



China Mn Metal Clean Production

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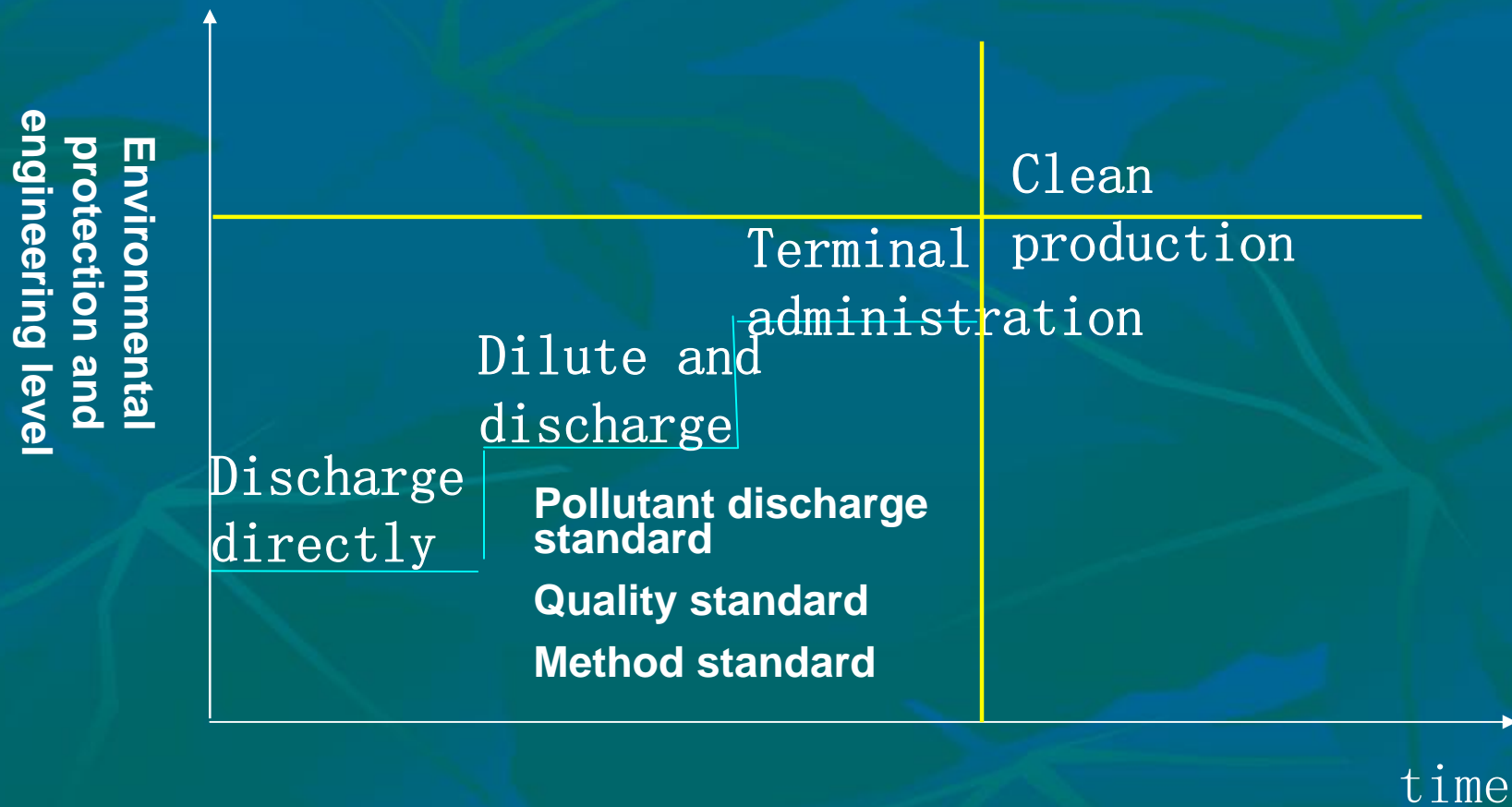
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1. The rise and development of clean production



1. The rise and development of clean production

❖ What is meant by clean production?
Why implement this environmental protection strategy?

❖ What is meant by clean production verification?

