

STUDY ON THE TECHNOLOGY OF PURIFICATION OF WELL-BRINE BY HYFLUX

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Abstract: The technology of purification of well-brine by Hyflux is a new process that based on the success experience of purification of brine in the field of chloro-alkali and soda industries. In the process, we remove $\text{NH}_3\text{-N}$ organic, humic acid & magnesium by advanced pretreatment technology, and remove solid precipitation, which produced in the chemical reaction, by HVM membrane filtration technology to produce pure well-brine. The pure well-brine not only can be used to produce high quality salt, but also make caustic soda in the electrolysis workshop of chloro-alkali plant and soda plant.

Key words: Hyflux, purification of well-brine, well salt

1. OVERVIEW

It is very common and in all over the world that refined salt to be made from rock salt brine. The resource of rock salt and well-brine is very rich in our country. It is estimated that total resource of sodium chloride is reached to more than 10 thousand billion tons. The preliminary basic proved reserves is more than one thousand billion tons. The resource of rock salt is distributed to 18 provinces, municipalities, cities in the country. There are two kinds of well-brine, one is Na_2SO_4 (Glauber), the other is CaSO_4 (gypsum). The production capacity of rock salt in 2004 is 15650 kilo ton per year, and it will reach 21800 kilo ton per year in 2005, 26000 kilo ton per year in 2006, 32950 kilo ton per year in 2010. The companies of producing rock salt are mostly distributed into 11 provinces, municipalities, cities such as Hu bei, Si chuan, Hu nan, Yun nan, Chong qing, He nan, Jiang su, Jiang xi, An hui, Shan xi, Shan dong etc. Most of plants and enterprise produce vacuum pure salt, the others produce liquid salt.

The majority of domestic companies did not purified the well-brine in the beginning.

During the late of eighties and early to nineties, four sets of equipments, which were used to produce vacuum refined salt, were imported from Sulzer Co. in Switzerland. All of them used purification process, and economic value of that salt was obviously better than the plants which did not purified well-brine.

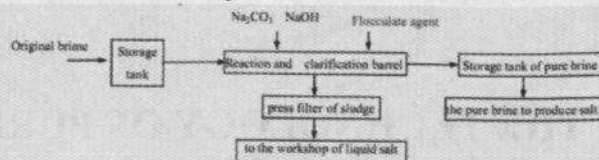
In the well-brine, there are lots of impurities such as $\text{NH}_3\text{-N}$, humic acid, organic, Ca^{2+} , Mg^{2+} , SS, CO_3^{2-} , HCO_3^- . All of those impurities will not only affect the quality of product, but also the normal operation of sodium chloride and anhydrous sodium sulfate. If we do not remove those impurities, some problems will be happened as described below:

(1) It will be scaling and plugged the evaporating concentrating system. The heater and evaporating pot need to be washed and cleaned frequently. It will waste the energy during production, increase consumption, shorten production cycle, decrease the efficiency of production, and depress the economic value of salt production and the economic benefit of company.

(2) The component of the scale are commonly natural organic, CaSO_4 , CaCO_3 , MgCO_3 ,

$\text{Mg}(\text{OH})_2$. All of those impurities are difficult to dissolved, and are not easily cleaned up by hot water. So it is needed to acid washing, such as HCl , to clean them. It is needed a lot of work and consumed lots chemical reagents.

(3) The scale reduces the thermal efficiency



of heat exchanger, increase system thermal resistance. It not only reduces the utilization efficiency of energy, but also decreased the quality of product and the capacity of evaporation of system.

