Application of closed-cycle technology in electroplating production line in China

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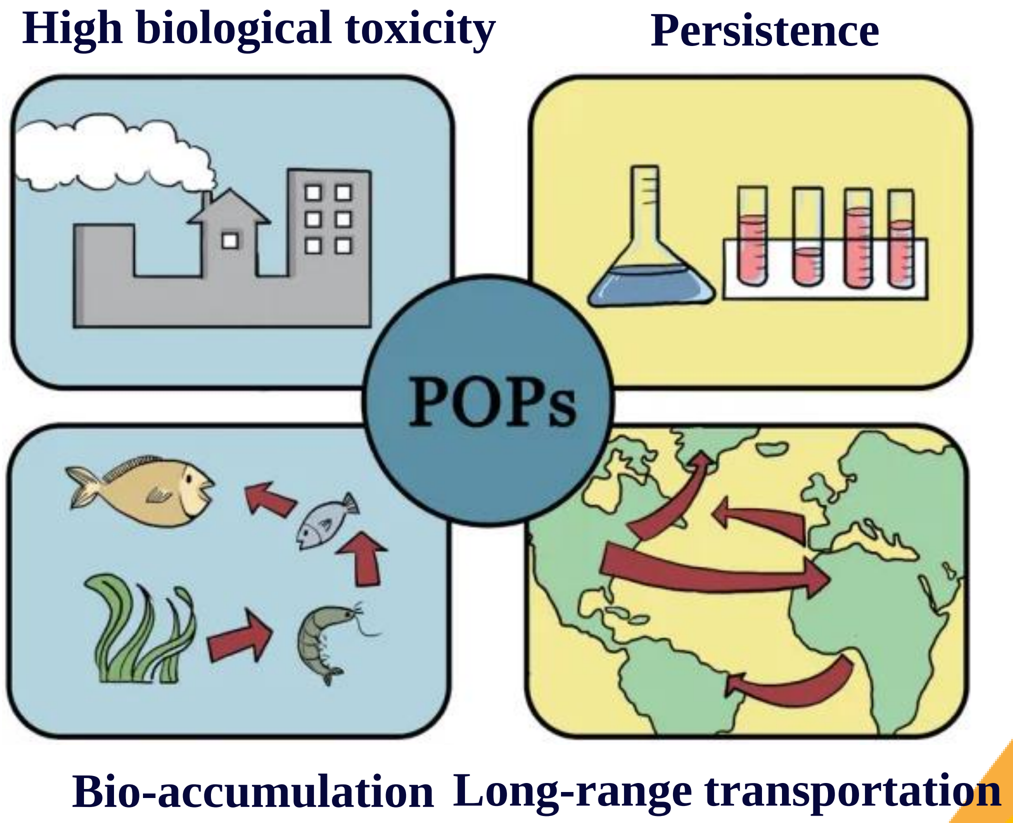
Chapter 1 Research Background

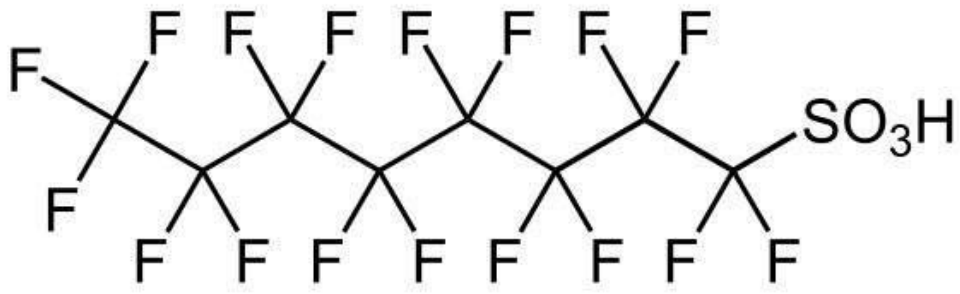
Persistent Organic Pollutants (POPs)

- Naturally occurring or synthetic organic compounds
- High biological toxicity
- Persistence
- Long-range transportation
- Bio-accumulation

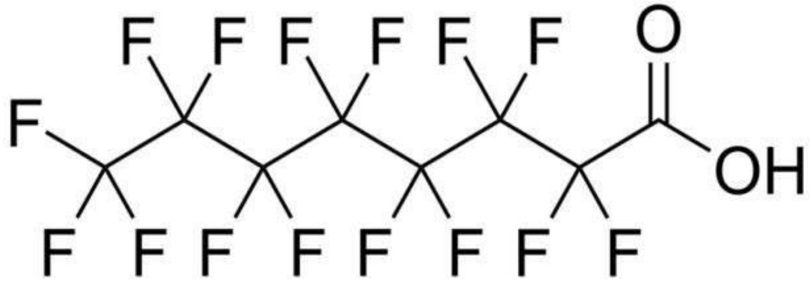


Polyfluoroalkyl substances (PFASs)

- Belongs to persistent organic pollutants (POPs)
- Widely used in electroplating, firefighting, pesticides, aviation, textiles
- In the electroplating industry, PFASs serves as a fluorocarbon surfactant to suppress the chromium mist generated during the electroplating process.
- PFOS and PFOA are typical PFASs



PFOS



PFOA

Chapter 1 Research Background

The Development of Regulation for PFASs as Fluorocarbon Surfactant in China

2009: Listed in Annex B (List of Substances Subject to Restriction) of the Stockholm Convention on Persistent Organic Pollutants

2013: The Standing Committee of the National People's Congress of China deliberated and approved the amendment

2014: The former Ministry of Environmental Protection, along with 11 other ministries and commissions, jointly issued a document prohibiting all production, circulation, use, and import/export of PFOS and PFOSF, except for specific exemptions and acceptable uses.

2019: The use of PFOS in the electroplating industry (except for closed-cycle systems) has been clearly listed as a target for complete phase-out

2023: The Ministry of Ecology and Environment, along with five other departments, jointly issued the "List of New Pollutants under Key Control (2023 Edition)", in which PFASs have been included in the list of new pollutants under key control.