1. The rise and development of clean production

clean production in the world

- ❖ America: chemical industry, Motorola, Nike
- ❖ European Union: Holland, Denmark, Britain, Norway.....
- ❖ The United Nations: central project of global national clean production
- ❖ International finance: World Bank, Asian Development Bank
- ❖



1. The rise and development of clean production

clean production in China

- ❖ B4 sub project
- ❖ Canada skill aids project
- ❖ American Environmental Protection Agency project
- ❖ Technological development and popularization
- ❖

1. The rise and development of clean production

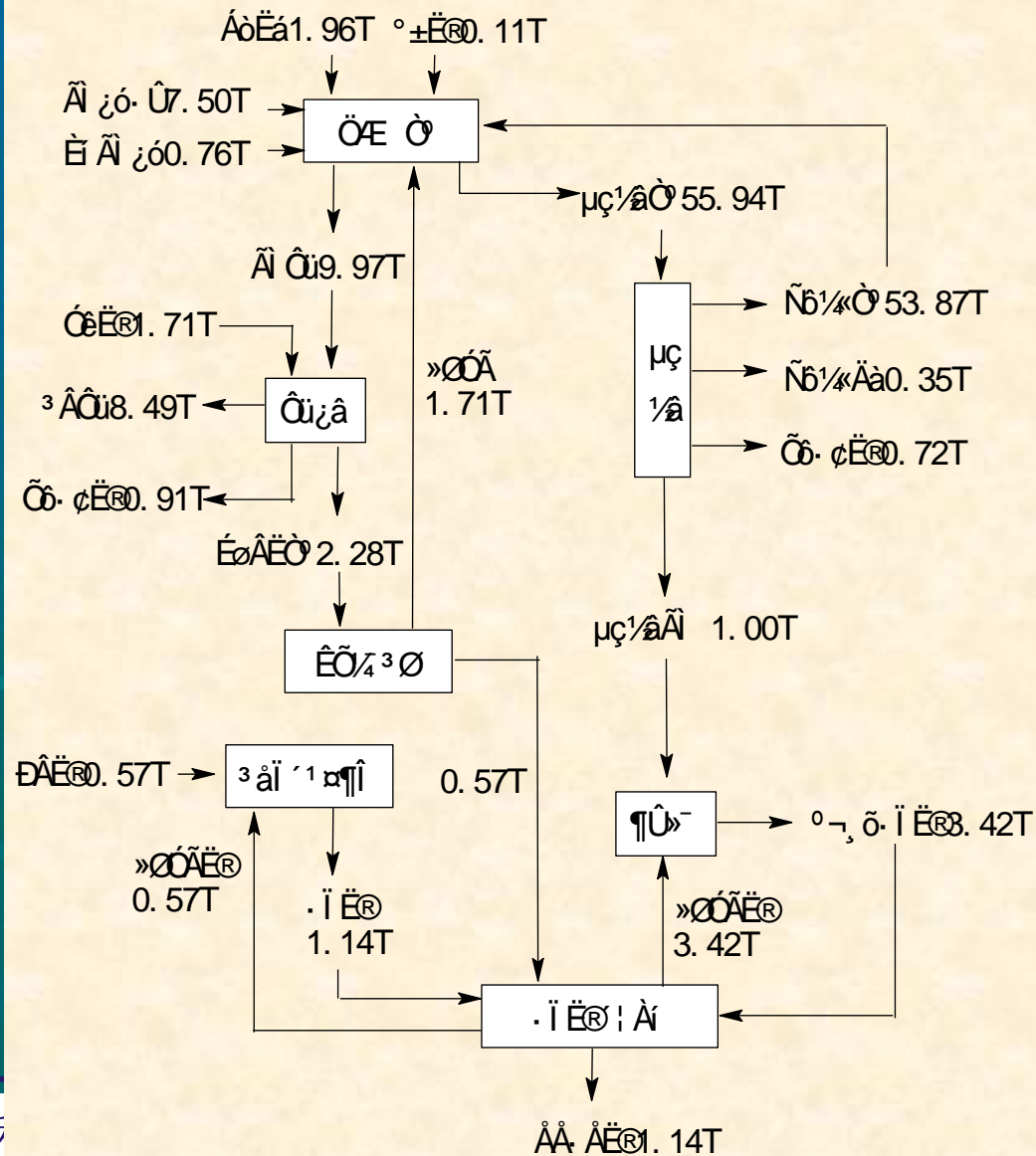
- ❖ Clean production promotion regulation
- ❖ Clean production standard
- ❖ No. 151 file

