Application and Product Standard of Purified Crystalline Salt from Desulfurization Wastewater of Thermal Power Plant

Zhengkun Li 1,2*, Ruozheng Li 1,2, Xiaoyu Liu 1,2, Chong Zhao 1,2 and Ying Tian 1,2

1 Beijing Guodian Futong Science and Technology Development Co., Ltd, Beijing 100070, China
2 Nari Group Corporation/State Grid Electric Power Research Institute, Nanjing, Jiangsu Province, 210000, China

Abstract: The shortage of water resources and the increasingly strict requirements of environmental protection make the zero discharge of waste water from thermal power plants imperative. The treatment of high salt desulfurization wastewater is the bottleneck of the application and promotion of "zero discharge" technology. The waste water zero discharge and resource recovery technologies such as salt separation and purification can be used to make sodium chloride crystal salt meeting the standards of "industrial salt" (GB/T 5462-2015) and sodium sulfate crystal salt meeting the standards of "industrial anhydrous sodium sulfate" (GB/T 6009-2014). However, due to the lack of related standards of certification index and certification method of crystal salt products, it is restricted to realize resource recovery as commodities. In this paper, the application field and product standard of purified crystalline salt from desulfurization wastewater are analyzed.

1 Introduction

As a large user of water and drainage, the water consumption of thermal power plants accounts for 20% of the total industrial water consumption. In the current situation of increasingly scarce water resources and increasingly strict environmental protection requirements, zero discharge of waste water from power plants has become a general trend. Desulfurization waste water is the end waste water of thermal power plant, because of its complex composition, high salt content and difficult reuse, its treatment has become the key and difficult point of zero discharge of power plant waste water[1-3].

The desulfurization wastewater is weakly acidic with high suspended solid and salt content, and contains a variety of heavy metals[4-5]. The traditional "zero discharge" treatment technology of high salt wastewater can realize zero discharge and reuse of water, but it will produce solid discharge, namely solid hybrid salt. Due to the presence of organic impurities and heavy metals, mixed salt cannot be recycled and is soluble, which poses a high risk of secondary pollution. Therefore, it needs to be managed as hazardous waste [6-7]. However, the number of units with the qualification of hazardous waste treatment and disposal in China is small, the treatment capacity is limited[8], and the treatment cost is high. Currently, the cost of treating hazardous waste in China is basically more than 3,000 yuan/ton[9], which is even higher than the cost of producing crystallized salt, making it difficult for enterprises to bear. Therefore, it is very important to purify the impurity salt in the process of zero waste water treatment to obtain high purity crystalline salt products instead of hazardous waste. How to solve the problem of crystal salt product marketing is also the key. As a product, crystalline salt should first meet the applicable product quality standards and be certified and recognized. This paper analyzes the application and product standard of purified crystalline salt from desulfurization wastewater of thermal power plant, and discusses the feasibility of its application in chlor-alkali and soda ash industries.

2 Salt separation and resource recovery of high salt wastewater

The recycling utilization of high salt wastewater from thermal power plants is to separate the recoverable crystalline salt such as sodium chloride and sodium sulfate from other impurities such as organic matter to realize salt separation, dry or incinerate a small amount of mother liquor, and use mixed salt or separated crystalline salt as raw material or for other purposes [10-11].

2.1 Elemental salt separation process

(1) Nanofiltration salt separation

Nanofiltration is a kind of filtration process between ultrafiltration and reverse osmosis membrane filtration, nanofiltration membrane can effectively intercept the bivalent and polyvalent anions in the water (e.g., SO\text{4}^2-) and organic pollutants, and for the univalent anion (e.g., Cl\text{-}) has good effect through, so for high salt wastewater in the mixed salt system has good choice separability[12-13]. Based on the phase diagram of salt solution of wastewater, high quality sodium chloride was

*Corresponding author’s e-mail: queenlz@sina.com

© The Authors, published by EDP Sciences. This is an open access article distributed under the terms of the Creative Commons Attribution License 4.0 (http://creativecommons.org/licenses/by/4.0/).
prepared by evaporation crystallization system. Nanofiltration has a high efficiency of salt separation, but the disadvantage is that the membrane performance attenuation, membrane pollution and other problems will occur during long-term operation[14].

