Analysis of Factors Influencing Flocculating and Sedimentation in Brine Purification

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Abstract: Through the experimental study on the clarification effect of the brine purification of Kunming Salt Mine, both internal and external factors influencing the clarification effect of the brine purification are analyzed theoretically and practicality and summarized, providing theoretical and practical evidences for resolving similar problems in the future.

Keywords: brine purification, flocculation, settlement, factors

Brine purification is one of the key processes in the vacuum salt manufacturing technology. Its aim and significance are to remove or reduce impurities in brine to increase the productive capacity of salt producing equipment, ensure the quality of products and provide high-quality and qualified raw materials for chemical production and comprehensive utilization.

Kunming Salt Mine introduced the advanced production technology and key equipment for its 200,000-ton salt production apparatus from the Sulzer Company of Switzerland which makes Kunming Salt Mine one of the modernized salt production enterprises. The feed brine is a kind of mirabilite type rock salt brine. In the technology of vacuum evaporation for producing salt, it is required that brine must have extremely high quality. The content of Ca^{2+}+Mg^{2+} in the refined brine should be below 10ppm. The poor effect of brine purification will exert direct influence on the normal production and lead to hard scaling on pipe wall of the heating chamber, or even blocking the pipe. Therefore, a series of harms will be caused, such as the reduction of heat transfer efficiency, the increase of tank washing frequency and the cut-down of the life of the equipment. These problems will affect the quality and output of products, thus exerting serious influence on the economic efficiency of the enterprise.

Since Kunming Salt Mine was put into operation after commissioning in June 1993, the problem of poor effect of clarification of brine occurred several times. Particularly at the later half of 1998, the problem became most severe, lasting for about half a year. The light transmittance of the brine after purification is extremely low in the tank. Tests were made by observing total 20 steps through the reaction tank containing brine. However, almost no steps could be seen in the worst case and about 10 steps could be seen in the best case. In the case with the normal purification effect, the bottom can be seen clearly, which is an extremely great contrast. At that time, it was fortunate that the filtering devices for brine clarification had been completed and could be used so that production could be maintained. The company attached great importance to this situation and organized a team to tackle the issue of brine purification and clarification effect. Through efforts, factors possibly influencing the effect of clarification in brine purification have been basically found. Now I hereby sum up as follows to have a discussion

with people in this field and provide some theoretical evidences for reference for the similar situation in the future.

1. BASIC SITUATION OF BRINE PURIFICATION IN KUNMING SALT MINE

1.1 Forms of impurities in brine

The brine of Kunming Salt Mine belongs to Glauber's salt brine, mainly containing Ca^{2+}, Mg^{2+}, AL, P, organic matters, a small quantity of clay, and etc.

1.2 Method of brine purification

Lime-soda ash one-step method is adopted.

1.3 Basic principle of brine purification reaction

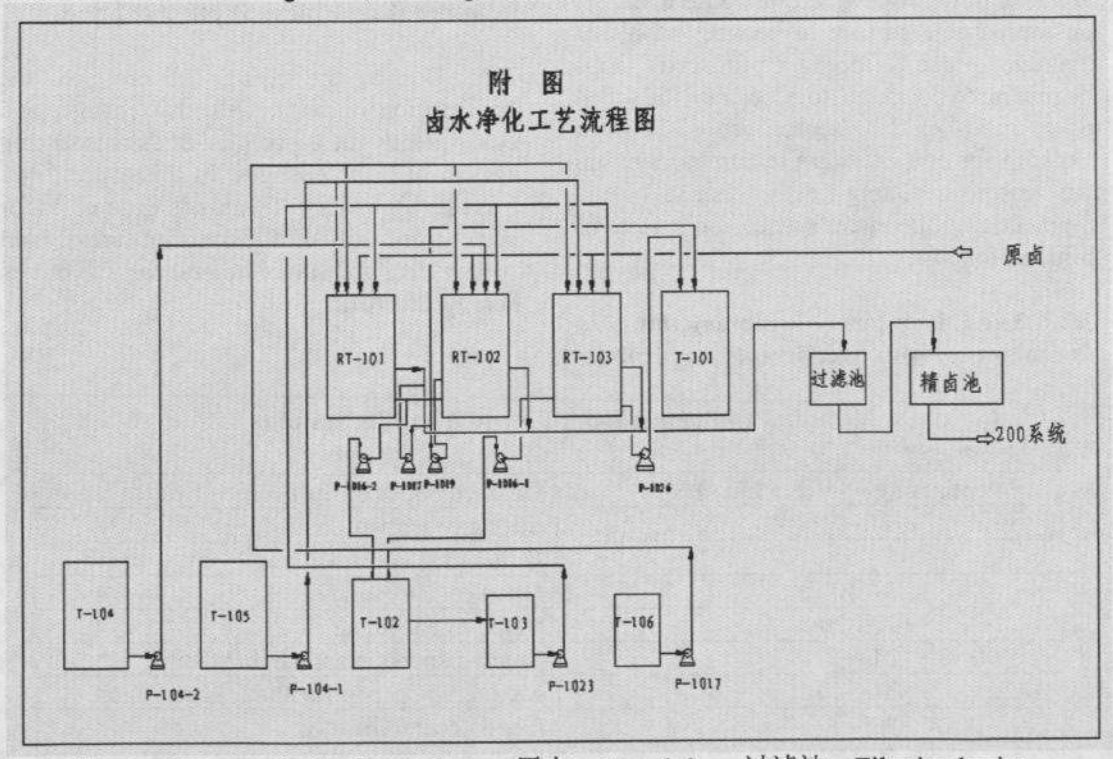
$$Mg^{2+}+CaO+H_2O \rightarrow Mg(OH)_2\downarrow+Ca^{2+}$$
$$Ca^{2+}+Na_2CO_3 \rightarrow CaCO_3\downarrow+2Na^{+}$$