1. The rise and development of clean production

There are laws and regulations to abide by

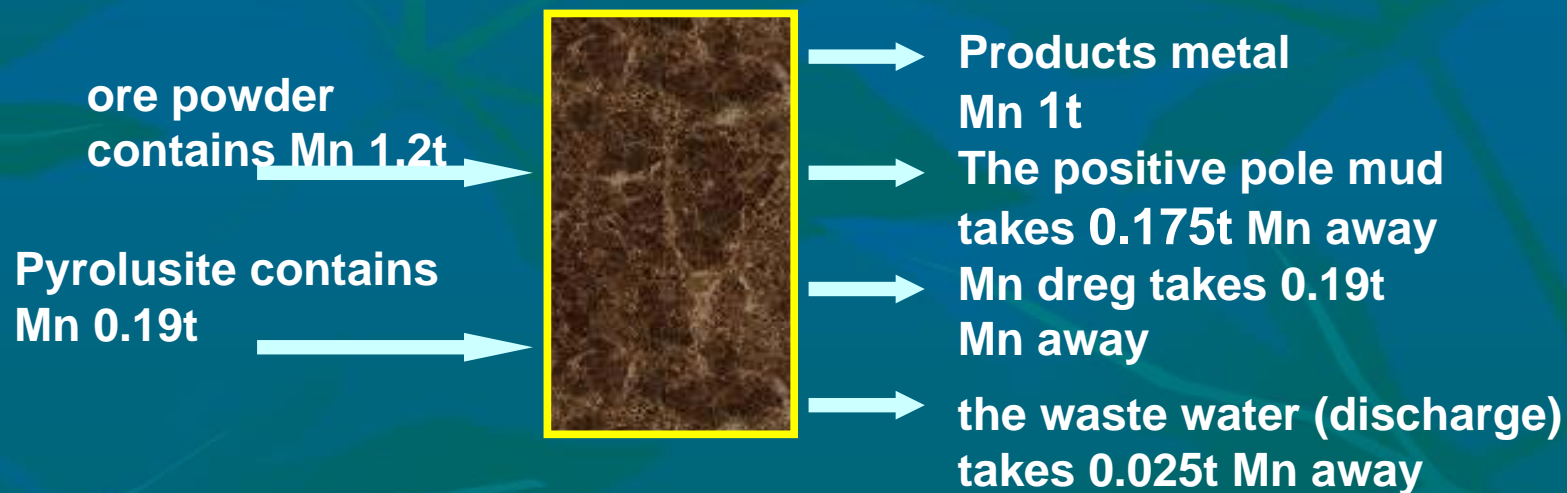


2. Chinese classic verification-clean production of electrolytic manganese



Typical enterprise's supply balance chart
(base on the production of a ton of
electrolytic manganese)

2. Chinese classic verification- clean production of electrolytic manganese



Mn balance chart (base on the production
of a ton of electrolytic manganese)

2. Chinese classic verification-clean production of electrolytic manganese

Add $K_2Cr_2O_7$ contains chromium 0.169kg



Product takes 0.004kg chromium away
the waste water takes 0.165kg chromium away

Chromium balance chart (base on the production of a ton of electrolytic manganese)

Add SeO_2 contains selenium 0.989kg



Product takes 0.6kg selenium away
The positive pole mud takes 0.221kg selenium away

The positive pole liquid take 0.168kg selenium away
Selenium balance chart (base on the production of a ton of electrolytic manganese)

2. Chinese classic verification- clean production of electrolytic

manganese

Add ammonia 82.78kg



the waste water takes 43.34kg

ammonia away

The positive pole mud takes

0.99kg ammonia away

Slay contains 36.5kg ammonia

Volatilize 1.95kg ammonia

Ammonia balance chart (base on the
production of a ton of electrolytic
manganese)

sulfuric acid contains
sulphur acid radical 1.676t



the waste water takes 0.746t

sulphur acid radical

The positive pole mud takes 0.004t

sulphur acid radical

Slay contains 0.926t sulphur

acid radical

sulphur acid radical balance chart (base on
the production of a ton of electrolytic
manganese)

