中南大學
CENTRAL SOUTH UNIVERSITY

Unit 17 tungsten metallurgy

lecturer: Xiyun Yang

School of Metallurgy and Environment

New words and expressions

tungsten *n* /'tʌŋstən/ 钨

tungstate *n* /'tʌŋ,stet/ 钨酸盐

molybdenum *n* / məˈlɪbdənəm / 钼

molybdate *n* / mə'lɪbdeɪt / 钼酸盐

devourer *n* / di'vauə/ 吞噬者

catalyst *n* /'kætəlɪst/ 催化剂

superalloy *n* /,sʊpə'ælɔi/ 高温合金，超级合金

cemented carbide *n* 硬质合金

inorganic pigment *n* 无机颜料

lubricant *n* /'lubrɪkənt/ 润滑剂

ferromagnetism *n* /,fɛroʊ'mægnətɪzəm/ 铁磁性

wolframite *n* / 'wʊlfrəm¸aɪt / 钨锰铁矿，黑钨矿

scheelite *n* / 'ʃilaɪt / 钨酸钙矿，白钨矿

Hacksaw钢锯 ['hæksɔ]

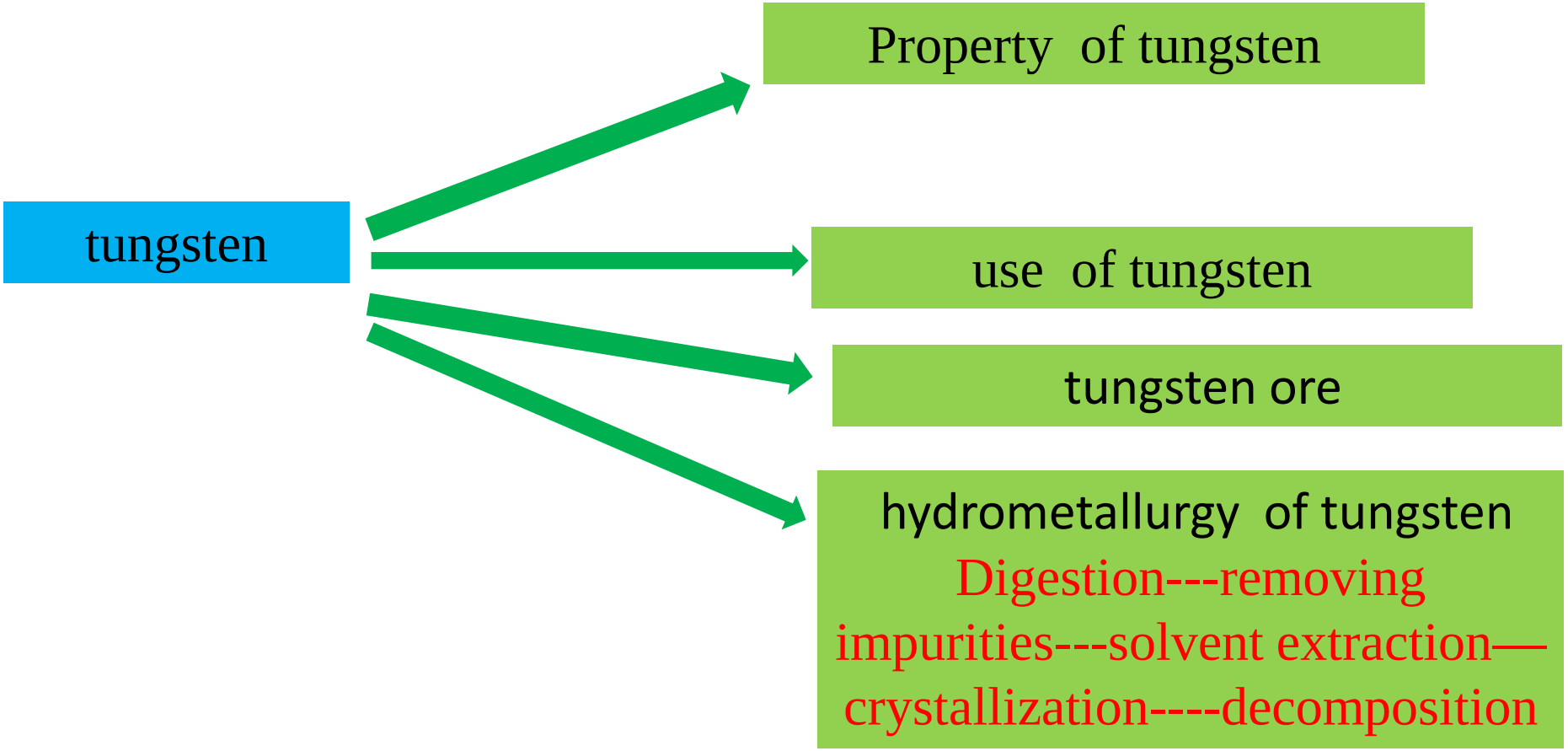
New words and expressions

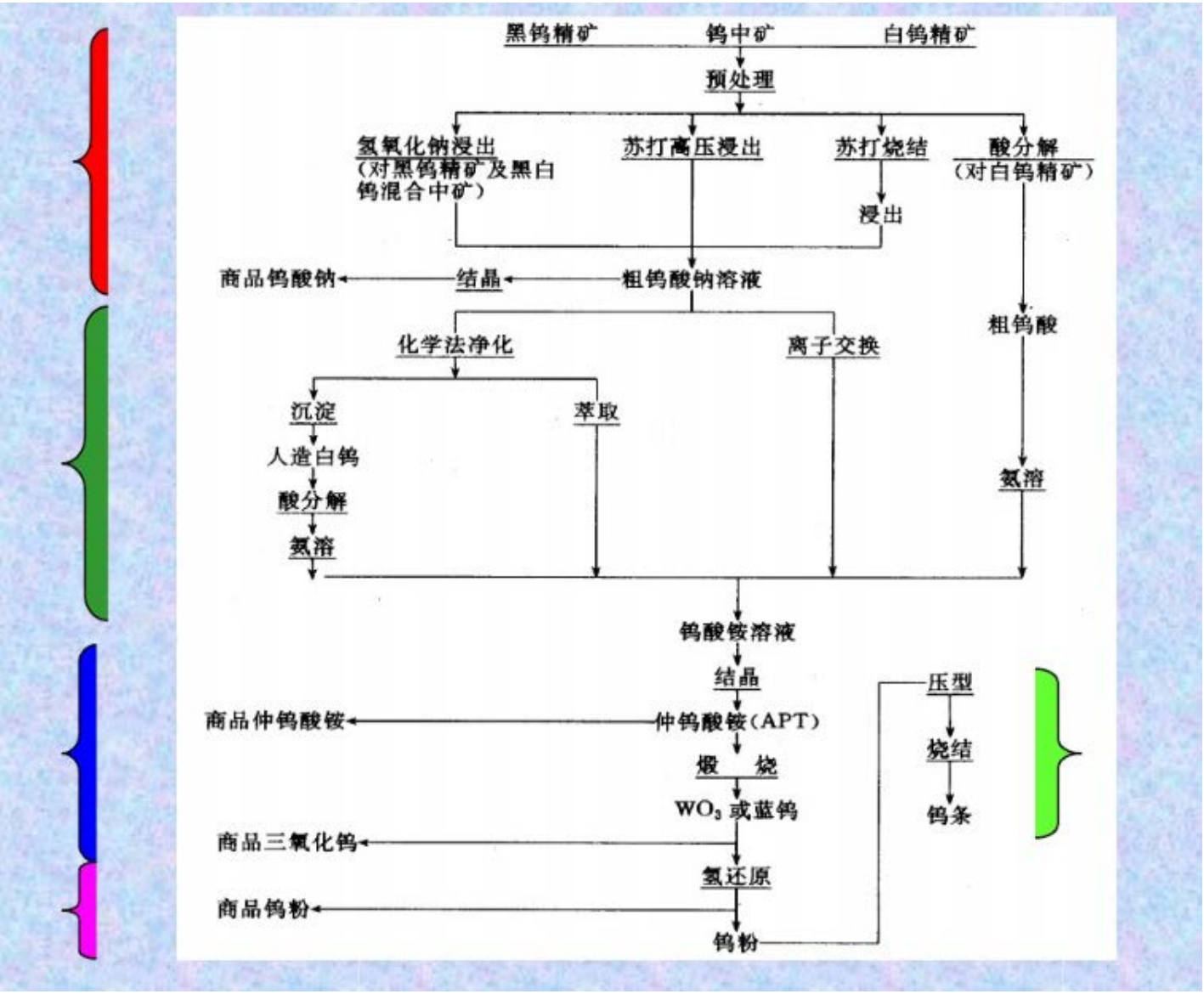
- comminution [,kɑmə'njʊʃən] 破碎
- grind *vt* /graɪnd / 磨碎
- vibratory screen *n* ['vaɪbrə,toʊri] 振动筛
- sodium hydroxide *n* 氢氧化钠
- sodium carbonate *n* 碳酸钠
- autoclave *n* /'ɔːtə(ʊ)kleɪv/ 高压釜
- alkaline digestion *n* / ˈælkəˈlaɪn / / daɪˈdʒɛstʃən / 碱分解
- affinity *n* /ə'fɪnəti/ 亲和力
- ion exchange resin *n* 离子交换树脂
- effluent *adj* /'ɛflʊənt/ 流出的
- stripping agent *n* 解吸剂，反萃剂
- regenerate *vt* 再生
- precipitation *n* /prɪ'sɪpə'teʃən/ 沉淀