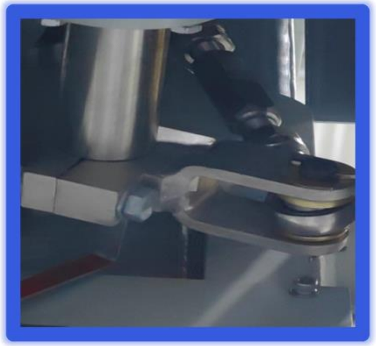
Introduction to electroplating process

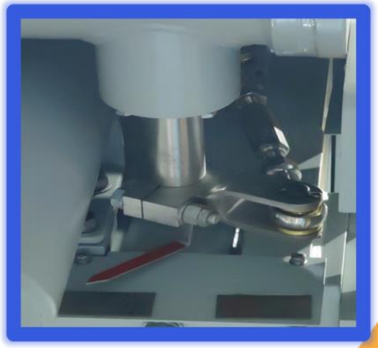
Electroplating technology is one of the key processes of high-end and the entire manufacturing industry, and the more developed the manufacturing industry, the more developed the supporting electroplating industry.

Electrochrome plating plays an important role in decorative and functional plating because the chromium layer of electrochrome plating has the following properties:

- High hardness
- Wear
- heat resisting
- Corrosion-resistant
- Not easy to change color

Bathroom products





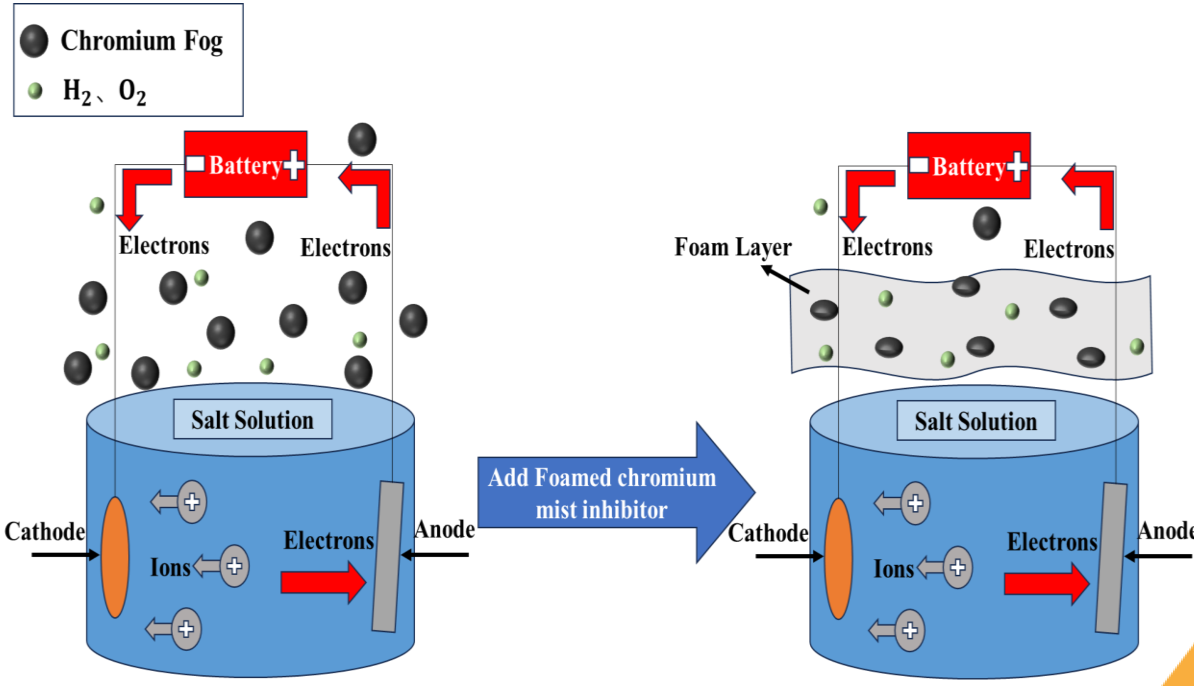
Electrical switches

Why Use PFASs in Chromium Plating?

Reason: during the electroplating process, the hydrogen of the cathode and the oxygen of the anode will overflow in the form of gas, taking away the chromium anhydride in the electroplating bath solution and producing chromium mist.

Chrome fog is **strongly corrosive** and has a **high carcinogenic risk** to humans.

The use of PFASs-containing chromium fog inhibitors such as F53 and FC-80 can solve the problem of chromium fog.



Conventional electrochrome plating process

Three main steps in plating hard chrome:

1. Pre-treatment: degreasing, cleaning; 2. Electroplating; 3. Post-treatment: all kinds of recycling, cleaning and spraying