(2) Evaporation-heating crystallization process

Evaporate the solvent, the solution from unsaturated become to saturated state, continue to heat, excess solute will be a crystal precipitation, that is evaporation crystallization. The method is suitable for salts whose solubility varies little with temperature, such as sodium chloride [15-17].

(3) Evaporation concentration-cooling crystallization process

Evaporative concentration-cooling crystallization process is to use evaporation technology to concentrate high-salt wastewater, and the concentrate precipitates crystalline salts by cooling. The process is suitable for the separation of the mixed salt system in which the inorganic salt solubility varies greatly with temperature, such as sodium chloride and sodium sulfate system, in which sodium chloride in water solubility change is not big with temperature, and sodium sulfate is more sensitive to temperature, therefore through the evaporation concentration-cooling crystallization process, the two kinds of inorganic salt can separate out respectively, to achieve the purpose of separation. By controlling the crystallization temperature, the process can obtain more pure crystalline salt products[12,18].

Evaporation-heating crystallization process and evaporation concentration-cooling crystallization process can be summed up as the thermal salt separation process. The thermal salt separation process and the membrane salt separation process have their own advantages and disadvantages. The process of thermal salt separation is simple, reliable, low investment and operation cost, and the shortage is that the quality of crystalline salt is slightly lower. The advantage of membrane method for salt separation is that the quality of sodium chloride is slightly higher, which is more suitable for wastewater with sodium chloride as the main component. The disadvantage is that the investment and operating cost are relatively high, and the operating reliability is not as good as that of thermal method for salt separation. The separation efficiency gradually decreases with the extension of operating time [10,19]. Different salt separation processes can be combined to form a multistage salt separation process, which can achieve better salt separation effect and make up for the shortcomings of a single process. It is the development direction of salt separation technology in the future[20].

2.2 Industrial pilot test of resource recovery of crystalline salt

A pilot test on zero discharge and recycling of high salt desulfurization wastewater from thermal power plant in hebei province was carried out. The raw water quality of desulfurization wastewater is shown in table 1.

| Table 1. Main characteristics of desulfurization wastewater from a thermal power plant in hebei province |
|-----------------|-----------------|-----------------|-----------------|
| Element         | Mass concentration/(mg L⁻¹) | Element         | Mass concentration/(mg L⁻¹) |
| pH              | 6~7*            | SiO₂             | 10~20           |
| Chromaticity (method of dilution multiple) | 30~50* | Na⁺             | 1500~4500       |
| SS              | ≤500            | Ca²⁺             | 1000~2000       |
| COD             | ≤150            | Mg²⁺             | 3000~6000       |
| NH₄⁺           | 15~30           | Fe               | 10~20           |
| SO₄²⁻           | ≤1.00           | Cu               | ≤0.5           |
| F               | ≤15             | Hg               | ≤0.05           |
| Cl              | ≤12000          | Cd               | ≤0.1           |
| SO₄²⁻           | 1000~2000       | TDS              | 15000~25000     |

Using the Calcium Sulfate Seed combine MVR evaporation crystallization process. In the pretreatment section of main additive lime and sodium sulfate, remove most of the hardness and heavy metal, and then into the evaporation crystallization system. In the beginning, the evaporation crystallization system was fed with a certain amount of calcium sulfate crystal seed. In the seeded slurry process, low solubility salts precipitate preferentially on calcium sulfate seed crystals suspended in the circulating brine in the evaporator, rather than precipitating as scale on the heat transfer surfaces. Condensate from the system can directly reuse and its produce sodium chloride salt crystals whose purity is up to 99.10%, which meets the standard requirements of industrial salt, and can be used as industrial raw materials. The details are shown in table 2.