2. Chinese classic verification- clean production of electrolytic manganese

- ❖ Calculate manganese's infusion rate and utilization ratio of China's electrolytic manganese production process according to the following formula:

$$\frac{1}{2}p^3 \hat{O} \hat{A} \hat{E} = \frac{\frac{1}{2}p^3 \hat{O} \mu \tilde{A} \times \tilde{U} \tilde{A} \tilde{I} \tilde{A} \zeta (E \tilde{U} \tilde{O}^0 \tilde{O} \tilde{D})}{\frac{1}{4} \hat{O} \hat{E} \hat{e} \mu \tilde{A} \times \tilde{U} \tilde{A} \tilde{I} \tilde{A} \zeta}$$

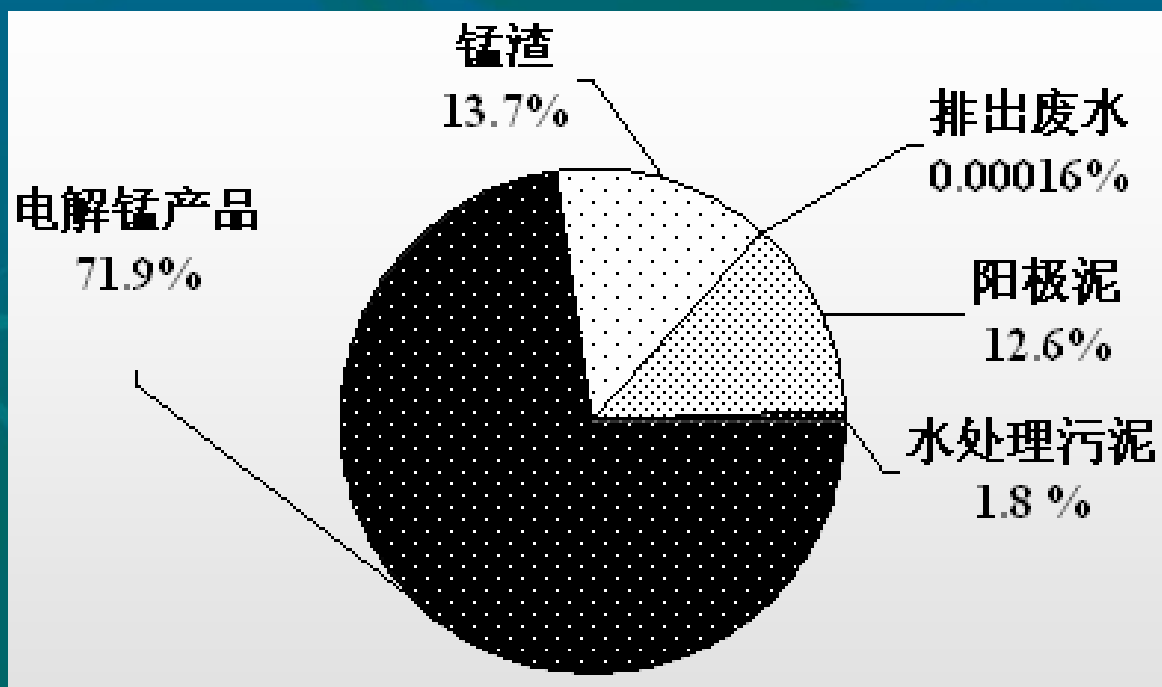
$$\hat{A} \hat{U} \hat{O} \tilde{A} \hat{E} = \frac{2 \hat{U} \hat{E} \cdot \tilde{O} \tilde{D}^0 \tilde{A} \tilde{I} \times \tilde{U} \tilde{A} \zeta}{\frac{1}{4} \hat{O} \hat{E} \hat{e} \mu \tilde{A} \tilde{I} \times \tilde{U} \tilde{A} \zeta}$$

2. Chinese classic verification- clean production of electrolytic manganese

- ❖ According to the two formulaes and supplies weighing apparatus described above, the infusion rate of manganese of typical electrolytic manganese enterprise $=((1.2+0.19)-0.19)/(1.2+0.19)=86.3\%$; utilization ratio $=1/(1.2+0.19)=71.9\%$ 。
- ❖ From the infusion rate and utilization ratio of the manganese, we know more than 10% of manganese enters the environment with the manganese dreg, which not only can not be utilized effectively but also caused environment pollution, at the same time, nearly 30% of the manganese has not got effective use in the whole production process of electrolytic manganese.