1.4 Selection and use of flocculating agent

The type of flocculating agent has great influence on the effect of flocculating sedimentation and it is usually a decisive factor in most cases. In general, the range of the applicable pH values of flocculant of non-ionic polyacrylamide (PAM) category is between 1 and 6. The range of the applicable pH values of anion PAM is between 6 and 10 and that of cationic PAM is between 0 and 10. The cationic PAM plays an important role in the treatment of waste water, and is suitable for some suspension systems which are extremely difficult to be treated. In the selection of the flocculant type, not only the factors of sedimentation effect should be considered, but also the filtration performance of sediment should be taken into consideration. Only when requirements in these two aspects are satisfied, the demand of production can be met.

Through small-scale experiment in the laboratory and large-scale pilot production for many times, the use of partially hydrolyzed polyacrylamide (PH-PAM) of anion type as a sedimentation aid has been decided. The content of solid substances is 2.5%, with average molecular weight of about 10,000,000 and hydrolysis degree is 30%.

2. Schematic diagram of brine purification process (see the diagram attached below)



Chinese characters in the figure above: 原卤— Raw brine; 过滤池—Filtering basin; 精卤池— Refined brine basin; 2000 系统— System 2000

3. ANALYSIS OF THE FACTORS INFLUENCING CLARIFICATION EFFECT OF BRINE PURIFICATION

3.1 The results of the changes of chemical constitution and electrical property on surface in the suspension system of brine

The parameter used for describing electrical property on surface is δ-potential. The value of δ-potential has a direct relation with the stability of the whole suspension system of brine (see attached table). It can be seen from Table 1 below that only when the δ-potential of particles is between ±20mV-30mV, it is easy to coagulate. The partially hydrolyzed polyacrylamide (PH-PAM) anion type is used as a sedimentation aid in Kunming Salt Mine. However, PH-PAM generally has flocculation effect only when the δ-potential of the suspension system is higher than 0. The end of the polymer chain is fixed on the surface of particles and the polymer segment that extends into the solution absorbs the blank part of adjacent particles. The polymer chain is stretched by the two particles linked by the polymer and forms a "bridge". The PH-PAM absorbs onto the part of positive charges and amido forming hydrogen bond with hydroxyl on the particle surface or between atoms of hydrogen and flocculi produced, thus beginning to coagulate to accelerate the speed of solid-liquid separation. Through experiments and literature research, I sum up the reasons resulting in the change of the δ-potential in the entire suspension system of brine as follows:

3.2 The long-term accumulation of flocculants with different hydrolysis degrees will result in the change of δ-potential in the suspension system.

Functional groups of PH-PAM have negative charge. During the process of modification, the hydrolysis degree has been excessively increased (about 50%~70% according to theoretical calculation). However, the process of actual modification is not complete, which leads to the excessive increase of NaOH and the increase of the steric hindrance of activated functional groups. Since sodium hydroxide (NaOH) itself is a kind of inorganic anion coagulant, thus it makes the δ-potential of the suspension system of brine move towards negative direction.

3.2.1 The lime-soda ash method is used for the brine purification. The content of lime and soda ash is not high, thus it is extremely possible to bring in other electrolytes and influence the electrical property on the surface of suspended particles and the thickness and the composition of the double electrical layer so as to influence the sorption process of the flocculant on the particle surface when they penetrate the double layer. Furthermore, lime and soda ash are also negative ion coagulants in some senses. If adding too much, they will accumulate day by day, thus making the δ-potential of the entire suspension system have a change so as to influence the clarification effect of brine.

