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Low-Cost Zero Sewage Discharge Strategy in Coal Chemical Industry

Xiaojuan Li*, Yingying Tian

Accounting Department of Hebei Finance University, Baoding 071000, China
LXJ4455@126.com

High salinity in the sewage discharged by coal chemistry companies has become the bottleneck to the development of this industry. In response to the zero discharge standard specified by the Ministry of Environmental Protection, this paper sheds new light on the development of low-cost zero discharge sewage treatment strategy for the coal chemistry industries based on coal chemistry brine TMC hot film coupling separation technology. A pretreatment test is conducted to determine the dosing conditions for any component. On this basis, taking a coal chemistry company as a study case, we conduct a pilot study on the evaporation and crystallization of industrial strong brine on the field. The findings show that PAC and FeSO4 can act as the best flocculant, while the optimal doses of Na2CO3, MgO, CaO, PAM and PAC are 70mg/L, 2500ug/L, 80mg/L, 2mg/L and 120mg/L, respectively; the purity of brine after evaporative crystallization reaches above 95%; the total treatment cost per ton brine is RMB 50.32 /t, so that the economic effect seems obvious. This study provides the clues for coal chemistry companies to reach the zero discharge of sewage and promote the steady development of the coal chemical industry.

1. Introduction

In order to fill the gaps of the energy structures such as petroleum and natural gas in China (Ericsson and Hallmans, 1996), the coal chemical industry is confronting with the status in quo of transition towards modern business model. But unfortunately, the modern coal chemical industry should be subject to the zero-discharge specification issued by the Ministry of Environmental Protection, as well as the environmental constraints for high pollution and water consumption in current industry (Jia et al., 2016). Against this background, how to achieve zero discharge, minimize environmental risks and maximize economic benefits has long caused concern in current coal chemical industries.

Coking, direct liquefaction and high-temperature pressurization vaporization and other processes produce various types of coal chemical sewage. Among them, the concentrated brine produced by circulating sewage and chemical regeneration water in coal chemical industry seems more challenging in sewage treatment (Dresscher, 1965). As a bottleneck to the zero-discharge in coal chemical industry, the concentrated brine contains a flood of toxic heavy metal ions such as cadmium, lead and copper, so that it is often treated most difficultly and at a high cost. But if untreated, these effluents discharged directly will have negative effect on neighboring environment (Barbosa et al., 2009). Thermal evaporation, natural evaporation and membrane separation technologies are commonly used for concentrated brine treatment (Yu et al., 2010). To complete strong brine concentration and crystallization, it is usually required to integrate the pretreatment with other technologies to form a whole set of processes. The purpose of the pretreatment is to primarily remove some heavy metals from the concentrated brine, reduce its alkalinity, hardness, etc., so as to relieve the burden of subsequent membrane treatment and the operation cost (Feng et al., 2009). By far, China has developed a relatively complete process of concentrated brine treatment, for example, the “Zero Discharge” projects of China Coal Tuck Fertilizer and the Guojiawan Power Plant, Shenhua Shendong Power, have basically achieved the zero sewage discharge with crystallized salt stacked in the factory area (Gai et al., 2008). The concentrated brine treatment technology adopted by foreign countries seems basically similar to that by China, but specific integrated processes may be more advanced. The U.S. C.A. Quist-Jensenet al., Heijman et al. and Polish Marian Turek et al. respectively applied different integrated processes to evaporate and

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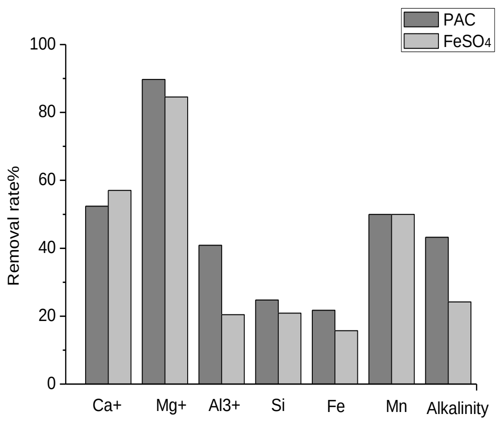
crystallize concentrated brine, and heaped up the finally formed crystalline carnallite (Keleti et al., 1982). From the studies at home and abroad, it is found that the zero sewage discharge in the plant area can be achieved by the integration of the membrane concentration and evaporation crystallization processes (Oberholster et al., 2008), but the formed crystalline salt can still cause secondary pollution if not properly treated.
Based on the above analysis, this paper expounds the low-cost sewage zero-discharge strategy for coal chemical industries. The comparative analysis method helps determine the PAC and $FeSO_4$ as the best flocculants. The optimal doses of Na_2CO_3, MgO, CaO, PAM and PAC are determined by the passivation-complexation process and the heavy metal ion removal test. On the basis of this, taking a coal chemical industry as an example, this paper introduces the field test and the process of concentrated brine thermal film coupling separation. The results from this separation test show that the purity of the evaporation crystallization brine reaches more than 95%, so that the resource recycling can be realized. The economic cost analysis suggests that the total cost per ton of concentrated brine is RMB 50.32 /t, and the economic effect is obvious.

