TECHNOLOGY FOR CONTROLLING SODIUM HYPOCHLORITE IN THE TREATMENT OF REMOVING AMMONIUM FROM BRINE

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Abstract: This paper systematically studies the technology for controlling the addition dosage of sodium hypochlorite in the process of removing ammonium from brine, and it also summarizes concrete controlling method, which is applicable and valuable for popularization.

Key words: Removing ammonium from brine; Sodium hypochlorite; dosage; Controlling technology

INTRUCTION

Shalongda Co., Ltd., Salt Mine of Hubei Province is a self-financing by enterprises and self-development of the salt mine. The contents of inorganic ammonium have always been high due to the geological structure. In order to protect the production safety, the content of inorganic ammonium should be reduced to 1 mg/L before entering the electrolysis process. Of course, the residual sodium hypochlorite content cannot higher than 10 mg/L. Therefore, it is very critical to control the addition of sodium hypochlorite.

TECHNOLOGY OF REMOVING AMMONIUM FROM BRINE

The technology of removing ammonium from brine is to drop sodium hypochlorite which is reacted with inorganic ammonium and to get removing ammonium objective.

The reaction principle of removing ammonium:

$NH_3+NaClO \rightarrow NH_2Cl$ (Compressed air to remove)

$NH_3+NaClO \rightarrow NH_2Cl_2$ (Compressed air to remove)

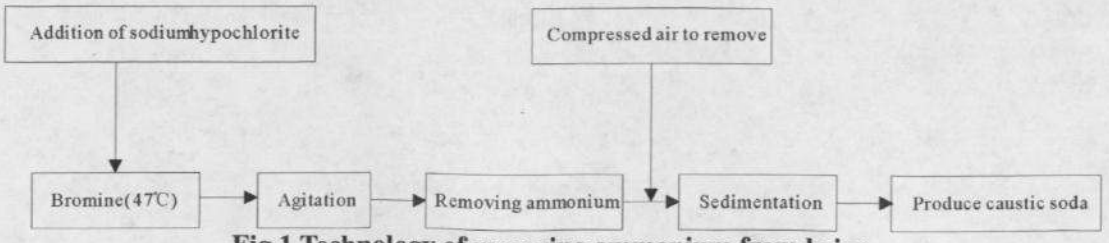

Fig.1 Technology of removing ammonium from brine

The requirement of the inorganic ammonium content in the brine should be less 1 mg/L during the caustic soda production. The free chlorine in the brine should be less 10 mg/L. Therefore, we must add optimum sodium hypochlorite in the treatment of the brine. Extra brine causes excessive free chlorine, free chlorine leads corrosion of iron equipments. The iron ions enter into the electrolytic cell, causing membrane perforate. The hydrogen content is over the standards in the chlorine header, which leads the unsafe production. The total ammonia should be higher if less sodium hypochlorite addition. nitrogen trichloride will be generated when ammonia meets chlorine in the electrolytic cell. And the nitrogen trichloride will explore when chlorine aggregation. In the production process, there are some aspects resulting in inorganic ammonium and free chlorine abnormal production. The reason is that as following: (1) hypochlorite has impurities plug glass cocket, stops sodium hypochlorite fluid; (2) it is not easy to control the glass cocket, and excessive addition of sodium hypochlorite. (3) it takes more than 30 min to analysis the inorganic ammonium and free chlorine in the salt brine. The analysis lagged behind, resulted the unqualified salt brine; (4) brine and sodium hypochlorite did not find a reasonable ratio parameters.

MEASURES TO SOLVE THESE PROBLEMS ABOVE

(1) A-type problem solving: the raw materials of sodium hypochlorite have impurities. These impurities will be agglomerated when they fluid the glass cocket and jam it. The jam will stop the sodium hypochlorite, and induce the higher inorganic ammonia. We installed a buffer filter screen at the exiting of sodium hypochlorite tank. This screen will filter the impurities in the sodium hypochlorite.

(2) B-type problem-solving: The brine and sodium hypochlorite should be added in certain of ratio. Glass cocket does not the gauging function. The operators can only be based on a sense, thus leading the free chlorine fluctuation. For such phenomena, we bought a JXMT-200/63 type metering pump. This pump has the fine tuning function, the minimum unit is 0.01 L/h. The installation of pumps can control the fluid and solve the difficulties of sodium hypochlorite addition volume.

(3) K-D method solves the problem of time lag.