2. Chinese classic verification-clean production of electrolytic manganese

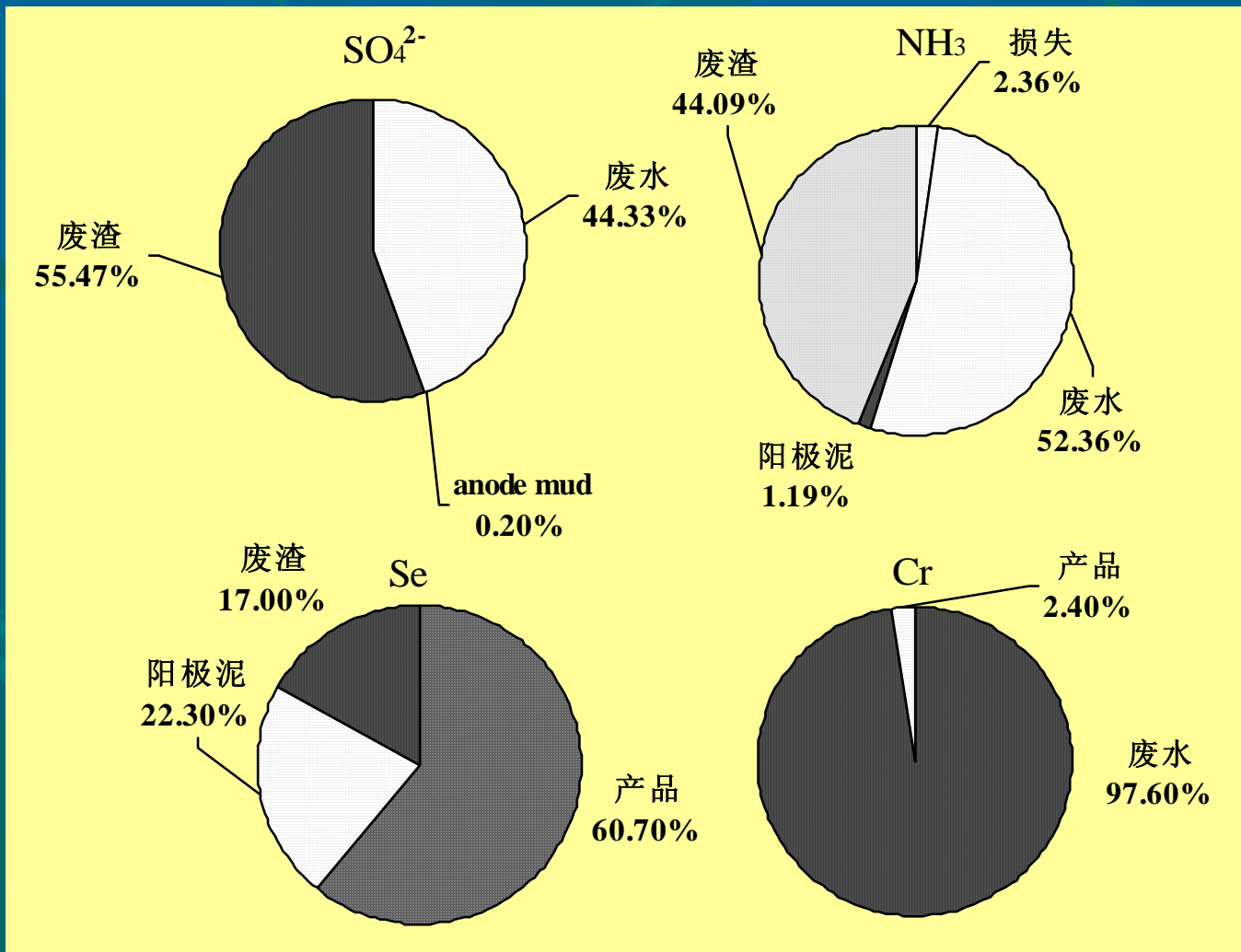
- ❖ According to supplies weighing apparatus, manganese entered in the products is $1-0.719=38.1\%$, among which, in dreg is $0.19/1.39=13.7\%$; in positive pole mud is $0.175/1.39=12.6\%$, discharge with waste water is $1.14 \times 2 \times 10^{-6} / 1.39=0.00016\%$, in mud is $(0.025-(1.14 \times 2 \times 10^{-6} / 1.39)) / 1.39=1.8\%$.




