressures (as high as 150 atm) and sometimes **longer** digestion times are required.

-

## Refining bauxite to alumina



- The gibbsite, boehmite or diasporite in the bauxites reacts with the caustic soda to form soluble sodium aluminate.
- The residue, <sup>非限制性定语</sup>known as red mud, contains the insoluble impurities and the sodium aluminum silicate compound, referred to as desilication product, formed by the reaction of clay minerals with the sodium aluminate-caustic soda solution.
- The red mud is separated from the solution by counter-current decantation and filtration.
- After cooling, the solution is supersaturated with respect to aluminum.

## seeding

- It is **seeded** with recycled synthetic gibbsite (alumina trihydrate) and agitated. A large part of the alumina in solution thus **crystallizes out** as gibbsite. This gibbsite is classified into product and seed, the seed **being recycled** and the product **washed**.
- Wash water and spent liquor, after **concentration by evaporation**, are **recycled** to the digestion system. For metal production, the product is calcined at temperature up to 1300°C to produce alumina **containing about 0.3-0.8% soda, less than 0.1% iron oxide plus silica, and trace amounts of other oxides.**

### Attention:

- 通过几个动词的连接，描述了溶出过程和种分过程
- 杂质含量的描述

## Use of alumina

- Some of the precipitated gibbsite is used for rubber, plastic and paper fillers, and paper coating.
- Activated aluminas having high internal surface area are made from the gibbsite by calcination at low to moderate temperatures. They are used as desiccants and catalysts. Fully calcined aluminas are used in the production of ceramics, abrasive, and refractories.

# electrolysis

- Electrolytic reduction(smelting). although unchanged in principle, the smelting process of today **differs in** detail and in scale from the original process discovered by Hall and Heroult.
- Modern technology has **effected** substantial improvements in equipment, materials and control of the process and has lowered the energy and labor requirements and the final cost of primary metal.

**differ in** 在。。。不同

**effect:v.**引起，使产生

# Inert anode technical specification.

- equation:  $\text{Al}_2\text{O}_3 \rightarrow \text{Al} + \text{O}_2 \uparrow$  (No carbon anode consumption)
- electrode: inert anode    wenable cathode
- The electrode pole pitch: <2.0 cm
- average cell voltage: ~ 3.6 V
- electrolytic temperature: ~ 850 °C
- the ton aluminum direct current consumes: <12000 kWh
- decrease of electricity consumption: >10%
- Anodic evolution:  $\text{O}_2$

## Hall-Héroult anode technical specification

- equation:  $\text{Al}_2\text{O}_3 + \text{C} \rightarrow \text{Al} + \text{CO}_2 \uparrow$
- cathode and anode: carbon materials
- The electrode pole pitch:  $\sim 4.0\text{cm}$
- average cell voltage:  $3.8 \sim 4.2\text{V}$
- electrolytic temperature:  $920 \sim 960^\circ\text{C}$
- the ton aluminum direct current consumes:  $\sim 13000\text{ kWh}$
- electric energy efficiency:  $\sim 50\%$
- Tons of aluminum carbon consumption:  $\sim 400\text{ kg}$
- Tons of aluminum equivalent  $\text{CO}_2$ :  $\sim 10.7\text{t}$  ( electrolytic process  $4.9\text{t}$ , power-generation process  $5.8\text{t}$  )