2. Test on removal of heavy metal ions in concentrated brine of coal chemical industry

2.1 Chemical precipitation and coagulation mechanism and selection of flocculants

In order to initially remove some of the anions and heavy metals (such as HCO_3^-, Cu^{2+}, etc.) in the concentrated brine of coal chemical industry, a chemical precipitation agent CaO may be introduced to precipitate corresponding oxides and hydroxides. The purpose of coagulation is to destabilize the suspended particles and colloids in the concentrated brine by adding the flocculant in order to form larger particle clusters, and then increase the collision of the particle clusters by adding chemical agents to form larger floc destabilization and precipitation (Yan et al., 2012).
In addition to the flocculation effect, we should also consider the cost, solubility and reduction of secondary pollution when selecting the flocculants. Inorganic polymers and salts are two types of commonly used flocculants (Liao et al., 2012). In this paper, based on the types and indicators of flocculants, the inorganic polymer flocculant PAC and the inorganic salt flocculant $FeSO_4$ are chosen for comparative test under the specific conditions, as shown in Fig. 1. In relation to $FeSO_4$, the removal rate of Si, alkalinity and Al^{3+}, etc., are highly removed by PAC, reaching 24.77%, 43.25% and 40.90%, respectively. At last, the PAC is chosen as the test flocculant.



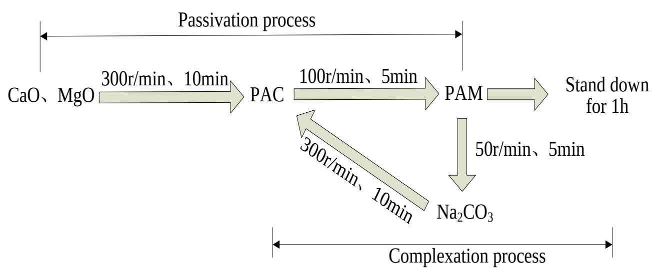


Figure1: Effect of PAC and $FeSO_4$ on ion Removal

Figure 2: Concentrated brine passivation-complexation process

2.2 Test for concentrated brine passivation-complexation process

The specific process of the concentrated brine passivation-complexation treatment is shown in Fig. 2. The purpose of this test is to pretreat the concentrated brine (Zhu et al., 2018). It includes passivation and complexation processes. The comparative test, as describes above, has determined the PAC as the best flocculant. The optimal dosage in each process is determined by the test below.

2.2.1. Test for passivation process

The main purpose of the passivation process is to remove heavy metal ions, alkalinity and hardness from the concentrated brine, while the precipitation-based removal effect is subjected to the doses of chemical agents

(Yang et al., 2016). To determine the optimal doses of CaO, MgO, PAC and PAM, the agents with different gradients of concentrations are tested respectively. The results show that the removal rate presents higher when the doses of CaO, MgO, PAC and PAM are 80mg/L, 2500ug/L, 120mg/L and 2mg/L, respectively. The specific results are shown in Table 1.

Table 1: Ion removal effect when CaO, MgO, PAC and PAM are optimally administered

——	CaO(80 mg/L)	MgO(2500ug/L)	PAC (120mg/L)	PAM(2mg/L)
Ca^{2+}（mg/L）	3.948	3.523	4.156	3.765
Mg^{2+}（mg/L）	0.376	1.36	0.678	0.666
Mn^{2+}（mg/L）	0.024	0.024	0.02	0.021
Al^{2+}（mg/L）	0.08	0.043	0.062	0.061
Total Si（mg/L）	55.84	55.29	52.76	52.69
Total Fe（mg/L）	4.732	4.529	4.314	4.314
HC O_3/ CO_3^{2-}（mg/L）	167.12	148.38	133.02	145.63

2.2.2 Test for complexation process

The complexation process further removes residual hardness and heavy metal ions on the basis of the passivation process while removing part of the COD and active silicon (Meng et al., 2016). As a result, based on the optimal doses of PAC and PAM determined by the passivation process, we analyze the overall removal rate of each ion when the Na_2CO_3 concentration gradient changes from 40 to 80 mg/L. Eventually, the optimal dose of Na_2CO_3 is determined as 70 mg/L, at this time, the total removal rate is 413.98%.