New words and expressions

- volatilize *vt* /'vɑlətl,aɪz/ 使挥发
- mother liquor *n* 母液
- filtration *n* 过滤
- deionized water *n* /di:'aɪənaɪzid/ 去离子水
- stoichiometric *adj* /s'tɔɪkɪ'ɔmɪtrɪk/ 化学计量的
- thiomolybdate *n* /θiəməli:b'deɪt/ 硫代钼酸盐
- ammonium *n* /ə'moʊniəm/ 铵
- paratungstate *n* /pærə'tʌŋsteɪt/ 仲钨酸盐
- ammonium paratungstate *n* /ə'məunjəm ˌpærə'tʌŋsteɪt/ 仲钨酸铵
- precursor *n* /pri:'kɜ:rsər/ 前驱体
- crystallize *vt* /'krɪstəlaɪz/ 使结晶
- intermediate *n* /ˌɪntər'mi:diət/ 中间物
- metatungstate *n* /metətʌŋs'teɪt/ 偏钨酸盐

- 数词的用法
- 复合形容词


tungsten
Property of tungsten
use of tungsten
tungsten ore
hydrometallurgy of tungsten
Digestion---removing impurities---solvent extraction—crystallization----decomposition


黑钨精矿
钨中矿
白钨精矿
预处理
氢氧化钠浸出
(对黑钨精矿及黑白钨混合中矿)
苏打高压浸出
苏打烧结
浸出
酸分解
(对白钨精矿)
商品钨酸钠
结晶
粗钨酸钠溶液
粗钨酸
化学法净化
离子交换
沉淀
萃取
人造白钨
酸分解
氨溶
氨溶
钨酸铵溶液
结晶
压型
商品仲钨酸铵
仲钨酸铵(APT)
烧结
煅 烧
WO_3 或蓝钨
钨条
商品三氧化钨
氢还原
商品钨粉
钨粉