2. Chinese classic verification- clean production of electrolytic manganese

- ❖ According to supplies weighing apparatus, chromium entered in the products is $0.004/0.169=2.4\%$; discharged with waste water is $0.165/0.169=97.6\%$ 。 Results show that, Cr^{6+} except 2.4% entered in products, the other 97.6% became environment pollutant discharging with the waste water.
- ❖ We could know by the same method:
 SO_4^{2-} in the production of electrolytic manganese, expect 0.2% entered in the positive pole mud, 99.8% entered in environment with waste water and waste residue ; ammonia, expect 1.19% entered in the positive pole mud, and production process lose 2.36%, 96.45% entered in environment with waste water and waste residue ; selenium, 60.70% entered in the products , 22.30% entered in environment with waste residue.

2. Chinese classic verification-clean production of electrolytic manganese





2. Chinese classic verification-
clean production of electrolytic
manganese

Liquid-making workshop



2. Chinese classic verification-clean production of electrolytic manganese

Besides sulfuric acid and ammonia water, the production of one ton of electrolytic manganese need liquid-making workshop put into 7.5 tons manganese spar powder and 0.76 tons of pyrolusite powder, reflux 53.87 tons of positive poles liquid, produce 55.94 tons of electrolytic liquid and 9.97 tons of manganese dregs. An electrolytic manganese enterprise producing 30,000 tons per year, liquid-making workshop discharge manganese dreg up to 299,100 tons every year, which seriously threaten the ecology and environment. By weight, the electrolytic liquid takes up 30% of the manganese dreg, the manganese content in the electrolytic liquid is 3.3%, so when producing a ton of electrolytic manganese, 9.97 tons of discharged manganese dregs include 0.099 tons of soluble manganese.

2. Chinese classic verification-clean production of electrolytic manganese

After the manganese mine transported to electrolytic manganese factory, firstly it would be broken, then rub into manganese mine powder with 100 mesh, then add sulfuric acid into manganese mine powder and get the sulfuric acid manganese solution, thus shift water soluble manganese from firm to liquid in the form divalent manganese ion, then put into manganese dioxide powder and ammonia to delete Fe^{2+} in the liquid. From the transportation of manganese mine to the electrolytic manganese factory to pressing, the electrolytic liquid included in the manganese dreg, which has cost a lot, while the processes from electrolytic liquid to the final production are few. The electrolytic liquid in manganese dreg is serious pollutant, however it has obvious value. Recycle the electrolytic liquid should be a very important means to decrease the environmental pollution.

2. Chinese classic verification-
clean production of electrolytic
manganese

wastewater
disposal
workshop



2. Chinese classic verification-clean production of electrolytic manganese

- ❖ When producing a ton of electrolytic manganese each time, there is 0.57 tons filtrate with 0.132% Mn, 1.14 tons cathodic cleaning waste water with 1.15% Mn, 3.42 tons passivation waste water (with chromium) with 0.074% Mn discharge into wastewater disposal workshop. The current discharge standard of density limit of Mn^{2+} in China is 2mg/L, supposed that the workshop has reached the standard, then there would be plenty of Mn^{2+} enter into the mud of this workshop. According to supplies weighing apparatus, when producing a ton of electrolytic manganese each time, there is 0.025 tons of manganese (before disposal) in the waste water. After disposal, the standard density is 2mg/L (max), through calculation, we know the total amount of manganese entered into mud is 0.0249 tons, then, it would be 0.165kg for chromium by the same method.