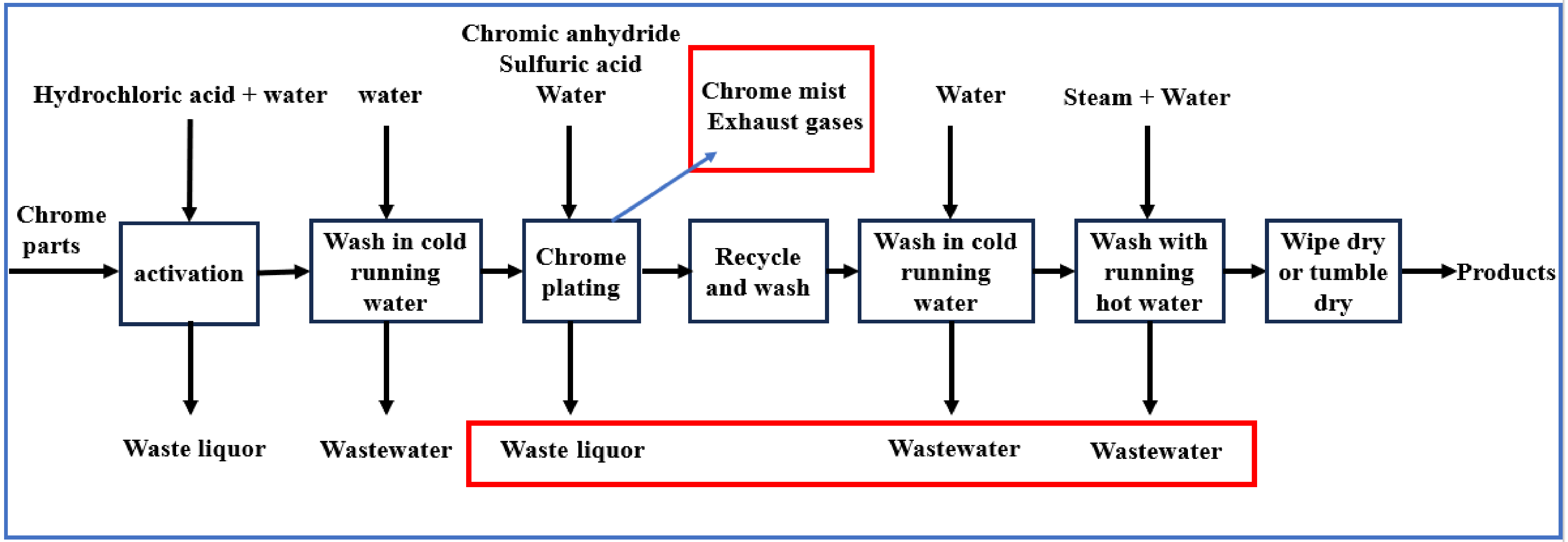


Fig.1 Schematic diagram of typical hexavalent chromium plating in China

PFOS Main discharge channels

Second: Introduction to the Plating Process

Emission pathways for PFASs

Emission pathways for PFASs

① **Exhaust gas**

- PFASs floats on the liquid surface and, as the exhaust gas of the system overflows, a small portion of gel-like PFASs is carried out into the external environment by the exhaust gas.
- The amount of PFASs carried out in this way accounts for approximately 30% of the total PFASs carried out from the entire system.
- Closed-cycle treatment of PFASs is required in each chromium exhaust gas system of the production line.

② **Rinsing water**

- A portion of the chromic acid solution and PFASs are adsorbed on the components after the electroplating process
- This portion accounts for approximately 70% of the entire PFASs system
- Closed-cycle treatment of PFASs is required in the rinsing water process.

What is the closed cycle of PFASs?

- One of the best environmental practices of hexavalent chromium electroplating production lines
- Near-zero environmental discharge of toxic and harmful substances such as PFASs by efficiently recycling the main substances hexavalent chromium
- This technology eliminates the application of PFASs in the electroplating industry, meets the requirements of China's implementation of international conventions

Difficulties in Technology

1. How to collect all chromic anhydride and chromium mist inhibitors in chromium mist?
2. How to renew and regenerate the refluxed chromium anhydride solution and remove the impurities of the recycled chromium mist?
3. How to improve the recycling rate of materials and water under the condition of low energy consumption?

Third: Introduction to the closed-cycle electroplating process

The current situation of closed-circuit circulation in China

Fig.1 Example of exhaust gas emissions in Longxi Electroplating Park

The 3-meter-high exhaust unit is too far from the surface of the chrome tank.

Fig.2 Hexavalent chromium plating line in China

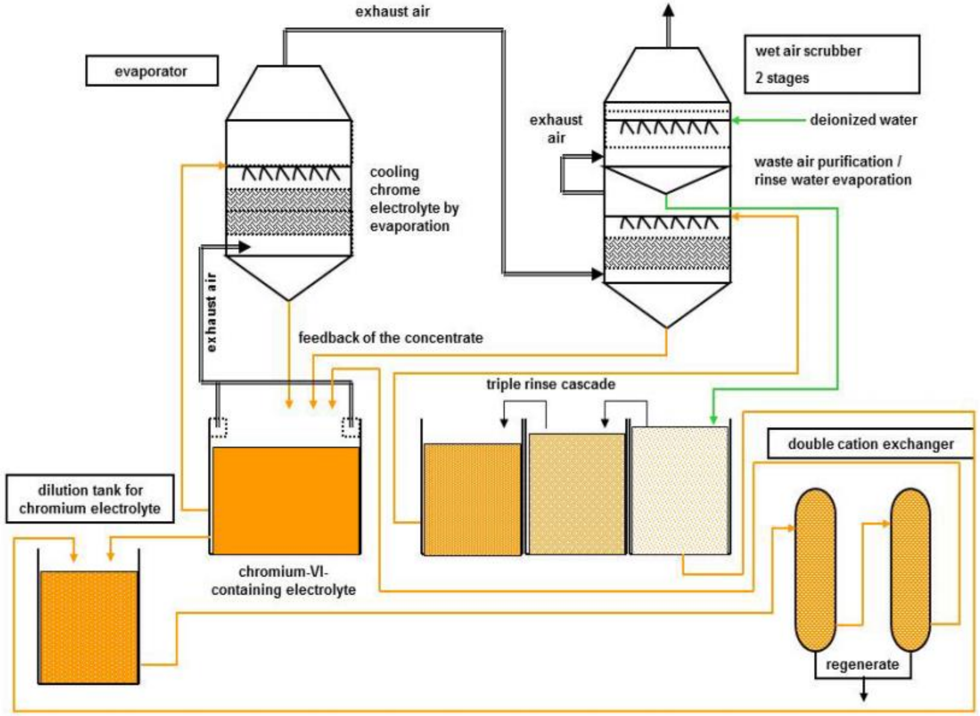
The exhaust device is close to the bath liquid.

Third: Introduction to the closed-cycle electroplating process

Application status of closed-cycle technology in Germany

The experience of the EU is that closed-cycle plating lines can be achieved by combining evaporation, condensation and ion exchange technologies

Chapter 4.4.4 of the draft BAT/BEP guidelines（UNEP / POPS / COP.7 / INF / 21 2015）contains a process flow diagram for the combination of multi-stage flushing technolog with evaporation technology, exhaust gas scrubbers and ion exchange for electrolyte purification.



Current status of closed-cycle technology application in United States

The KCH Spectra U-Series chromium mist remover with HEPA/ULPA filtration complies with the latest federal EPA emission limits for hexavalent chromium at 0.006 mg/dcsm (dry standard cubic meter), eliminating the need for PFASs or non-PFASs chromium mist suppressants.