| Table 2. Purified Sodium Chloride from Wastewater in Thermal Power Plant |
|-----------------|-----------------|-----------------|
| Element         | Testing standard | Mass concentration |
| Water content / (g/100g) | GB/T 13025.3-2012/2 | 0.13           |
| NaCl/ (g/100g)  | GB 5461-2000/5.15 | 99.10          |
2.3 Cases of crystal salt recycling project

Guangdong heyuan power plant [21] is the first power plant in China to realize zero waste water discharge in a real sense. The zero waste water discharge system adopts the process of "pretreatment +4 effect evaporative crystallization", and the designed treatment water amount is 22 m³/h, among which the desulfurization wastewater is 21 m³/h. The pretreatment system includes coagulation and sedimentation system, water quality softening system and sludge treatment system. The water from the pretreatment enters into 1~4 effect evaporative crystallization tank for evaporative crystallization, and the resulting crystalline salt meets the requirements of industrial salt, and the industrial salt yield is 3~4 t/d. The third phase of expansion project of the desulfurization wastewater deep treatment (evaporation crystallization) project by Guodian Hanchuan power generation co., LTD., is the national first adopting mechanical vapor recompression (MVR) evaporation crystallization technology to power plant desulfurization wastewater treatment project, using the process of "pretreatment + NF+ RO + MVR" to dispose the desulfurization wastewater, the sodium chloride crystallization salt whose purity is up to 97.5%, satisfies the requirement of industrial salt [22].

3 Application field analysis of crystal salt

3.1 Raw salt market analysis

Raw salt is one of the most important raw materials for caustic soda and soda ash. The statistical data shows that in the consumption of raw salt in China, the salt used in the production of both alkali and soda has been taking a large proportion. The overall operation trend of the two alkali industries plays a key role in the development of the raw salt industry. In 2018, the sales volume of raw salt in China was 55.5402 million tons, down 8.6% year-on-year. Although the amount of salt used by two alkali is increasing, the growth rate of salt used by two alkali is decreasing[23-25]. For one thing, soda ash industry is overcapacity, and its profit space is small. For another caustic soda industry presents serious overcapacity, high energy consumption, mercury pollution and other environmental problems [26], which are unfavorable to the market of raw salt. Therefore, if low-price raw salt or industrial salt from wastewater purification is used as production raw material in the two-alkali industry, the production cost of the enterprise can be reduced. In the case of overcapacity and market downturn, the profit of the enterprise can be improved, which has practical significance for the survival and development of the enterprise. Sodium sulfate use requirements are not high, not too much discussion here.

3.2 Application analysis in chlor-alkali industry

The chlor-alkali industry refers to the preparation of NaOH, Cl₂ and H₂ by means of electrolysis of saturated NaCl solution, and the production of a series of chemical products with them as raw materials. As the main raw material of chlor-alkali industry, the quality of raw salt is very important. The main content, impurity and properties of different kinds of raw salt are quite different. According to the difference of different kinds of raw salt in the control of brine refining process, it is necessary to change different process control methods or even adopt different equipment when using different raw salt [27].

Ion-exchange membrane process is the main process of chlor-alkali production in China. Excessive TOC in the brine will directly cover the anodic active coating, leading to the disappearance of anodic activity and the imbalance of current distribution, which will lead to the increase of electrolytic voltage and the decrease of current efficiency and affect the service life of the ion-exchange membrane[28-30]. Therefore, it is necessary to set restrictions on organics.According to the determination of raw salt in a chemical industry in binzhou, the TOC is 63.5 mg/kg. Compared with the data in table 2, it can be seen that the TOC of crystallized salt from desulfurization wastewater is less than 50 mg/kg, which meets the requirements.