ORIGIN OF ANALYSIS METHOD

Process standards stipulate chemical analyzers analysis the finished brine tank. The times of analysis is as high as 7. It takes 20 min to analysis one sample. This method is too time-consuming and reaction lags. This operation also results some of the unqualified brine entering the system. At the same time, some metal ions, like magnesium and ferric ion, also interfere the analyzing results.

The reasons of disturbance are as follows: In the past, the determination of inorganic ammonia brine adopted Sodium Reagent Photoelectric Colorimetry. The sodium reagent contains sodium hydroxide. The liquid presents suspension after adding sodium reagent.

$Mg^{2+}+NaOH=Mg(OH)_2\downarrow$ (white flocculent precipitate)

$Fe^{3+}+NaOH=Fe(OH)_3\downarrow$ (red brown flocculent precipitate)

Sodium Reagent Photoelectric Colorimetry uses the Lambert-Beer Law. This law is just suitable for uniform colorful solution. So it has defects to be used in analyzing the inorganic ammonia brine. Since the analysis is time-consuming, lagging operation, big error. All of these pushed us to searching new technologies. We began to use test paper to determine the inorganic ammonia brine. We found that inorganic ammonia has color effects to the sodium reagent and chloride high-mercury reagent.

We found that the content of inorganic ammonia in the brine was very low after many experiments. And the color effects were not obvious. We modified the previous analysis methods. The distillation was used to analyze inorganic bromide brine. Although this analysis eliminated the metal ions interference in the brine, the analysis data was accurate. It needed as long as 30 min to finish the analysis. At the same time, the free chloride was higher in the brine. The higher free level of free chlorine resulted excessive hydrogen content in the chlorine gas header. It influenced the safe production of the electro-chemical plant. So we re-examined the use of test paper to test the inorganic ammonia brine. We found the free chloride had some features as following after searching the references and many experiments.

$Cl_2+2KI=2KCl+I_2$

Iodine reacts with the starch in blue color. Then we used dissolved starch and potassium iodine to get comparative consistency potassium iodine-starch mixture reagent. The test paper immersed potassium iodine-starch mixture tested brine. The color of the test paper deepened with the increasing of the concentration of free chloride. This site sodium hypochlorite control was opened by using this method. The free chlorine content can be controlled when the color of the test paper is lighter than the standard coloration of the free chlorine.

ANALYSIS OF SMALL-SCALE TEST

Step One: according to the related standards of chlorine and caustic industry, the content of free chl-
orine in the brine should be less 10 mg/L. 15 groups experiments have been done to compare the free chlorine brine and distillation method. Experimental data are as follows.

Table 1 Analysis data for free chlorine brine and distillation method

Number	Free chlorine content (mg/L)	Inorganic ammonia content (mg/L)
1	5.62	0.38
2	4.07	0.51
3	3.46	0.66
4	9.82	0.20
5	9.04	0.16
6	7.56	0.46
7	7.14	0.43
8	7.33	0.45
9	6.25	0.49
10	3.57	0.65
11	2.01	0.72
12	1.08	0.82
13	8.65	0.33
14	8.73	0.36
15	3.09	0.68

It was found that the content of free chlorine is lower than 10 mg/L, the content of inorganic ammonia brine is lower than 1 mg/L. It indicates that the controls of free chlorine are equally qualified with control the inorganic ammonia brine.

The second step: we used potassium iodide starch test paper changed dark properties with the increasing of the free chlorine concentration. We prepared the

standard salt solution, 5 mg/L, 10 mg/L, 15 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, 50 mg/L, 60 mg/L, 80 mg/L, 100 mg/L. The coloration conditions were recoded with the photo. This is because iodine is very easy to sublimate, the color will be disappeared after 2 min. The operators just need take out the color card to compare the color, they can control the free chlorine and the inorganic ammonia brine content. This method omitted the tedious steps such as sealing in the free chlorine analysis and distill and coloration in the inorganic ammonia analysis. The analyzing time reduced 5 seconds from 30 min. This method is convenient and greatly reduced the amount of workers labor operations, and ensured on time observation and control.

APPLIATIONS IN THE PRODUCTION PROCESS

After the small-scale test work, we applied this technology to the production process. Firstly, the salt technology branch organized technical training. The operators should know how to use the potassium iodide starch paper and color card. The passing rates of free chlorine brine increased from 40.3% to 100% in the operating process. The passing rate of the inorganic ammonia brine reached 100%. We investigated several results randomly, as shown in Table 2.