It is achieved by effectively trapping chrome mist in the treatment tank and achieving ultra-efficient removal in the Spectra U chrome mist remover.

KCH Spectra system mainly includes:：

- Washable composite mesh mats
- Removable sprinkler design for reduced water consumption
- Fiberglass-covered PVC bottom for double leak protection
- Access door, for cleaning, maintenance

Fig.3 Closed-cycle external diagram of KCH cycle plating line in United States

Design principles of closed-cycle hexavalent chromium plating process line

difficulties in technology

- How to collect all chromic anhydride and chromium mist inhibitors in chromium mist
- How to renew and regenerate the refluxed chromium anhydride solution and remove the impurities of the recycled chromium mist?
- How to improve the recycling rate of materials and water under the condition of low energy consumption?

Key technologies

- Chromium mist graded multi-layer barrier
- Reverse osmosis, ultrafiltration technology
- ion exchange resin
- Low-temperature evaporation technology

Key technologies 1:
Chromium mist graded multi-layer barrier

Level 1
- 10 micron gel pellets

Level 2
- 2-10 micron gel pellets

Level 3
- 0.2-2 micron gels

Level 4
- Less than 0.2 micron particles

With this structure, it can stably discharge lower than the national standard (Cr^{6+}0.05mg/m^3).

In addition, no chemicals are used to complete the recovery of PFOS in the system.

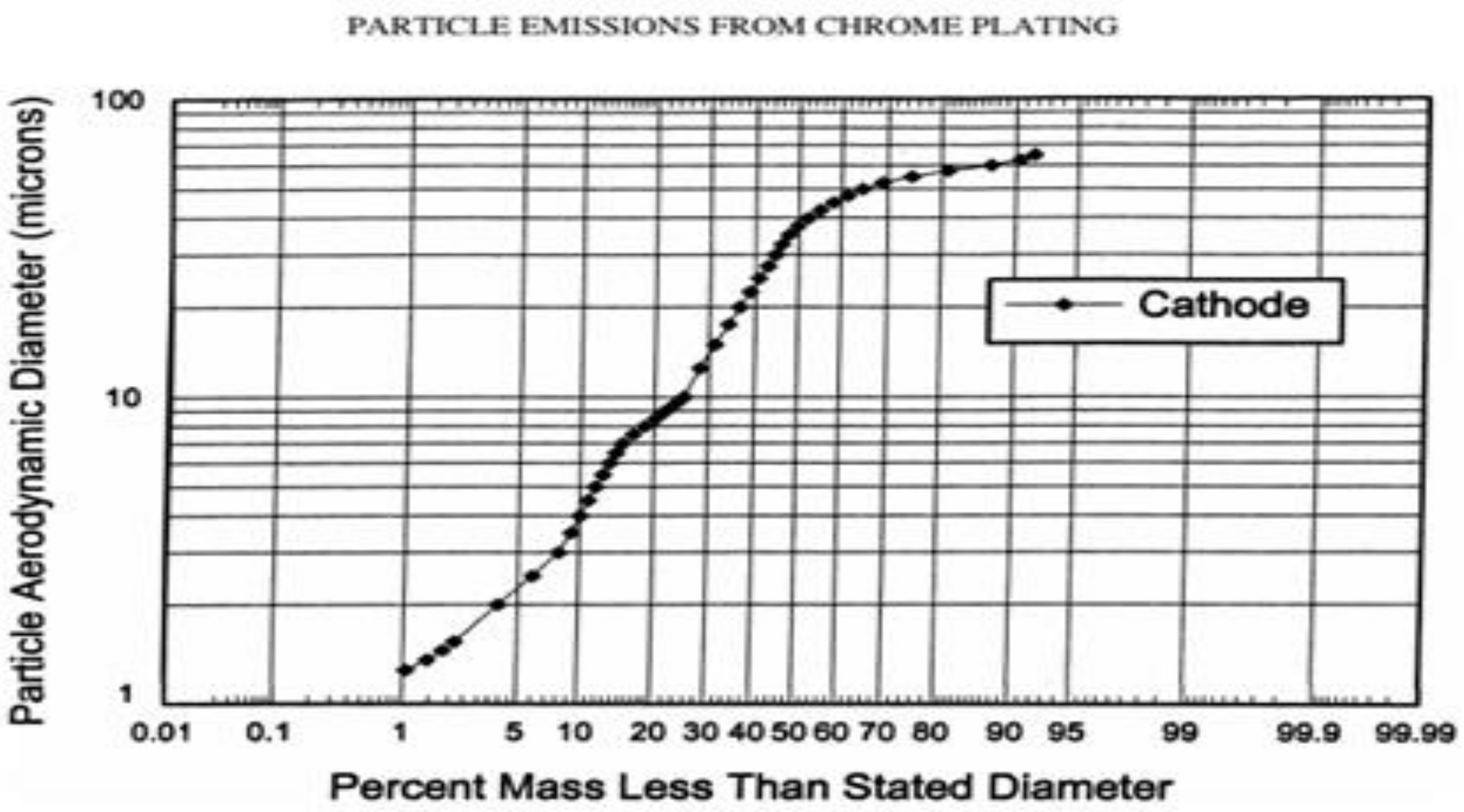


Figure 5: Particle size of chromium mist from hydrogen precipitation from the cathode（Aerosol Science and Technology, 40:639–648, 2006）and recovery distribution

More than 95% of the chromium mist particles brought out by hydrogen precipitation from the cathode are between 1 μm and 70 μm, and the distribution is shown in the figure.