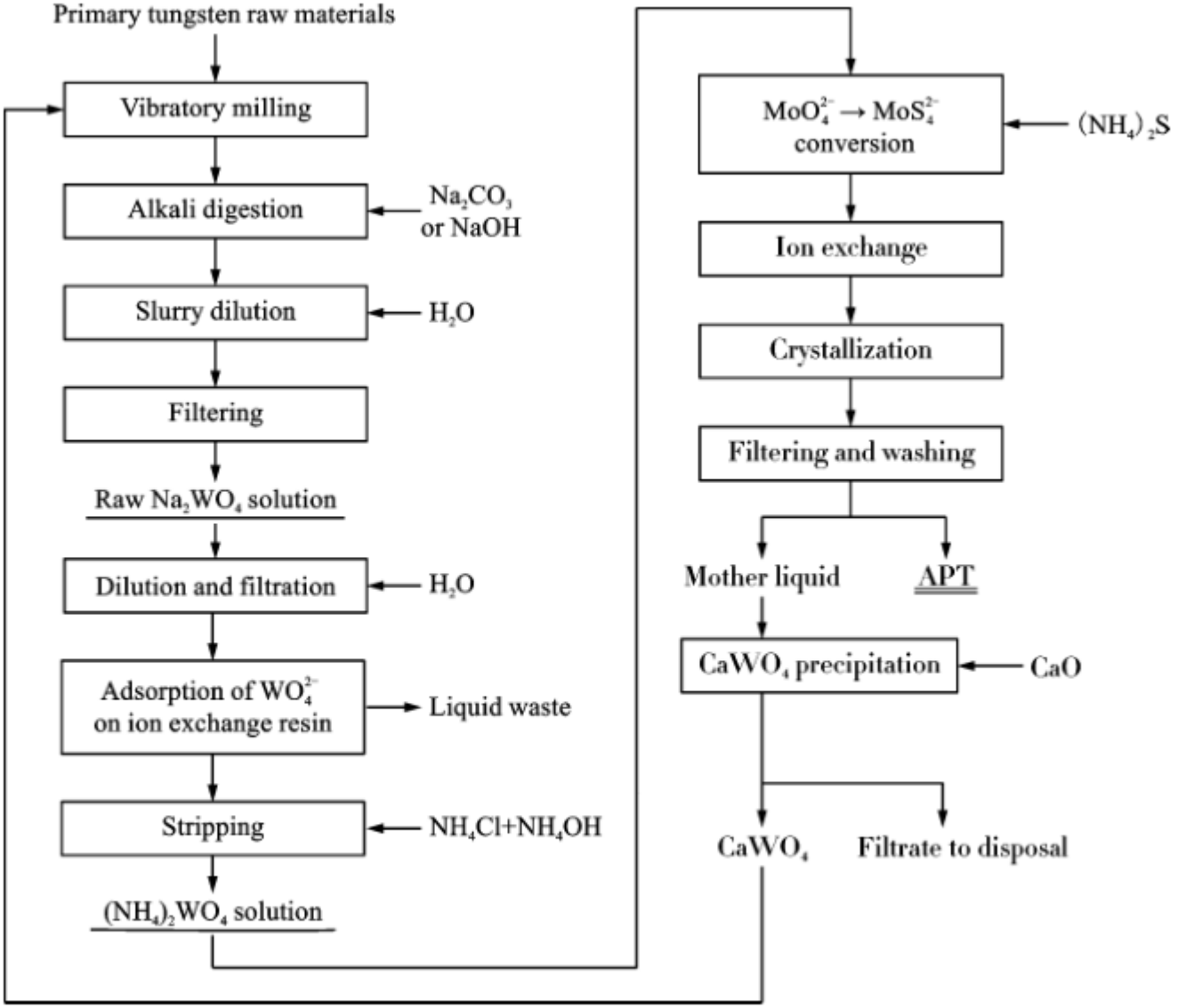


Fig. 17-1 Flowsheet of modern tungsten hydrometallurgy

Tungsten property

- Tungsten is a metallic transition element. Its position in the Periodic Table is characterized by period 6, group 6, atomic number 74, average relative atomic mass 183.85.

- Pure tungsten is a light gray or whitish metal that is soft enough to be cut with a hacksaw and ductile enough to be drawn into wire or extruded into various shapes.

- If contaminated with other materials, tungsten becomes brittle and difficult to work with.