2.3 Test for removal of concentrated brine ion

2.3.1 Determine target heavy metals and flocculants

After the passivation-complexation process, most of the heavy metals such as Al^{2+}, Mg^{2+} can be removed, but some of them still have a poor removal efficiency, as shown in Table 2. In order to reduce the operation cost and relieve the burden of subsequent treatment, this paper removes heavy metals by the conventional chemical methods (Barbosa et al., 2009). As shown in Fig. 3, four flocculants (PAC, $FeCl_3$, $FeSO_4$, Al_2（SO_4）$_3$) are chosen hereof. According to the efficiency comparison, it is obvious that the total removal rate of heavy metals increases as the dose of flocculant goes up, but the removal rate of $FeSO_4$ is the highest among the four flocculants. When $FeSO_4$ is 25 mg/L, the total removal rate reaches 112.82%. Although the removal rate of Cu^{2+} is higher than that of $FeSO_4$, $FeSO_4$ has a better removal effect on other heavy metals. Therefore, after comprehensive comparison, $FeSO_4$ is finally chosen as flocculant.

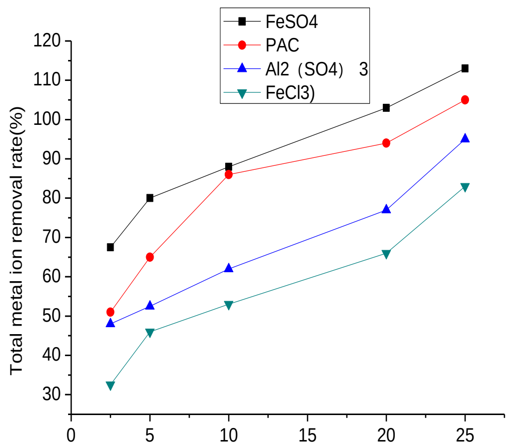


Figure 3: Comparison of four flocculants

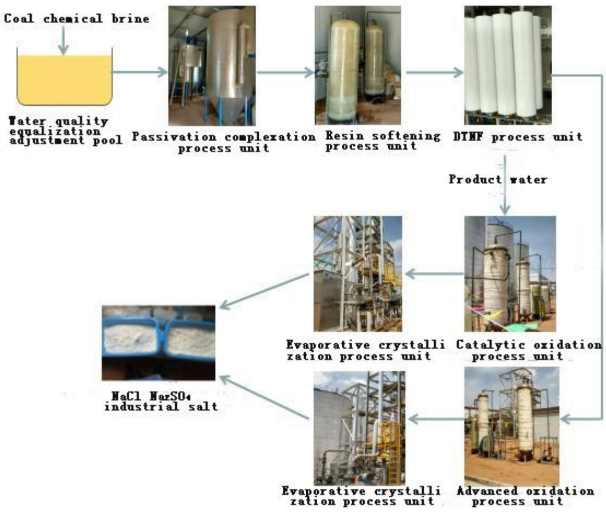


Figure 4: Field test equipment and process

Table 2: Removal of heavy metal ions by passivation-complexation process

Heavy metal ion	Total As	Cu^{2+}	Total Cr	Ni^{2+}	Pb^{2+}	Sr^{2+}
Raw water	0.074	0.127	0.044	0.117	0.029	0.028
After pretreatment	0.059	0.093	0.033	0.083	0.022	0.021
Removal rate（%）	20.27	26.77	25	29.06	24.14	25

2.3.2 Dose of enhanced $FeSO_4$

The removal rate of Ni^{2+}, total As and Cu^{2+} will increase as the dose of $FeSO_4$ lifts up. However, in order to avoid secondary pollution and save the cost, its dosage can not increase indefinitely. Therefore, its optimal dosage should be determined by the test. The results are shown in Table 3. It is known that the removal effect is optimal when the dosage of F $FeSO_4$ is 90 mg/L.

Table 3: Strengthening the effect of $FeSO_4$ on Cu^{2+}, total As, and Ni^{2+}

$FeSO_4$'s increase in volume	Cu^{2+}（mg/L）	Total As（mg/L）	Ni^{2+}（mg/L）
50	0.282	0.156	0.258
70	0.261	0.134	0.229
90	0.228	0.119	0.211
120	0.224	0.114	0.211
150	0.219	0.110	0.204

3. Evaporation crystallization effect of industrial salt

3.1 System debugging and operation

As shown in Fig. 4, the field test equipment and process are given for the thermal film separation of concentrated brine in coal industrial industry. Based on the above-mentioned the best dosage determined by the passivation-complexation process and heavy metal ion removal tests as above. The pre-treatment unit and the deep treatment system unit are debugged and operated to make sure the DTNF unit and HCOS units work normally. Due to limited space, this paper focuses on the commissioning and operation results of the evaporative crystallization unit.