2. Chinese classic verification-clean production of electrolytic manganese

There still exist some problems in current waste water terminal treatment method:

(1) Adjusting of two Ph values

- ❖ solubility product of $\text{Mn}(\text{OH})_2$, $K_{\text{SP}} = 1.9 \times 10^{-13}$, when pH is 9, $[\text{OH}^-] = 10^{-5}$, $[\text{Mn}^{2+}] = 1.9 \times 10^{-13} / 10^{-10} = 1.9 \times 10^{-3} \text{mol/L}$, density of manganese = $1.9 \times 10^{-3} \text{mol/L} \times 55 \text{mg/mol} \times 10^3 = 104.5 \text{mg/L}$. So when the pH value of manganese waste water is 9.0 (within standard), manganese is precipitated incompletely, and can not reach the discharge standard (2mg/L).
- ❖ If we change the pH value above 10, manganese in waste water can reach standard, and in order to make the pH value of waste water reach the standard, pH value must be adjusted again, we change pH value of effluent water back to 6-9, the process is unchanged and the cost increases, which caused some enterprises not adjust pH value for the second time.

2. Chinese classic verification-clean production of electrolytic manganese

(2) mud disposal problems in wastewater disposal workshop

After waste water treatment, there will be a large amount of mud, because the mud includes manganese as well as chromium, so it must be handled as dangerous wastes, which cause the big amount and high cost. Currently, the factories adopt the method of deposit after dehydration, which lead that the amount increases day by day.

(3) Ammonia nitrogen disposal problems

Ammonia nitrogen in waste water can not removed, so it is directly discharged in water.