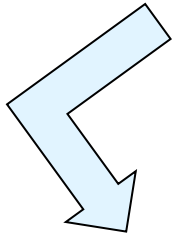
# Electrolyte

**main part:**

**molten  $\text{Na}_3\text{AlF}_6\text{-AlF}_3\text{-Al}_2\text{O}_3$**

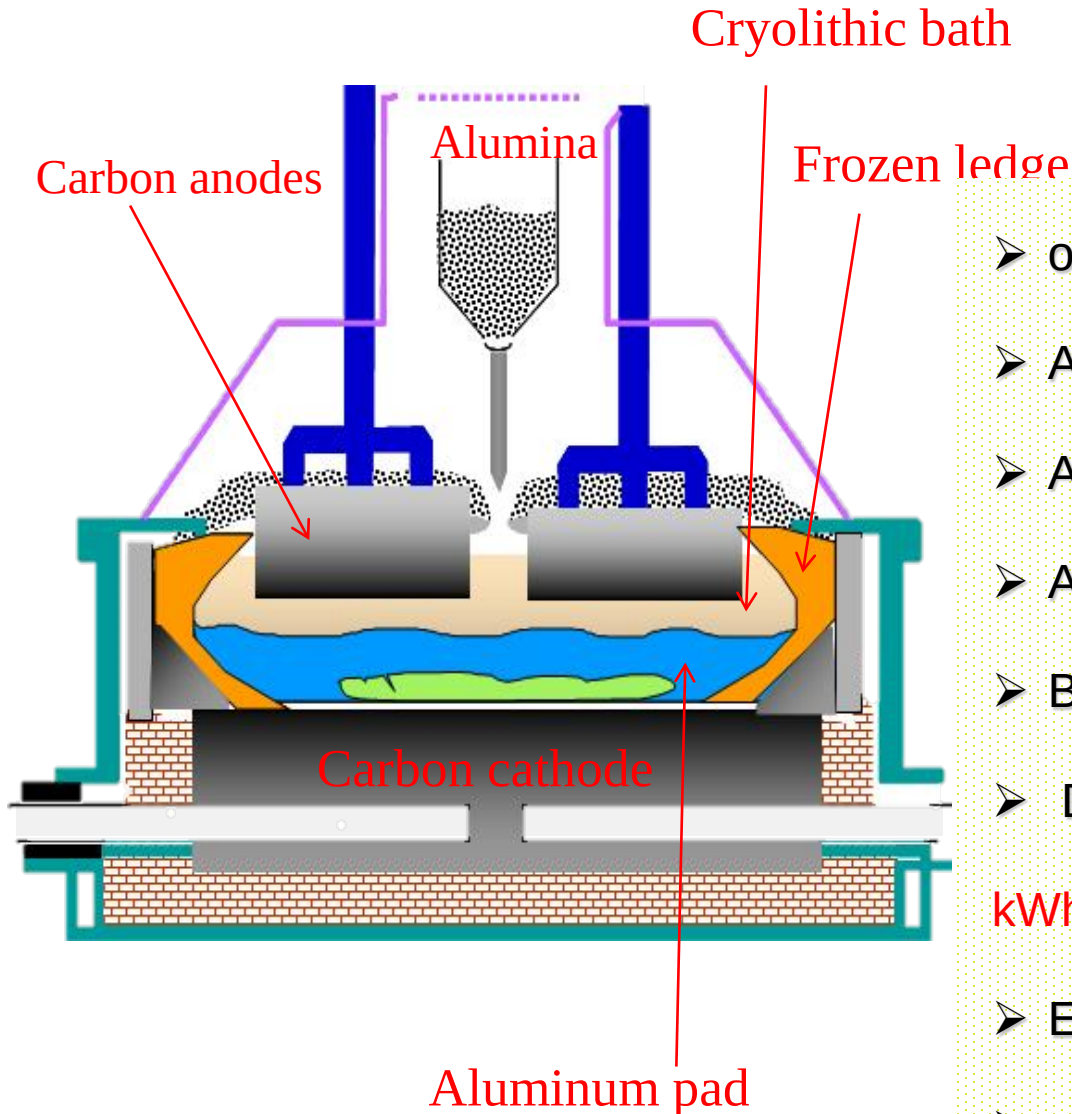
**additives:**

**$\text{CaF}_2$ 、  $\text{MgF}_2$ 、  $\text{NaF}$ 、  $\text{Na}_2\text{CO}_3$ 、  $\text{LiF}$**



to **regulate** the electrolyte performance : **fusibility、 density**  
**viscosity、 surface properties**  
**conductivity**