Under the condition that the pH of the anode solution in the electrolyzer is 2~4, ammonium in the brine reacts to form nitrogen trichloride. Nitrogen trichloride explosive temperature is 95°C , but when its concentration in the chlorine reaches more than 5%, vibration or ultrasonic can cause decomposition and explosion at 60°C , and it will explode instantaneously under the direct sunlight and magnesium light, it is also induced to explode when contacting with ozone, nitrogen oxides, grease or organic matter. Therefore, Total ammonium content is strictly controlled in chlor-alkali production[31]. According to the industrial requirements, the basic requirement for total ammonium is below 10mg/kg. As shown in table 2, both TOC and ammonium of crystallized salt from desulfurization wastewater can meet the requirements.

The toxicity test of crystallization salt from desulfurization wastewater was carried out, and the indexes were all below the limit of "Identification standards for hazardous wastes-Identification for extraction toxicity" (GB 5085.3-2007).

Therefore, crystal salt purified from desulfurization wastewater can be used as raw salt in enterprises.
3.3 Application analysis in soda ash industry

Soda ash is one of the important chemical raw materials, used in the manufacture of chemicals, detergents, pharmaceuticals, etc.[33]. At present, in the downstream products of soda ash plate, glass and daily glass continue to grow at a high speed. In terms of flat glass industry demand, 80% of plate glass is applied in the construction industry, which will continue to drive the market demand of soda ash.

According to the investigation on the quality of raw salt in domestic alkali plants, the content of sodium chloride such as Qingdao raw salt, Dahua washing salt and Changlu salt is 92.3% to 94.84%, while only the content of salt in zigong mineral salt in sichuan province is 98.55%[17]. In general, compared with chlor-alkali industry, soda ash industry has a lower requirement on the index of salt, without the requirement on the index of organic matter TOC and total ammonium, which is one of the best ways to apply salt in wastewater purification industry.

4 Preliminary preparation for standard of crystal salt

Compared with the national standard of industrial salt and the indexes of zero discharge and recycling system of waste water, the content of sodium chloride in crystal salt from desulfurization waste water of thermal power plant can meet the requirements. Corresponding to the indicators of salt used in chlor-alkali and soda ash industry, the requirements of sodium chloride content of raw salt are not high, for organic matter and total ammonium, chlor-alkali has requirements, while the soda ash industry has no requirements. Therefore, soda ash salt is one of the best ways to purify industrial salt from wastewater. The index of organic matter and total ammonium should be well controlled. As the raw salt in chlor-alkali industry, crystallized salt in wastewater is also the main application direction.

Table 3. physical-chemical indexes of Purified Sodium Chloride

| Element                              | Index                  | Industrial dry salt | Industrial wet salt |
|--------------------------------------|------------------------|---------------------|---------------------|
| Identification for extraction toxicity| Below the standard limit on the basis of GB 5085.3 | 98.5 | 97.5 | 96.0 | 95.5 | 93.5 | 91.0 |
| Sodium chloride (g/100g) ≥          | Primary standard       | 0.40               | 0.60               | 0.35               | 0.70               | 1.10               |
| Water content (g/100g) ≤            | Secondary standard     | 0.10               | 0.20               | 0.10               | 0.20               | 0.40               |
| Insoluble matter (g/100g) ≤         | Qualified standard     | 0.30               | 0.40               | 0.40               | 0.60               | 1.10               |
| Ca²⁺ and Mg²⁺/ (g/100g) ≤           | Total ammonium (mg/Kg) ≤ | 8.00               | 75                 | 67                 | 58                 | 70                 |
| SO₄²⁻/ (g/100g) ≤                   | Whiteness ≥            | 3.00               | -                  | -                  | -                  | -                  |
| TOC /mg/Kg) ≤                       | Fe³⁺ / (mg/Kg) ≤       | 75                 | 67                 | 58                 | 70                 | 60                 | 53                 |

Regardless of the application field, as a product the waste water crystal salt must have the corresponding standard, to be more easily recognized. In terms of product standards for crystallized salt products in high salinity wastewater, two group standards "Coal chemical industry—By-product industrial sodium sulfate" (T/CCT 001-2019) and "Coal chemical industry—By-product industrial sodium chloride" (T/CCT 002-2019) have been formally implemented since January 1, 2020, which provide certification and recognition basis for crystallized salt products in high salinity wastewater of coal chemical industry. Therefore, the product standard of crystallized salt in desulfurization wastewater of thermal power plants is urgently needed.