3.2.2 Due to the change of ore bed, the composition of brine will also change, and consequently the δ-potential of the suspension system of brine changes. In this aspect, it is necessary to make full analysis of samples for brine from different extracting areas, and collect data for future reference. Table 1 is hereby attached:

Table 1 Colloform Ion δ-Potential and Its Stability

δ-Potential of Colloform Ion (mV)	Characteristics of Suspension System
+30~0	Strong coacervation
-1~-5	Quite good coacervation
-5~-10	Good coacervation
-11~-20	Begin to coagulate
-21~-30	Slight dispersion and slight stability
-31~-40	Medium dispersion without aggregation
-40~-50	Good decentralization
-50~-70	Quite good decentralization
Below -80	Strongest decentralization

3.3 Influence of Temperature of Brine Suspension System on Flocculant Effect

Chemical reaction will occur by adding CaO and Na_2CO_3 into raw brine, and the precipitate of $CaCO_3$, $Mg(OH)_2$ is produced. There is also a trace of precipitate of $MgCO_3$. However, $MgCO_3$ is easy to deposit on the surface of $CaCO_3$ to form alum grain-like precipitate [$CaMg_3(CO_3)_4$]. When the system temperature is lower than 15℃, with the rise of temperature, the viscosity will gradually decrease and the sedimentation rate of flocculation will gradually increase when flocculating. However, when the temperature is excessively high, the hydration of alum grain will increase, thus influencing the absorption of PH-PAM on the particle surface so as to affect the effect of settlement of purification. When temperature is lower, the chance of collision among suspended particles will decrease, and the bridging chance between PH-PAM and particles decreases. Therefore, excessive high or low temperature will influence the flocculation effect in brine purification. Experiments prove that the temperature at 15~30℃ is beneficial to the settlement of flocculation.

3.4 Influence of Graininess and Specific Gravity of Solid Substances in Brine Suspension System on Flocculation Effect

Excessively large or small graininess of solid content is not beneficial to flocculation. Only moderate graininess of solid phase will be beneficial to the settlement of flocculation. Too small graininess is not favorable for flocculant to catch suspended particles, but too large graininess is not beneficial to the bonding and bridging functions of the long chain of flocculant. Therefore, it is important to control the time of reaction of brine, and tests should be further carried out to select better time for adding flocculant. Particularly, the quantitative test of graininess distribution for solid content is very important for the analysis of factors influencing the flocculation effect in brine purification.

3.5 Influence of Solid Phase Concentration of Brine Suspension on Flocculation Effect

The content of suspending particles in the suspension system (solid phase concentration) will affect the effect of flocculation. Excessively large solid content (>30%) will hinder the free settlement and excessively small solid content (<1%) will reduce the chance of collision of particles and influence the formation of flocculi. Therefore, in the process of brine purification, the times of slurry pumping and the quantity of slurry cleaning during shutdown should be carefully observed in order to find out empirical data to guide production.

3.6 Influence of Molecular Weight of Flocculant on Effect of Flocculation

According to the principle of flocculant bridging, PH-PAM must have enough flexible molecular chain for bridging among particles. Its flocculating effect should increase with the increase of molecular weight. However, it is not the case. Excessively high molecular weight ($M>1\times10^7$) and too high speed of flocculi coacervation will increase the velocity of sedimentation and result that fine particles suspend at the upper part of the supernatant liquor. A layer of flocculating film formed on the surface of these fine residual particles, thus being in a stable state due to their excessively small particles and existing in the suspension system of brine so as to lead to poor light transmittance. Therefore, it is very important to master the particle range of suspended grains of brine for the correct selection of the molecular weight of flocculant.

3.7 Influence of Agitating Time and Intensity on of Flocculation Effect

PH-PAM mainly depends on the absorption between amido and suspended particle, in which the linkage energy is only dozens of kcal/mol with weak force. Therefore, the strength of mechanical agitation should be moderate. Otherwise, the flocculi will be easy to become broken by agitation and influence the flocculation effect. Because PH-PAM acts with suspended particles in a very fast way, the time for agitation should not be too long to eliminate the breaking of the flocculi and depress the influence on the clarification effect of brine.

3.8 In the suspension system of brine, the excessively high concentration of brine will lead to the increase of the content of Na^+. However, the -COONa- in PH-PAM dissociates into -COO- and equilibrium movement of Na+ will be affected, thus reducing the linkage efficiency of effective functional group and influencing the effect of flocculation. In addition, the increase of the content and density of brine will result in the increase of the buoyancy of suspended particles in the system and the decrease of the settlement velocity so as to influence the sedimentation effect.

4. CONCLUSION

There are many factors influencing the flocculation effect in the brine purification. In addition, some factors come from the preparation of flocculants, dosage, etc. Special analysis is required for particular conditions. For the above-mentioned factors, several factors may work together and sometimes only one factor independently plays its role in such influence. For such conditions, comprehensive analysis should be made to eliminate factors of interference and treat problems with a definite purpose in mind. Of course, it is very important to collect primary data; hence the analysis can be carried out well. Judgment should be made through certain experimental means and empirical data to finally find out critical factors and existing problems so as to timely solve the problems and ensure the smooth implementation of production.

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