3.2 Effect of evaporative crystallization separation for industrial salt

First, the mechanical falling film evaporator is started, and water in the HCOS unit is input for atmospheric pressure evaporation. The concentrated materials are fed into the forced circulation crystallizer for continuous heating and concentration to obtain the Na_2SO_4 crystal. When the NO_3^- of the discharged mother liquor reaches a certain concentration, $NaNO_3$ can be prepared in a cooling crystallizer. The purity and mass changes of NaCl and Na_2SO_4 during the commissioning process are shown in Fig. 5, 6. It is obvious that the purity and quality of the salt produced by the system tend to be stable after 5 or 6 times of debugging.

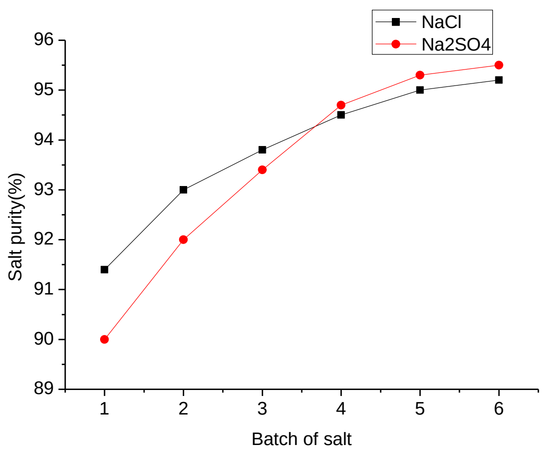


Figure 5: Purity change of NaCl and Na2SO4 during commissioning

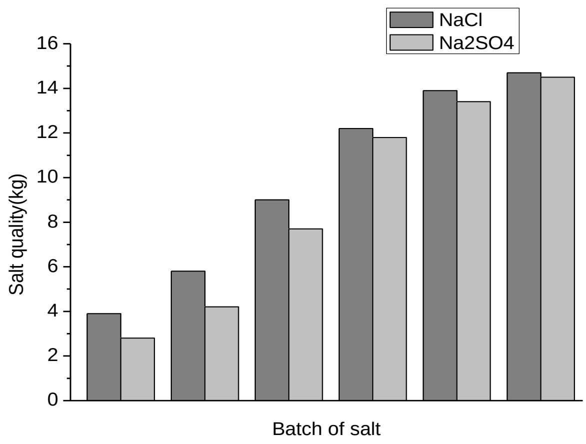


Figure 6: Mass change of NaCl and Na2SO4 during commissioning

As shown in Fig. 7, the live images of the evaporation crystallization salts and abraum salt in plant area are compared. It can be seen that the visual effect and purity of the evaporation crystallization salt are higher. The analysis results after the submission also show that the evaporation crystallization salt can reach the relevant provisions of physicochemical indicators for the industrial salt. Hence, the system can achieve the separation of industrial salt from concentrated brine and realize resource recycling.

(a) Evaporation crystallization *(b)Plant crystal salt*

Figure 7: Comparison of evaporation crystallization salt and solid crystal salt in the plant area

3.3 Economic cost analysis

In this paper, the economic costs of four process units, i.e. strong brine separation crystallization pretreatment unit, disc-type nanofiltration (DTNF) unit, multiphase co-crystal catalytic oxidation (HCOS) unit and evaporative crystallization unit, for concentrated brine separation in coal chemical industry are separately settled and consolidated. The total cost of treatment per ton of concentrated brine is RMB 50.32 /t. By consulting the relevant references, it can be concluded that the total treatment cost per ton of concentrated brine using natural evaporation (evaporation pond) and tetra-effect evaporation crystallization reaches RMB 204.35 /t and RMB234.34 /t, respectively. It is obvious that the evaporative crystallization separation of concentrated brine has low-cost and obvious economy.

4. Conclusion

For the purpose of achieving low-cost sewage zero-discharge in coal chemistry industry, this paper conducts the concentrated brine pretreatment and separation tests in a coal chemistry company. Here are conclusions:
(1) Tests are compared to determine that the best flocculants for the test are PAC and $FeSO_4$.
(2) Two pretreatment tests, i.e. passivation-complexation process and heavy metal ion removal, determine the optimal doses of Na_2CO_3, MgO, CaO, PAM and PAC.
(3) Based on the pre-treatment test results, the hot film coupling separation technology is introduced to carry out the field test on industrial brine evaporation, crystallization and separation in coal chemical industry. The results show that the purity of the industrial salt after system evaporation, crystallization and separation reaches more than 95%. The economic cost analysis shows that concentrated brine evaporation, crystallization and separation in coal chemical industry has the lowest cost and more obvious economy than other methods.

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