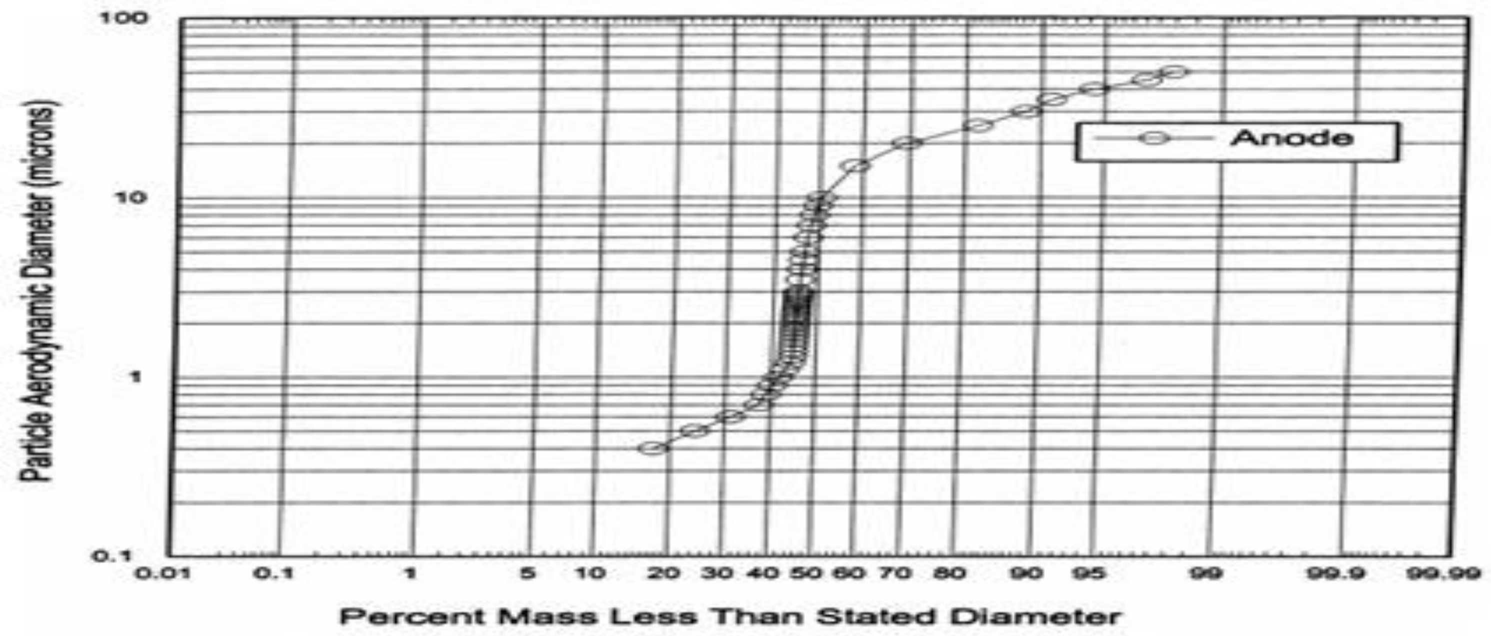


Figure 6: Particle size and recovery distribution of chromium mist from oxygen precipitation from the anode

（Aerosol Science and Technology, 40:639–648, 2006）

More than 98% of the chromium mist particles carried out by the oxygen precipitated from the anode are concentrated between 0.5 μm and 65 μm, and the particle size distribution is shown in Figure 6. The above particle size ranges are in the collection range of "chromium collection" and "leaching tower".

Chapter 4 Closed-cycle Circulation System Technology

- Hexavalent chromium colloids collected from the recovery tower for analysis：

More than 98% of the chromium mist particles carried out by the oxygen precipitated from the anode are concentrated between 0.5 μm and 65 μm.

More than 95% of the chromium mist particles brought out by hydrogen precipitation from the cathode are between 1 μm and 70 μm.

- With the method of four-stage recovery, all the particle sizes of hexavalent chromium chromium mist gel particles are basically covered.
- It provides a new way for the reuse and disposal of heavy metals such as hexavalent chromium, water and industrial solid waste, and reduces or eliminates the discharge of heavy metals such as hexavalent chromium to the environment；The transformation and improvement of the intelligent electroplating line has promoted the development of China's electroplating industry in the direction of green, clean and intelligent. (Heavy Metals Policy)

Key technologies 2:
Reverse osmosis, Ultrafiltration technology

- Evaporator module Evaporation to recover PFOS from rinse water

The evaporator is used to evaporate and recover the rinse water, and the evaporated distilled water is cooled and returned to the cleaning tank for recycling, and the concentrated chromic acid solution is returned to the plating tank for use, which not only ensures the cleaning effect, but also closes the PFOS cycle.

At present, the domestic production line uses a large amount of rinse water to clean the plating parts, because the parts from the chromic acid tank out of the groove bring out the chromic acid and PFOS, resulting in the rinse water contains PFOS, part of the rinse water to supplement the natural evaporation and heating and working evaporation of the chromic acid tank.

However, the excess rinse water is discharged to the wastewater treatment facility, and the wastewater treatment plant is unable to degrade the PFOS in the exhaust air of the production line。

Key technologies 2: Reverse osmosis, Ultrafiltration technology

Reverse osmosis Ultrafiltration

- Most rinse water is reusable
- Reduced evaporation process
- Save energy
- Reduced turbidity to meet ion exchanger requirements

Technology critical → **Acid resistance and strong oxidation performance of the filter membrane material**

Key technologies 2:
Reverse osmosis, Ultrafiltration technology

- Dish tube reverse osmosis membrane material and shape design

1） Two parts of the membrane module effluent： Concentrates and Permeates.

The concentrate is discharged into the brine tank for further processing；The permeate enters the permeate tank for reuse.

2） DTRO high-pressure reverse osmosis membrane is the core element to achieve the separation of fresh water and impurities, and has excellent chemical properties and polymer material composition.

Key technologies 3：
Ion exchange resin technology

Regeneration technology-Ion Exchange Resin

Removal of low-valent impurity ions in electrochrome acid solution：Cu、Ni、Zn、Fe

Technology critical

High selectivity
Resistant to strong acids
Corrosion-resistant
Resin

Key technologies 4: Low-temperature evaporation technology

The evaporator uses vacuum concentration equipment to evaporate the rinse water and pure water spray water through thermal cycle technology, and the evaporated distilled water is cooled and returned to the cleaning tank for recycling, and the chromatic acid concentrate is returned to the chrome plating tank for use, which not only ensures the cleaning effect, but also allows the PFOS and hexavalent chromium in the rinse water to be recycled.