Tungsten property

- Tungsten has the highest melting point(3422° C) of all metallic elements and a high density (19.3 grams per cubic centimeter) near to that of gold.
- Tungsten can be considered as a rather inert metal, which is resistant to many elements and compounds. It is compatible with most ceramics and glasses up to high temperatures and shows good resistance to many molten metals. Tungsten is stable to mineral acids in the cold and is only slightly attacked at higher temperatures

Compatible:兼容的

Mineral acid:无机酸

Attack：腐蚀，侵蚀（v,n）

当受到氯离子的侵蚀，钝化膜穿孔了passive film

Tungsten use

- Tungsten is a metal with a wide range of uses, the largest of which is as tungsten carbide in cemented carbides. Cemented carbides (also called hardmetals) are wear-resistant materials used by the metalworking, mining, and construction industries. Tungsten metal wires, electrodes, and/or contacts 触头are consumed in lighting, electronic, electrical, heating, and welding applications.

Tungsten use

- Other applications of tungsten are to make heavy metal alloys for armaments, heat sinks散热片, and high-density applications, such as weights砝码 and counterweights秤砣, superalloys for turbine blades, tool steels, and wear-resistant alloy parts and coatings.
- Tungsten composites are also a substitute for lead in bullets and shot子弹和炮弹.
- Tungsten chemical compounds are used in catalysts, inorganic pigments, and high-temperature lubricants. Tungsten disulfide (WS_2) is a dry lubricant that can resist temperatures as high as 500° C.

Tungsten occurrence

- Tungsten minerals that occur in sufficient abundance to be of economic significance can be divided into the wolframite and scheelite groups.
- The majority of tungsten deposits only contains some tenths of a percent of WO_3. On the other hand, ore concentrates in international trading require 65-75% WO_3.
- Therefore, a very high amount of gangue material must be separated. Companies which process their own concentrates produce low-grade concentrates(6-40% WO_3) in order to minimize the loss of tungsten minerals which increases with increasing concentration grade.

- some tenths of a percent千分之几
- 千分之六

occurrence

- In regard to the beneficiation of ore, the positive properties of tungsten minerals are the high specific gravity(scheelite and wolframite) and ferromagnetism(wolframite). A negative property is their brittleness, leading to a partial loss by too fine particles formed during the disintegration steps.破碎阶段

Ore beneficiation

- Ore beneficiation consists of two main steps: comminution and concentration. Comminution is first performed by crushing. Equipment in use comprises jaw, cone, or impact crushers冲击式 working mostly in closed circuits with vibratory screens.
- The second step in comminution is grinding, which is undertaken in rod or ball mills working in closed circuits with classifiers分级器. For concentration(separation of gangue minerals) several methods can be applied, depending mainly on the composition of the ore. They include ore sorting, gravity methods, flotation, magnetic, and electrostatic separation.

Hydrometallurgy of tungsten

- **3.1 Grinding of Ore concentrates**
  - Flotation-derived concentrates in most cases are fine enough to provide a complete dissolution during digestion.
  - In contrast, concentrates prepared by gravity procedures are much too coarse and must be disintegrated磨碎 by grinding in ball mills. Particle size plays a crucial role, especially in wolframite digestion. Mostly<325mesh(44um) is recommended and seldom<200mesh. For scheelite, <200mesh is sufficient.

digestion

- The aim of this step is to dissolve WO_3 or the tungstates and convert them into water-soluble sodium tungstate. Besides, a partial or total separation of gangue minerals can be achieved, depending on the type of compounds present.
- Raw materials consisting of fine grains can be treated by aqueous solutions of sodium hydroxide or sodium carbonate. The latter is more selective(it does not dissolve so much of gangue minerals) compared to sodium hydroxide.
- The usual equipment for pressure digestion consists of horizontal roll autoclaves or vertical autoclaves equipped with a stirrer. Heating is performed by steam jacket.