# Modern Hall-Heroult process cell



- overall reaction:  $\text{Al}_2\text{O}_3 + \text{C} \rightarrow \text{Al} + \text{CO}_2 \uparrow$
- Anode and cathode: carbon electrodes
- Anode-cathode distance:  $\sim 4.0\text{cm}$
- Average cell voltage :  $3.8 \sim 4.2\text{V}$
- Bath temperature:  $920 \sim 970^\circ\text{C}$
- Direct current consumption :  $\sim 13000$  kWh/t-Al
- Energy efficiency:  $\sim 50\%$
- carbon consumption :  $\sim 400$  kg/t-Al

## cell

- In a modern smelter, alumina is dissolved in cells(pots)-rectangular steel shells lined with carbon containing a molten electrolyte (bath) consisting mostly of cryolite.
- The bath usually contains 2-8% alumina. Excess aluminum fluoride and calcium fluoride are added to lower the melting point and to improve operation.
- Carbon anodes are hung from above the cells with their lower ends extending to within about 1.5 in (3.8cm) of the molten metal, which forms a layer under the molten bath.

Within到熔体里面

## heat

- The heat required to keep the bath molten is supplied by the electrical resistance of the bath as current passes through it.
- The amount of heat developed with a given current depends on the length of the current path through the electrolyte, that is, anode-cathode distance which is adjusted to maintain the desired operating temperature, **usually 960-970°C**.
- A crust of frozen bath, **2.5-7.6 cm thick**, forms on the top surface of the bath and on the sidewalls of cell.
- Alumina is added to the bath or on the crust, where its sorbed moisture is driven off by heat from the cell. While preheating on the crust, the alumina charge serves as thermal insulation. Periodically the crust is broken and the alumina is stirred into the bath to maintain proper concentration.

- The passage of direct current through the electrolyte decomposes the dissolved alumina.
- Metal is deposited on the cathode, and oxygen on the gradually consumed anode . About 0.23 kg of carbon is consumed for every pound of aluminum produced.
- The smelting process is continuous. Alumina is added, anodes replaced, and molten aluminum is periodically siphoned off **without interrupting current to the cells.**

## current efficiency

- Current efficiencies in the industrial electrolytic process are about 92-96%, and the energy is about 50%.
- The voltage at the cell terminals is 4-5V, depending on the size and condition of the cell.
- Voltage is required to force the current through the entire cell and the amount of power required to maintain the temperature is a smaller proportion of the total power input in large cells than in the small ones because of the lower ratio of surface to volume.

### 重点句子的分析

- Thus power consumed per pound of metal is somewhat less in large than in small cells. Consumption of 13-18 kwh/kg of aluminum produced includes bus-bar, transformer变压器, and rectifier losses整流器.

- 阳极材料可分为阳极糊和预焙阳极炭块两大类。阳极糊未经焙烧，直接用在自焙铝电解槽上作阳极；阳极炭块已经成型和焙烧，用于预焙铝电解槽作阳极。
- 炭素阳极安装在电解槽上部，强大的直流电（30 ~ 300 kA）通过炭素阳极导入铝电解槽，在炭素阳极底部发生分解氧化铝的复杂的电化学反应（阳极反应），阳极最终产物是CO和CO<sub>2</sub>。铝电解生产中，炭阳极参与反应而逐渐消耗，每生产一吨铝净耗炭素阳极420 ~ 650 kg。生产时，需定期向电解槽中添加新阳极糊（对自焙阳极）或更换新阳极块（对预焙阳极），以保持正常连续工作。
- $\text{Al}_2\text{O}_3 + \text{C} = 2\text{Al} + \text{CO} + \text{CO}_2$

- A **potline**(电解槽系列) may consist of 50-200 cells with a total **line voltage** of up to 1000V at current loads of 50000-225000A. Electric power is one of the most costly raw materials in aluminum production.
- Aluminum producers have continually searched for sources of cheap hydroelectric power, but have also had to construct facilities that produce power from fossil fuels.

译文：一个铝电解系列由50-200个电解槽组成，在负载50000-2250000安培的电流情况下有着高达1000伏的线电压。在铝的生产当中，电能是最昂贵的原料之一。生产铝的人们已经在不断寻找廉价的水利发电资源，但还是不得不建造从化石燃料中获得能量的设备。



- In the past half century, technological advances have significantly reduced the amount of electrical energy necessary to produce a pound of aluminum. In 1930 the requirement was 12kwh. In the 1970s a single cell can produce about 1.5 tons (1400kg) of metal per day and uses only **6kwh/Ib**(13kwh/kg). This level of energy consumption has been maintained to the present time.