According to the requirements of salt used in chlor-alkali industry and soda ash industry, and according to the conventional requirements of metal ions, and referring to the standards of crystallized salt from by-products of coal chemical industry, the standards for purifying crystallized sodium chloride from desulfurization wastewater of thermal power plants are proposed, as shown in table 3. Primary products are mainly used in non-edible alkali soda ash industry. Secondary products are mainly used in non-edible alkali soda ash industry. Qualified products are mainly used in small industrial salt production industry.

In the same way, the standard for purifying sodium sulphate from desulfurization wastewater of thermal power plants can be drawn up. The recommended index value can be referred to table 3 corresponding index of sodium chloride.

5 Conclusion

The purified crystallization salt from desulfurization wastewater of thermal power plant can meet the requirements of industrial salt, and meet the requirements of TOC < 50 mg/kg and total ammonia < 10 mg/kg. As a raw salt can be used in two alkali, especially chlor-alkali industry. On the basis of industrial salt (GB/T 5462-2015) standard and two group standards "Coal chemical industry—By-product industrial sodium sulfate" (T/CCT 001-2019) and "Coal chemical industry—By-product industrial sodium chloride" (T/CCT 002-2019), the standards of purified crystallization sodium chloride from
desulfurization wastewater of thermal power plants were formulated combined with the raw salt index requirements of downstream potential salt industry. In order to further analyze the index of purified crystallization salt from wastewater and form the standard, it is necessary to carry out the applied test and pilot test.