Series "VsHp" concentrator Working diagram

1. *Freon Compressor*
2. *Boiling Exchanger*
3. *Sub cooler*
4. *Expansion Valve*
5. *Condensing Exchanger*
6. *Vacuum Ejector*
7. *Pump*
8. *Distillate Tank*
9. *Concentrate Pump*

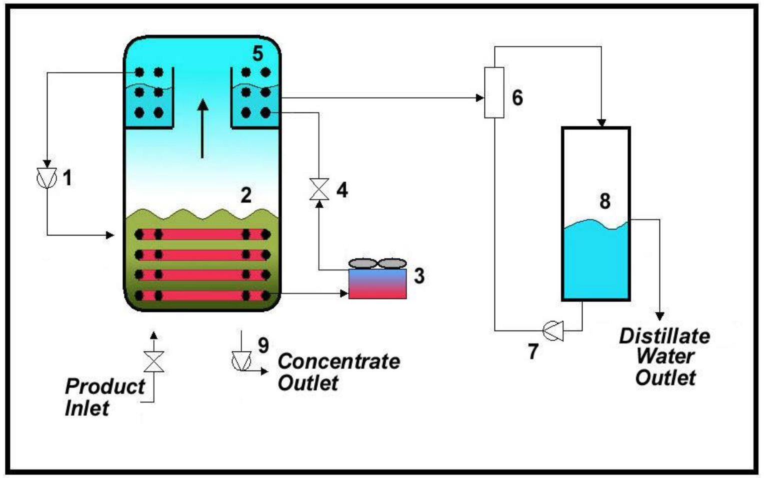
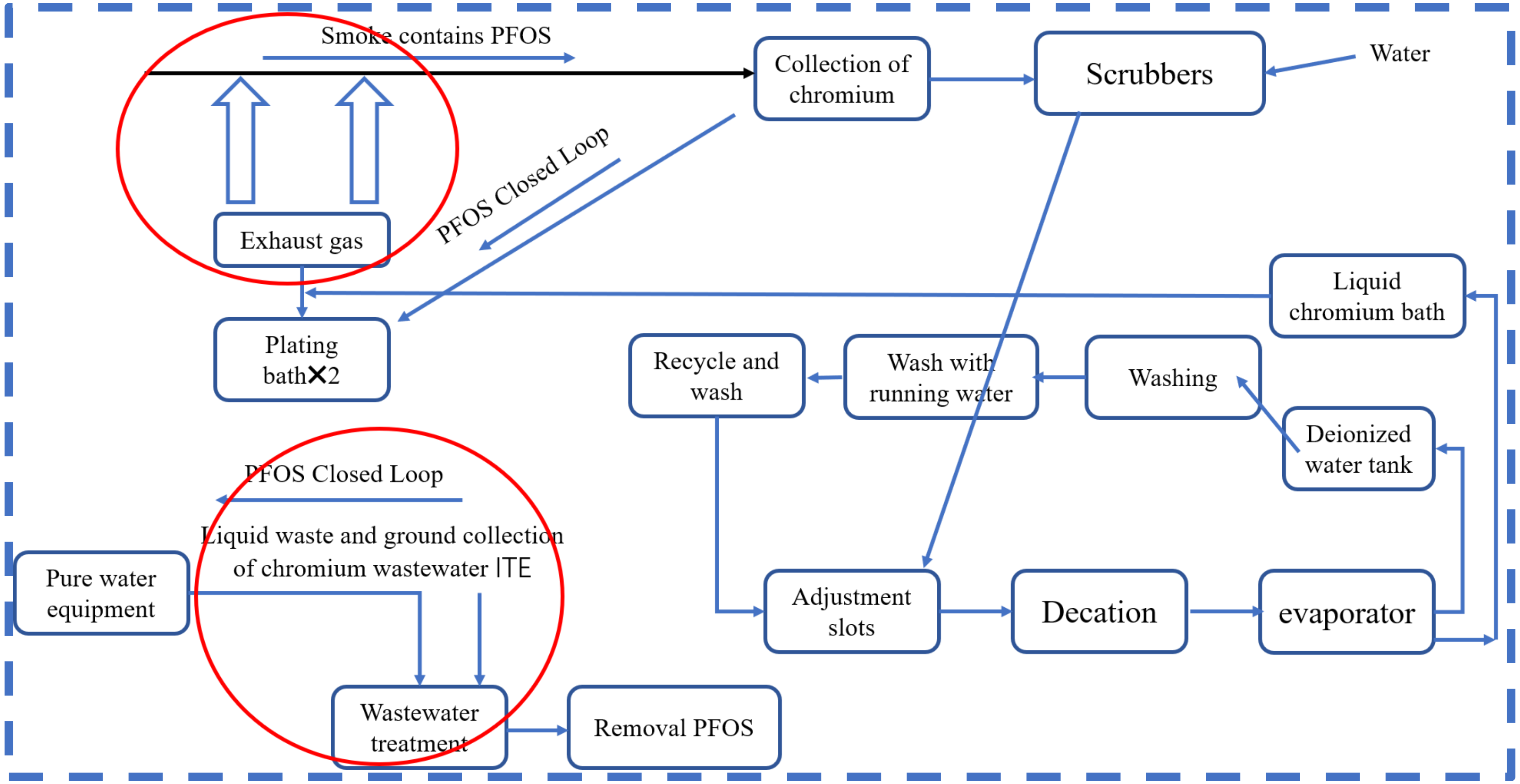