注: **6kwh/Ib** 6千瓦时每英镑

译文: 在过去的半个世纪, 技术上的进步已经明显减少了生产1英镑 (相当于**0.454千克**) 铝所需要的电能。在1930年, 生产1英镑铝所需电能是12千瓦时, 而在20世纪70年代, 一个简单的电解槽一天能够产1.5吨金属而且产1英镑铝只需要6千瓦时的电能。

- Current is led out of the cell to the anode **busbar**（阳极母线） by a number of **carbon block anodes**(炭块阳极) suspended in **parallel**（平行的） rows on vertical conducting rods of copper or aluminum.

译文：电流通过炭块阳极从电解槽中导出到阳极母线上，这些阳极炭块呈平行的一排在竖直的铜或者铝导电棒上悬浮着。

## Pre-baked anode cell VS Self-baking anode cell

### Self-baking cell

- continuous anodes
- no need for specialized factory to produce anodes;
- serious fume injury
- higher cell voltage and more energy consumption
- higher cost and lower mechanization level.

### Pre-baked cell

- lower cell voltage and less energy consumption
- less construction cost
- can be large-scale and higher mechanization level.
- discontinuous pre-baked anodes need to be changed regularly, which is difficult
- need specialized factory to bake anodes

- Because impurities in the anodes dissolve in the bath as they are consumed, pure carbon (**calcined petroleum coke** or **pitch coke**) is used as raw material. The ground coke is mixed hot with enough coal tar (煤焦油) or petroleum pitch (石油沥青) to bond it into a block when pressed in a mold to form the “green” anode (生阳极) .