References

1. Zhang, Q.B., Zhou, Q.F., Liang, J. (2019) Technology review and application research of zero discharge for desulfurization wastewater of coal-fired power plant. Environmental Science Survey, 38(4): 59-64.
2. Cao, F. (2018) Research progress of wastewater zero discharge technology of thermal power plant. Industrial Water & Wastewater, 49 (3): 6-11.
3. Li, Y, Zhang, Q, Wang, Q. (2016) Application of evaporative crystallization process in the zero discharge of desulfurization waste water in thermal power plant. Technology of Water Treatment, 42(11): 121-122.
4. Chao, L, Shao, X, Hu, C, et al. (2011) Research progress on the treatment technology of wastewater with high salinity. Journal of Anhui Agricultural Sciences, 39(31): 19387-19389.
5. Woolard., C R, Irvine, R L. (1995) Treatment of hypersaline wastewater in the sequencing batch reactor. Water Research, 29(4): 1160-1168.
6. Zheng, L., Wei, Y.C., Jiao, Y.Y., et al. (2019) Status and prospect of zero liquid discharge technologies for flue gas desulfurization wastewater in thermal power plant. Chemical Industry and Engineering, 36(1): 24-37.
7. Huang, X., Chen, Y.G., Su, N.N., et al. (2019) Research on fractional crystallization technologies for recovering salts from high salinity wastewater. Chemical Industry and Engineering, 36(1): 10-23.
8. Tang, Y.P. (2018) Current situation of hazardous waste in China. http://www.cement.com/news/content/9400233951842.html.
9. Wei, S.J. (2019) Waste disposal price rises again in 2019, becoming the "hot property". http://www.sohu.com/a/333352004_100301299.
10. Fan, Z.S. (2016) Key index control of zero emission from coal-chemical industry and selection for resource tenique about crystallization salt resource. Coal Processing & Comprehensive Utilization, 10: 5-8.
11. Wu, Y.F., Zhang, J.L., Li, N., et al. (2017) Study on the operation effect of recycling zero discharge technology of high salt wastewater from coal chemical industry. Coal Processing & Comprehensive Utilization, 6: 32-35.
12. Bian, X.T., Huang, Y.M., Guo, R.T., et al. (2019) Research progress on salt separation and resource utilization in high salinity wastewater. Inorganic Chemicals Industry, 51(8): 7-12.
13. Mohammad, A. W., Teow, Y. H., Ang, W. L., et al. (2015) Nanofiltration membranes review: recent advances and future prospects. Desalination, 356: 226-254.
14. Wu, Z.B. (2017) Application of membrane concentration+multi-effect evaporation in treatment of high concentration salt-containing wastewater. China Chlor-Alkali, 4: 36-38.
15. Zhou, H.F., Shi, W.B., Ding, Z.G., et al. (2017) Resource utilization of high concentration salt moisture in coal chemical industry. Coal Processing & Comprehensive Utilization, 12: 23-26.
16. Cui, C.C., L.R., Luo, L., et al. (2017) Advances and countermeasures of salt wastewater treatment in modern coal chemical industry. Clean Coal Technology, 22(6): 32-35.
17. Wang, G.h., Wang, J., Yang L.D., et al. (2019) Technical progress of evaporation/crystallization for saline wastewater in Chinese thermal power plants. Thermal Power Generation, 48(3): 1-6.
18. Li, B.Y., Liu, G.Q., Wang, Y., et al. (2014) The formation of high salt wastewater and advances in its treatment. Chemical Industry and Engineering Progress, 33(2):493-497.
19. Guo, Y., Wang, X.T. (2017) Mechanism, characterization and control of nanofiltration membrane contamination. Water & Wastewater Engineering, 53(9): 120-131.
20. Sai, S.J., Dang, P., Liu, H., et al. (2017) Study on the operation effect of salt separation process for zero discharge technology of high salt wastewater from coal chemical industry. Coal Processing & Comprehensive Utilization, 4: 52-55.
21. Liu, J. (2017) Thermal power plant waste water zero-emission technology proposal. Huadian Technology, 39(9): 58-62.
22. Wan, Y.G., Xu, F., Tian, X.F., et al. (2017) Guodian Hanchuan Power Generation Company Limited desulfurization waste water evaporative crystallization project process analysis. Huadian Technology, 39(10): 74-76.
23. Song, X B. (2019) According to the analysis of the current situation and development trend of China's raw salt industry in 2019, leading salt manufacturing enterprises may stand out. http://www.huaon.com/story/428802.
24. Wang, J.C., Zhu, W.J. (2012) Current situation of salt chemical industry development at home and abroad. Economic Vision, 6: 23-25.
25. Shao, B.R., Gao, Y.B., Ding, X.L. (2008) The general situation of domestic raw salt and the development direction of salt for caustic soda. Chlor-Alkali Industry, 44(4): 7-10.
26. Zhu, G.L., Ding, J. (2016) Analysis and trend prospect of China national salt industry market. Journal of Salt and Chemical Industry, 45(2): 1-9.
27. Chen, X.S. (2009) Research on using of mixed raw salts. Chlor-alkali Industry, 54(5): 9-11.
28. Hao, M.S., Zhou, L., Qiu, M.Y. (2009) Influence of TOC on ion-exchange membrane electrolyzers. Chlor-alkali Industry, 45(11): 18-20.
29. Wei, J., Yu, C.G., Wang, X.J., et al. (2016) Matters of operation of China-made ion-exchange membranes. Chlor-alkali Industry, 52(1): 21-23.

30. Dong, C.S., Wang, X.J., Zhang, Y.M. (2015) Interpretation of national standard GB/T 30297-2013. Chlor-Alkali Industry, 51(4): 9-13.

31. Dai, X.T., Zhu, K.S., Cheng, W.B. (2005) Several key problems in preventing the explosion accident in chlorine-alkali plant. In: China Occupational Safety and Health Association 2005 Annual Conference. Yichang City. pp. 249-251.

32. Yu, H. (2014) Soda ash: overcapacity need to be improved. Chemical Enterprise Management, 7: 51-51.

33. Lin, J.Q. (1988) Influence of raw salt quality on soda ash quality and countermeasures for reducing nitrate content of raw salt in soda production. Soda Ash Industry, 4: 32-37.