Fig.7. Schematic diagram of evaporation recovery of rinse water by evaporator

Chapter 4 Closed-cycle Circulation System Technology



Process flow diagram of the new closed-cycle chrome plating production line

- PFOS Gas Outlet

Workshop exhaust gas, air outlet after gas collection and treatment

- PFOS Liquid Outlet

Waste water is spilled on the ground

Ion exchange resin reclaimed water

New Northeast Electric Group chrome plating closed-circuit cycle production line

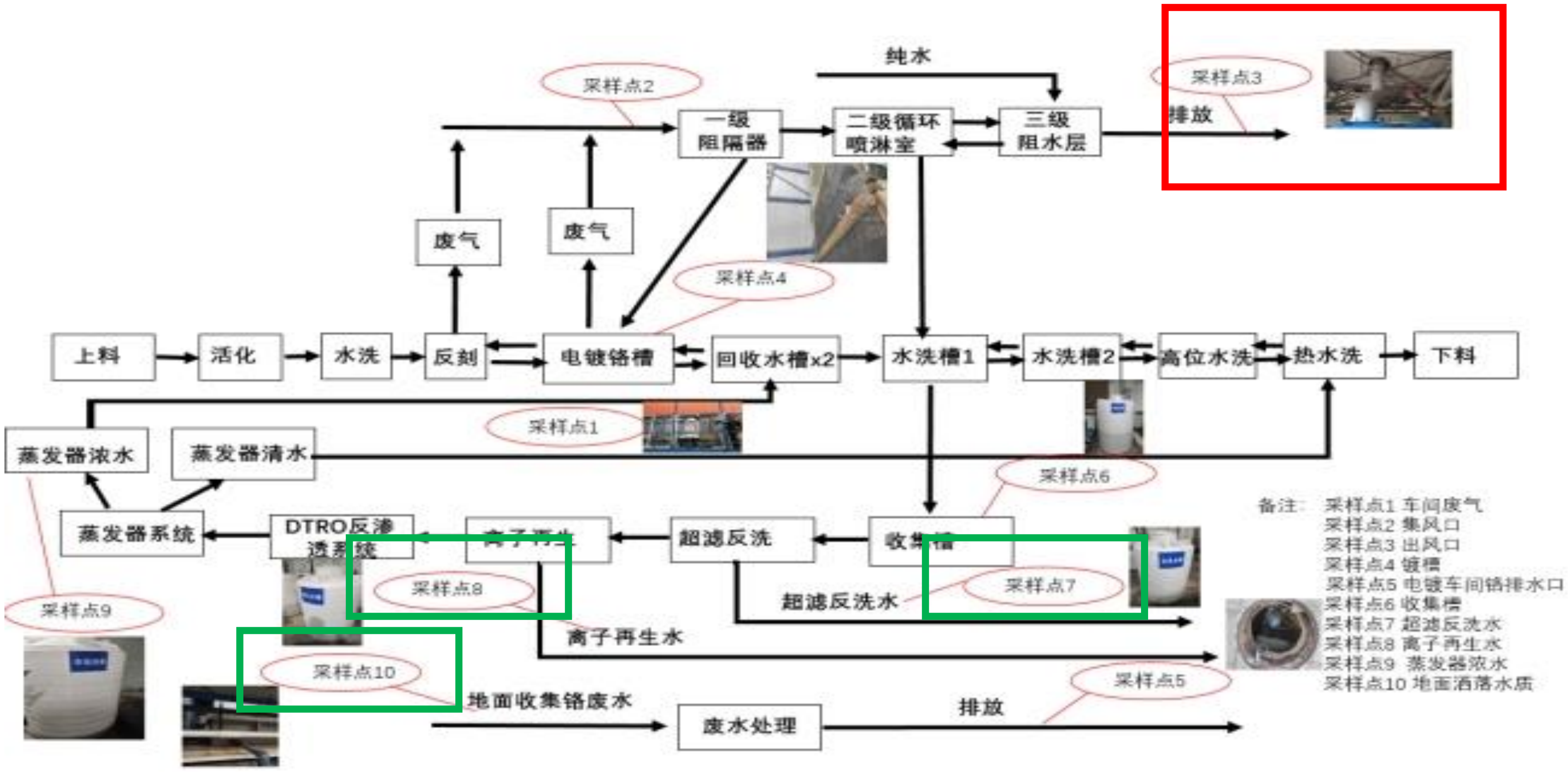
Third-party testing solutions

(1) Detection metrics： Exhaust gas——Chromic anhydride、Fluoride、PFOS
Wastewater——Chromic anhydride、Total chromium、fluoride、PFOS
Solid waste——Total chromium, fluoride, PFOS
Plating bath solution——Chromic anhydride, Total chromium, Fluoride, PFOS

(2) Executive Standard：

1) 《Determination of chromic acid mist in the exhaust gas of stationary pollution sources, diphenylcarboyl dihydrazine spectrophotometry》 HJ/T 29-1999
2) 《Determination of Atmospheric Stationary Pollution Sources Ion-selective electrode method for fluoride》 HJ/T 67-2001
3) 《Determination of Solid Waste Fluorine Alkali Fusion-Ion Selective Electrode Method》 HJ/T 999-2018
4) 《Hazardous Waste Identification Criteria Leaching Toxicity Identification Flame Atomic Absorption Spectrometry》 GB 5085.3-2007
5) 《Solid waste leaching toxic leaching method sulfuric acid nitric acid method》 HJ/T 299-2007
6) 《Water quality Determination of hexavalent chromium Diphenylcarboyl dihydrazine spectrophotometry》 GB/T 7467-1987
7) 《Water quality Determination of total chromium》 GB/T 7466-1987
8) 《Water quality Determination of fluoride Ion-selective electrode method》 GB 7484-1987
9) 《Soil and sediment Determination of perfluorooctane sulfonic acid and perfluorooctane carboxylic acid by liquid chromatography-triple quadrupole mass spectrometry》 HJ-Draft for Comments
10) 《Water Quality Determination of PFOS and PFOS Solid Phase Extraction, Liquid Chromatography-Triple Quadrupole Mass Spectrometry》 HJ-Draft for Comments

Layout of the Closed-cycle Electroplating Line



- ➢ PFASs Gas Outlet
- Workshop exhaust gas
- Air outlet after gas collection and treatment.
- ➢ PFASs Liquid Outlet
- Spilled wastewater
- Rinsing water from ion exchange resin
- Backflushing water from ultrafiltration

Reuse Rate Test Table

$$\text{The reuse rate of each substance in the circulatory system} = \frac{\text{The amount of } Cr, PFOS, \text{and water in the return water}}{\text{The amount of } Cr, PFOS, \text{and water in the influent water}}$$