calcined petroleum coke: 煅烧石油焦炭

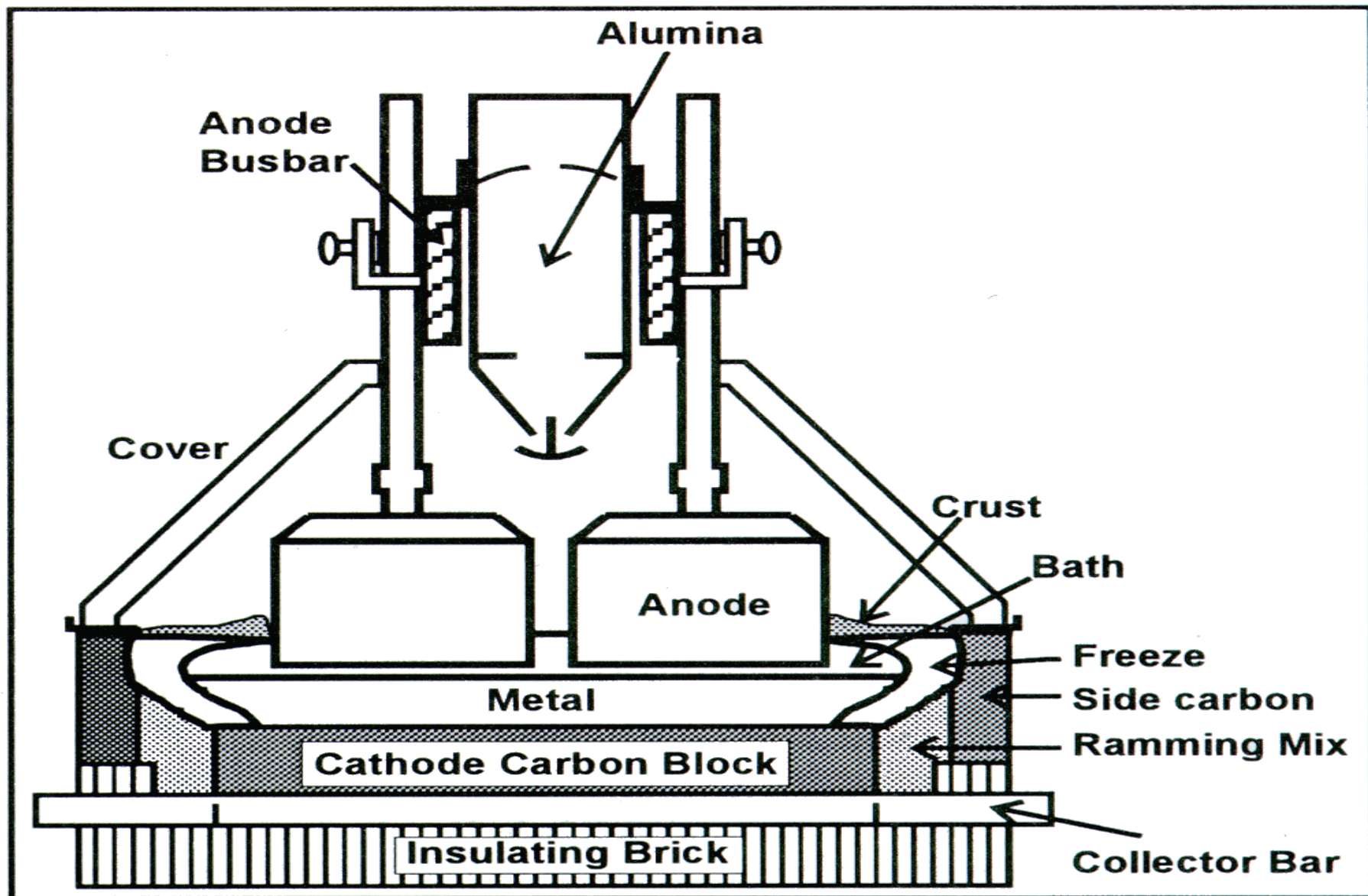
pitch coke: 沥青焦炭

ground coke: 粉状焦炭 (焦炭粉)

因为在阳极里面的杂质在阳极消耗的时候会溶解到电解质里面，所以纯的碳用来作为原料。将焦炭粉与足够的煤焦油或者石油沥青热混合在一起然后在模子里加压成块，即形成了生阳极块。