3.3 Ion Exchange Technology in Processing Sodium Tungstate

- As a result of alkaline digestion, the raw sodium tungstate solution is formed. Impurity elements like Mo, P, As, and Si are also partly dissolved by alkaline, which must be removed. In the ion exchange process, ions with higher affinity to the resin can replace those with lower affinity. A strong basic anion exchange resin(type 201×7) is used. There are several anions like WO_4^{2-}, MoO_4^{2-}, AsO_4^{3-}, PO_4^{3-}, SiO_3^{2-},OH^-,etc. in the sodium tungstate solution. The affinities of these ions can be arranged in a decreasing series:

$$WO_4^{2-} \approx MoO_4^{2-} > AsO_4^{3-} > PO_4^{3-} > SiO_3^{2-} > Cl^- > OH^-$$

Ion exchange

- Normally, the raw sodium tungstate solution after NaOH digestion contains 200g WO_3/L, which is too high for ion exchange process and must be diluted to a lower concentration with 20-25g WO_3/L.
- The ion exchange capacity decreases with increasing WO_3 concentration. Anions with higher affinities than Cl^- can be adsorbed by the resin as follows:

$$(R_4N)_2Anion+WO_4^{2-} \rightarrow (R_4N)_2WO_4+Anion^{2-}$$

Ion exchange

- During the early stage of adsorption, all ions with higher affinities than that of Cl^- can be adsorbed on the resin. However, when the diluted tungstate solution continuously passes through the ion exchange column, anions with smaller affinities, adsorbed already on the resin, are replaced by tungstate and removed by effluent solution, as described by the following equation:

$$(R_4N)_2Anion+WO_4^{2-} \rightarrow (R_4N)_2WO_4+Anion^{2-}$$

Ion exchange

- ion exchange technology is not only used for purification of the tungstate solution, but also for converting it into ammonium tungstate solution. The conversion is done while stripping the tungstate from the loaded resin, using ammonium salts as stripping agents. It is seen that ammonium chloride is the most suitable agent. In addition, it regenerates the resin to the desired form:

3.4 Separation of Molybdenum

- A process for separating molybdate from tungstate using ion exchange was patented in China and used in commercially to produce APT of high purity.
- An ammonium tungstate solution containing Mo as the main impurity element is purified by a single ion exchange technique.
- After pH adjustment, $(NH_4)_2S$ is added to convert molybdate into thiomolybdate. The solution passes a column of strongly basic anion exchange resin(type D201). Thiomolybdate is adsorbed and the effluent contains the tungstate purified from Mo. In order to regenerate the anion exchange resin, a solution of an oxidizer is used to desorb the thiomolybdate.
- The original Mo/WO_3 concentration ratio in the feed solution of 0.06-0.84% decreases to 0.001-0.0015% in the effluent. The recovery of the operation is better than 99%.

3.5 Ammonium Paratungstate Crystallization

- The purified ammonium tungstate solution is evaporated, whereby ammonia and water are volatilized.
- The ammonia concentration in the mother liquor decreases(pH drop) and at the same time the WO_3 concentration increases. Paratungstate $[H_2W_{12}O_{42}]^{10-}$ is formed whose ammonium salt has low solubility. Crystallization of $(NH_4)_{10}H_2W_{12}O_{42}\cdot 4H_2O$ is the result. The degree of evaporation depends on the purity of the feed solution and the required purity of the APT. Usually, if proper purification was performed in the foregoing steps it ranges somewhere between 90 and 99%.

3.5 Ammonium Paratungstate Crystallization

- The physical properties of the crystallized APT can be influenced by crystallization conditions to some extent. They are of importance for further processing to metal powder by hydrogen reduction.
- The crystallization is not only a conversion of the dissolved to the solid salt, but the last purification step in the hydrometallurgical process.
- Most of the impurity elements still present in the process solution, have much higher solubility than APT and are consequently enriched in the mother liquor. The crystal slurry is separated from the mother liquor by filtration and washing with deionized water. Filtrate and wash water are recycled and, finally, the APT is dried.

4 APT – A intermediate for tungsten products

- Today, APT is the most important and almost exclusively used precursor for tungsten products. Tungsten trioxide, tungsten blue oxide, tungstic acid, and ammonium metatungstate can be derived from APT, either by partial or complete thermal decomposition or by chemical attack.
- Tungsten metal powders are produced via hydrogen reduction of tungsten oxides. Changes in the reduction parameters allow the production of tungsten powders with various characteristics such as different grain size, grain size distribution, and powder density.

THANKS

End

lecturer: Xiyun Yang

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