Table 2 The results of the free chlorine and inorganic ammonia analysis

Number	Colorimetry Results	Free chlorine content (mg/L)	Inorganic ammonia content (mg/L)
1	<10 mg/L	7.09	0.49
2	<5 mg/L	3.05	0.65
3	<5 mg/L	2.51	0.77
4	<10 mg/L	7.66	0.43
5	<5 mg/L	3.22	0.61
6	<10 mg/L	8.69	0.23
7	<10 mg/L	7.34	0.44
8	<10 mg/L	7.25	0.42
9	<5 mg/L	1.69	0.85
10	<10 mg/L	9.52	0.17
11	<10 mg/L	9.44	0.18
12	<10 mg/L	8.99	0.30
13	<10 mg/L	8.65	0.29
14	<5 mg/L	3.69	0.64
15	<5 mg/L	2.13	0.71

We found potassium iodide-starch test paper and color card used properly through a period of production practice. We achieved good operation results combining the quantitative analysis originally. The inorganic ammonia brine content is lower 1 mg/L when the free chlorine content controlled within 10 mg/L. The inorganic ammonia content meets the industry requirement of less than l mg/L.

Shalongda salt mine adopts the butt joint well technology. Brine is heated by terrestrial heat resources, and the temperature of brine is 47 ℃ constantly at the exit of brine. The concentration of the sodium hypochlorite and inorganic ammonia can be acquired by analyzing. The flow rate

of the original brine can be shown on the electromagnetic flowmeter. These parameters above are proportional Parameter value=(9.83×75.6)÷(79.5×0.072)= 129.83

For example, when the brine flow is 80 m3/h, the original inorganic ammonia brine is 10.2 mg/L, sodium hypochlorite concentration is 90g/L, so the flow rate of relationship, therefore, we can find a parameter values (see Table 3, free chlorine is 5mg/L, inorganic ammonium is 0.4mg/L). the sodium hypochlorite is:

$(10.2\times80) \div(90\times129.83) = 0.0798\ m^{3}/h$

The brine quality can be very controlled by observing the K-D method. We selected 10 samples at the scene to verify the value, as shown in table 4.

Table 3 A group of parameter values in the experiment

Original inorganic brine content	Original flow rate per volume	Sodium hypochlorite content	Sodium hypochlorite flow rate per volume
9.83 mg/L	75.6 m^3/h	79.5 g/L	0.072 m^3/h

Table 4 Verifying parameter values for 10 samples

Sample	Flow rate of brine m3/h	Flow rate of sodium hypochlorite m3/h	Original brine concentration mg/L	Sodium hypochlorite content mg/L	Inorganic ammonia after treatment mg/L	Free chlorine content after treatment mg/L
1	73.5	0.057	10.1	100.5	0.4	4.2
2	74.2	0.07	9.5	85.2	0.38	4.9
3	75.0	0.07	8.4	90.7	0.30	5.6
4	72.2	0.04	9.7	143.2	0.25	5.8
5	50.6	0.07	9.6	125.6	0.23	6.1
6	51.6	0.67	9.4	129.8	0.20	6.3
7	75.2	0.55	9.3	111.4	0.39	4.7
8	77.4	0.05	9.0	120.0	0.30	4.0
9	62.4	0.65	9.7	108.5	0.25	5.4
10	68.5	0.06	9.6	103.6	0.26	5.8

As shown in Table 4, the brine inorganic ammonia content controlled at less than 1 mg/L, brine free chlorine less than 10 mg/L through the parameter values control.

CONCLUSIONS

Above control technology applied to production in the future, resulting in the following:

The economic benefits can be achieved by using this control technology in the production process. (1) the quality of brine was improved and the corrosion of the metal cationic coating layer by sodium hypochlorite. The life of coating was extended. The cost can be saved of 300,000 ruan per year. (2) the cost of sodium hypochlorite can save 42,000 yuan

annually; (3) the higher amount of hydrogen in the brine and nitrogen trichloride problems were solved. The electro-chemical plant security production level was improved. (4) the quality of brine was improved, the corrosion of the sodium hypochlorite to the equipments was reduced, the equipments life in the salt mine and electro-chemical plant

were prolonged.

The brine inorganic ammonia and free chlorine had a pass rate of 100% after the technology application in production within three months of practice. Their qualities can meet ion membrane caustic soda production requirements of brine. The control technology lies the industry leading level among the salt industry, it has great value to be used in chlorine and alkaline industry.