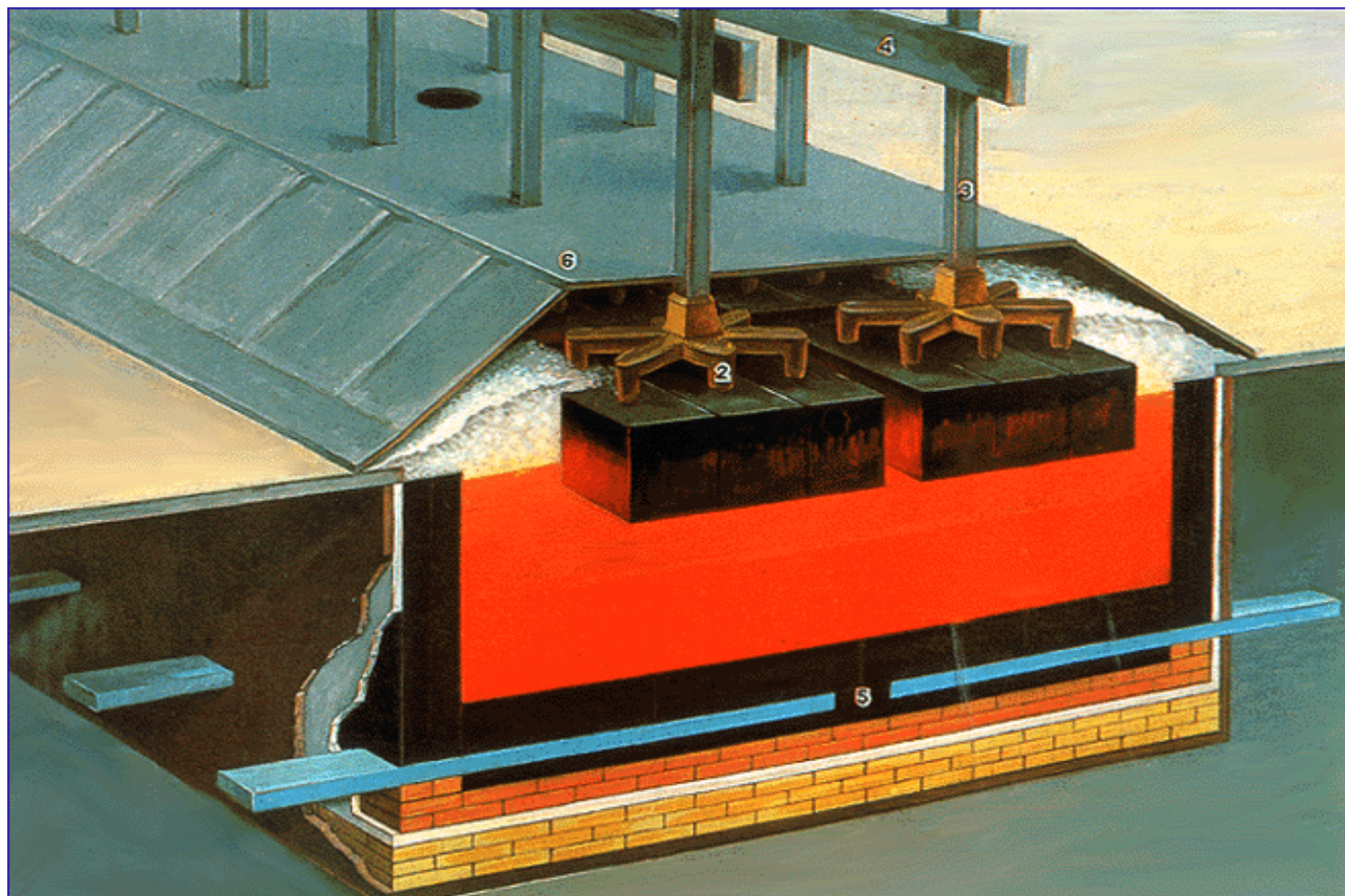
- This is then **baked** (焙烧) slowly at temperatures up to 1100-1200°C . In a **cavity** (洞) molded in the top of each block, a **steel stub** (钢爪) is **embedded** (插入、嵌入) by casting molten iron around it or by using a carbonaceous paste; the conducting bar is **bolted** (闷上, 拴住) to this stub.

译文：生阳极块接着在高达1100-1200°C 的温度下被焙烧。在每个炭块顶部所塑造的洞里面，钢爪通过在其周围浇筑熔融铁或者使用碳糊而被嵌入，导电棒（导杆）被闷在钢爪上面。





# 铝电解槽



1. 炭块    2. 钢爪    3. 铝导杆    4. 阳极母线    5. 阴极炭块组    6. 槽罩

铝电解槽是炼铝的主要设备，本幅绘示的是预焙阳极电解槽的纵剖面示意图。(1) 阳极装置。一般有10-20个阳极炭块组，每个炭块组包括炭块、钢爪和铝导杆。(2) 阴极装置和电解槽内衬。阴极装置就是阴极炭块组。(3) 槽壳、槽罩。(4) 导电系统。(5) 电解时的化学反应。

- Such an electrode is termed a **prebaked anode**（预焙阳极） to distinguish it from the **soderberg anode**（自焙阳极）, in which the electrode (single anode to cell) is formed in place from a carbonaceous paste which is baked by heat from the pot as gradually **descends**（下降） into the electrolyte.

译文：这种电极被称为预焙阳极，从而把它与自焙阳极区分开，自焙阳极是由碳糊在电解槽中直接形成的，碳糊在逐渐下降到电解质的过程中被来自锅（铝箱）的热焙烧。



| Process        | Product                                                     |  |
|----------------|-------------------------------------------------------------|--|
| Ore processing | Finer bauxite                                               |  |
| Bayer process  | Bauxite → sodium aluminate → gibbsite → alumina;<br>Red mud |  |
| Electrolysis   | Aluminum ingot                                              |  |

- Write a summary of the text.
- introduce the Bayer process
- Introduce the electrolyte for production of aluminum



# End



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