The reuse rate of Cr, PFOS, and water is more than the required 95%

Number	Time				Reuse rate of chrome particles: (CI-TCR)/TCI				Water reuse rate: reused water/influent water
1	2022.11.4-2022.11.18	TCI	22.32	g		Influent Water	55.8	m^3	
		TCR	0.79	g	96.50%	Reuse of water	53.2	m^3	95.9%
2	2022.11.21-2022.11.30	TCI	45.5	g		Influent Water	55.1	m^3	
		TCR	1.08	g	97.6%	Reuse of water	53.1	m^3	96.4%
3	2022.12.1-2022.12.12	TCI	42.5	g		Influent Water	52.2	m^3	
		TCR	1.92	g	95.5%	Reuse of water	50.3	m^3	96.44%
4	2023.2.1-2023.2.28	TCI	130.9	g		Influent Water	77	m^3	
		TCR	2.52	g	98.1%	Reuse of water	75	m^3	97.4%
5	2023.3.1-2023.3.23	TCI	455.3	g		Influent Water	413.9	m^3	
		TCR	9.76	g	97.9%	Reuse of water	402	m^3	97.1%

CI: Chromium in Influent water TCI: Total Chromium in the Influent water TCR: Total Chromium in the Return water

Comparison of Previous and New Technology

Previous technology	New technology
Terminal process	Process treatment
Reducing agents needed Hazardous substances generated	No waste is generated
Heavy metal emissions	Heavy metals can be reused

Advantages of Closed-cycle Technology

Drawbacks of the previous production line	Measures taken	Key technologies	Improvement
➢ PFASs in the exhaust gas cannot be degraded in the sewage treatment plant ➢ Sodium bisulfite used to reduce Cr(VI) to Cr(III), can not be recycled	Scrubbing Tower	➢ Pure water spray barrier was adopted ➢ Gel-like chromic acid and PFASs droplet from exhaust gas were collected and recycled to the production line	➢ Stable discharge according to the national standards (Cr(VI) $\leq 0.05 mg/m^3$) ➢ No extra additives ➢ PFASs recycling completed
➢ Chromic acid and PFASs in the plating tank were brought out due to the large amount of rinse water	Evaporator	➢ Distilled water from the evaporator was cooled and returned to the cleaning tank for recycling ➢ Concentrated chromic acid solution was returned to the plating tank for use	➢ Concentrated chromic acid solution from the evaporator returned to the chrome plating tank
➢ Fe(III) and Cu(II) can be found in the chromic acid treatment column and cannot be returned	Special treatment for impurities	➢ Ion-exchange resin able to adsorb the target ions (Fe(III) and Cu(II) impurities) ➢ The purified chromic acid solution can be used for a long time	➢ Purifying the chromic acid solution before in can be sent to the Evaporator

Cost

Number	Content	Ordinary production line	Expenses	Closed-cycle lines	Expenses
1	Rinse water treatment after plating	3000L/H	240.00	150L/H	12.00
2	The consumption of Chromic anhydride brings out	3L/H	37.50	0	0.00
3	The consumption of PFASs brings out	20g/H	0.50	0	0
4	Equipment depreciation (60,000H/ 10 years)	Calculated at 17.58 million	293.00	Calculated at 23.58 million	393.00
5	Electricity consumption	1800kW Electrovalence:0.7 Yuan	1260	2100kW, Electrovalence:0.7 Yuan	1470
6	Environmental factors	Emission ($20000m^3$/H)	40.5	Emission-free	0
	Subtotal		1871.50		1875.00

In summary : In the case of continuous work, it is about 4 Yuan /H

Benefit Analysis and Actual Operating Costs

Benefit Analysis (Half-year)

Project	Quantity	Unit	Unit Price(Yuan)	Savable Cost（Yuan）(Half-year)	Remark
Reduction of chromium-containing wastewater	2569	ton	11.82	30,365.58	
Reduction of trivalent chromium-containing sludge	1547	kg	0.4	618.80	
Reduce the dosage of fresh water	2569	ton	5.25	13,487.25	
Reduce chromic anhydride addition	150	kg	28	4,200.00	
Reduce chrome fog inhibitor addition	98.08	liter	1200.00	117,696.00	
An increase in the power consumption of new devices	28545.9	kw	0.77	Increased costs-21980.34	According to the production situation, the average daily operation is 8H
Reduce the amount of steam used	3.4	ton	265	901.00	According to the production situation, the average daily operation is 8H
Reduction of labor	1	person	5000Yuan/month	30000	
Total				175,288.29	

Equipment and installation and commissioning fees for chrome plating closed circuit system： 5,809,000 Yuan
The chrome plating closed-cycle system is put into operation and the estimated return of investment： 16.57 years

Promotion of technology

- **（1）Organize industry promotion and application meetings**
- Industry annual meetings (organized by industry associations) ; Project achievement promotion meetings (organized by the Department of Ecology and Environment of Guangdong Province)
- The Global Environment Facility (GEF) "China PFOS Priority Industry Reduction and Phase-out Project" and the demonstration technology of closed-circuit system transformation in the electroplating industry will be publicized and promoted.
- By building an efficient information exchange platform, managers in the environmental department, leading enterprises in the electroplating industry and other closely related industry partners can have a deep understanding of the core value and implementation effectiveness of the closed-cycle process, and help the electroplating industry and the wider field to achieve green transformation and upgrading.
- **（2）Establish a closed-circuit circulation technical scheme for hexavalent chromium production line**

Promotion of technology

- **(3) Published monographs**

- Published the monograph "Research on PFOS-based Environmental Management and Compliance Countermeasures in China" (Yu Lifeng, Sun Yangzhao et al.) (ISBN 978-7-5111-3196-6). We reviewed the compliance measures for PFASs and the management process of the domestic and foreign environment, that make the China's environment, industry, agriculture and other related fields and electroplating, pesticides, fire protection and other industries and enterprises systematically understand the policy requirements of environmental management of PFOS substances and the necessity of elimination and substitution.

- **(4) Published papers**

- ①Zhe Zheng, WengJing Chen, **An Lin**, Jie Ma, XiaoWei Liu,《Suggestions on the realization of functional hexavalent chromium electroplating closed-cycle system in China》.Material protection,2021,54(05):126-130.

- ②Zhe Zheng, WengJing Chen, **An Lin**, et al.《Chromium-chromium process closed-cycle technology》. 2022 China Surface Engineering Association ProSF.

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Thanks for your attention!