2. Chinese classic verification-clean production of electrolytic manganese

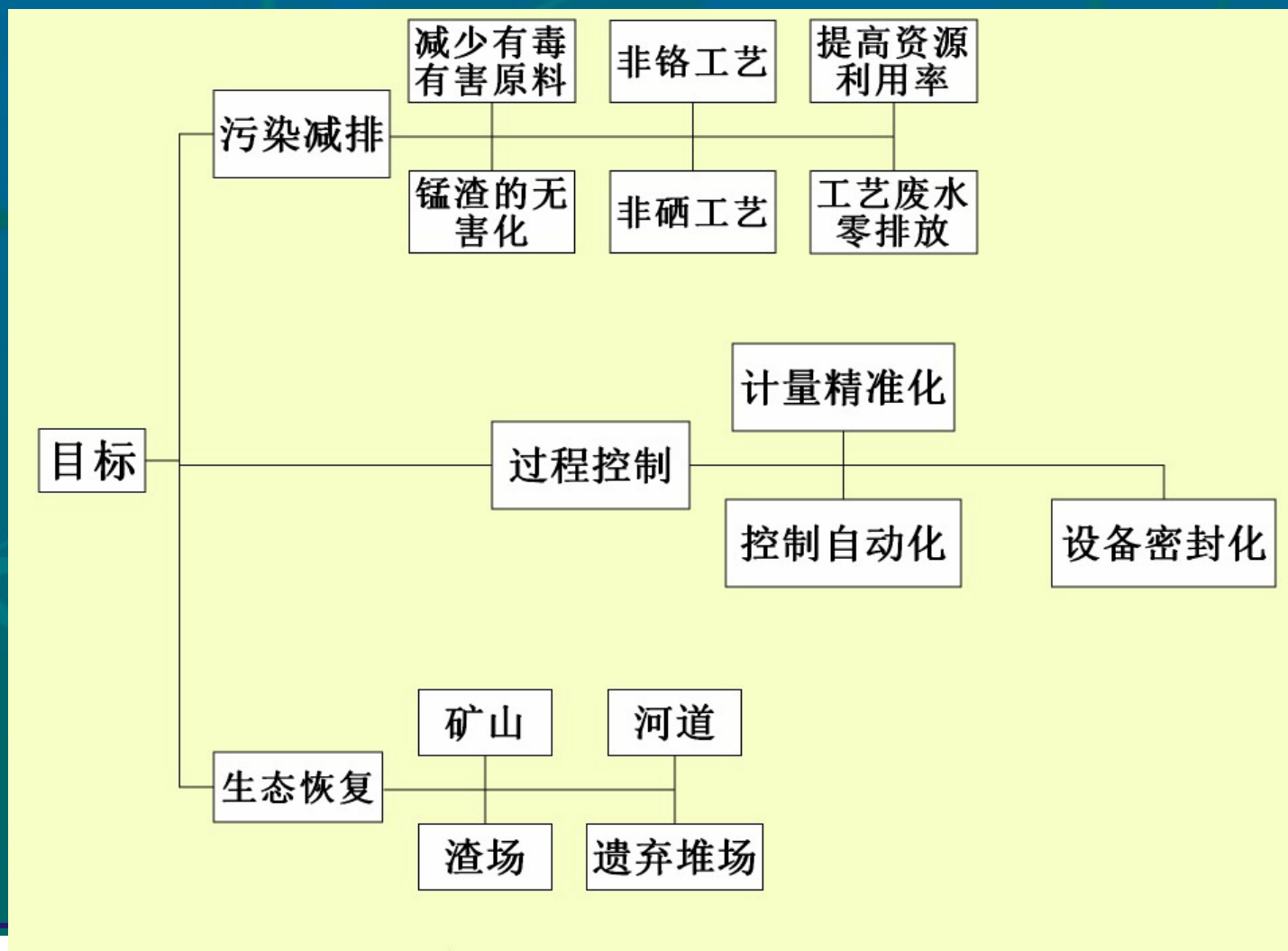
waste residue
piling factory



2. Chinese classic verification-clean production of electrolytic manganese

- ❖ A large number of manganese and chromium dreg bringing the great potential environment and ecological risk to locality and surrounding area. According to surveying, the contents such as sulphate, ammonia nitrogen, manganese, etc. in the manganese dreg respectively reach at 63324、2987、34762mg/kg, the density of arsenic, mercury, selenium is relatively high too, the maximum respectively reach at 38.9、32.3、30.8mg/kg, among which, the density of sulphate, manganese and selenium exceed 300 times of the reference of *electrolytic manganese clean production evaluating indicator system*. The treatment way of the manganese dreg in the electrolytic manganese enterprises of our country are still at quite primitive stage, many of them choose the local mountain or valley to pile the dreg, some dreg dams are even piled up with the stone, there is not a measure of prevention of seepage at all.
- ❖ The chromium dreg has been piled up alone only, has not handled safely as a kind of pollutant, there are obvious hidden

3. The clean production techniques of electrolytic manganese industry



3. The clean production techniques of electrolytic manganese industry

- ❖ Manganese dreg second extract techniques
- ❖ Recycle techniques of manganese and chromium ion in terminal waste water
- ❖ Wash and passivate manganese and chromium ion, collection and recycle techniques
- ❖ Manganese dreg preparation techniques

3. The clean production techniques of electrolytic manganese industry

❖ Manganese dreg second extract techniques

The rate of recovery of soluble manganese is more than 50% in the manganese dreg.

❖ Recycle techniques of manganese and chromium ion in terminal waste water

The manganese, chromium resource are more than 90% in waste water, 70% of the waste water will be reused in production after disposal.

❖ Wash and passivate manganese and chromium ion, collection and recycle techniques

Reduce manganese, chromium waste water 65%.

❖ Manganese dreg preparation techniques

The adding amount of manganese dreg is above 50%, the properties of product reach relevant standards of national building materials.

3. The clean production techniques of electrolytic manganese industry

Expect benefit (regard producing 30,000 tons of electrolytic manganese factory per year as the example)

❖ Manganese dreg second extract techniques

Retrieve 1260 tons of manganese every year, it is worth 25,200,000 yuan to increase production newly.

❖ Recycle techniques of manganese and chromium ion in terminal waste water

Reduce 240 tons and manganese, 10 tons of chromium through circulation and retrieve every year; It is worth 5 million yuan to increase production newly.

❖ Wash and passivate manganese and chromium ion, collection and recycle techniques

Reduce manganese, chromium waste water 65%, it is worth about 4 million tons to reduce the cost and increase production newly.

❖ Manganese dreg preparation techniques

Reduce more than 200,000 tons of manganese dreg, solve the problem of environmental pollution and ecological risk from manganese dreg, realize nearly 20 million yuan.



Thanks!





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