(4) The quality of products such as sodium chloride and some others will also be affected. Most of oversea companies purify the well-brine by removing Ca^{2+} , Mg^{2+} . The purification process contribute to the efficiency of heat-exchanger can be improved significantly, the cleaning frequency of heater and evaporating pot can be reduced, the consumption of energy can be decreased, the quality of products can be improved. The production time can be extended. Its consumption of steam is lower than 1 tone per ton salt (the consumption of steam in the un-purified process is over 1.2 ton per ton salt), the consumption of electric power is far lower than the un-purified process. And the operating time is more than 320 day per year (comparing to the un-purified process it is about 300 days). Every indicator is better than the un-purified process. So it is necessary to purify the well-brine by the removal of the impurities such as calcium and magnesium to improve the quality of well-brine in the field of salt and alkali industry.

2. THE TRADITIONAL PROCESS OF PURIFYING WELL-BRINE

We usually used chemicals to remove organic, calcium and magnesium to by forming precipitation and separate the insoluble or hard-soluble solids, such as $\text{Mg}(\text{OH})_2$, CaCO_3 , $\text{Fe}(\text{OH})_3$, by sedimentation to obtain pure brine. So the most critical part of this purification process is to remove the organics and separate the solids after the precipitation from well-brine.

There are three methods used in the traditional well-brine purifying processes to remove Ca^{2+} and Mg^{2+} . One is to use caustic

soda & soda process. It is very common practice, but the primary reaction equipment is very tall and big, and it needs stirring device. The second method is to use lime and soda process, the investment of capital construction of this method is very high. The third method is to use lime, Glauber's salt and

carbon dioxide process, the investment of capital construction is also very high and the process is very complex.

The caustic soda & soda process is shown as below:

The process adopted batch operation mode, the flow of process is shown as below: Original brine from mine is pumped into reaction tank, and reacted with caustic soda and soda, which are added into the tank, and then stirred and settled after the addition of flocculating agent. Then the liquid supernatant is pumped into pure brine storage tank, and the sludge is pumped to filter press, and the filtrate after the filter press is send to the workshop of liquid salt to further remove sulfate ion. The quality of pure well-brine has $\text{SS} < 10\text{mg/l}$, $\text{Mg}^{2+} < 5\text{mg/l}$, $\text{Ca}^{2+} < 10\text{mg/l}$. This process needs a very big storage tank. So the reaction and settlement can take place in the same container. Also it needs several reaction storage tanks to make the continuous operation, this cause the great instability during the reaction and settlement. This process can not remove $\text{NH}_3\text{-N}$ and organics, which will affect the quality of pure brine. So this process can not completely achieve the purpose of purifying brine, but brings adverse influence to production, especially to alkali factory, because their pure brine need to be farther treated to remove organic and calcium and magnesium.

In order to get same quality of purified brine as Hyflux process, this traditional process needs to add equipment to remove organic, concentrated sludge and the dewatering equipment.

3. BRINE PURIFICATION TECHNOLOGY FROM HYFLUX FILTECH

The technology of well brine purification from Hyflux Filtech is a process that based on

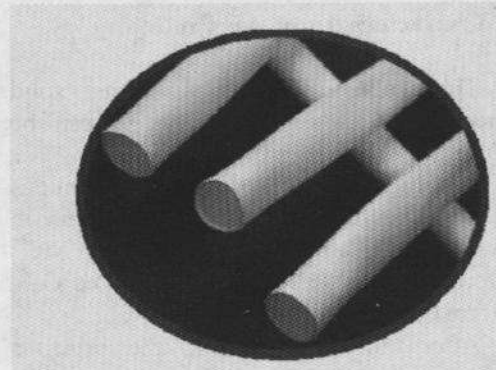
successful experience of well brine treatment in the field of chlor-alkali and soda industries. In this process, we design advanced process to remove $\text{NH}_3\text{-N}$ organics, humic acid, magnesium during pretreatment, and use HVM membrane technology as separation method to remove solid sedimentation, which produced in the reaction, to produce pure well brine.

The difference between the technology of well brine purification by Hyflux Filtech and traditional technology of flocculation and sedimentation is ① we have pretreatment system to remove organic materials, ② we use membrane filter to completely separate sediments from well brine instead of nature settlement. The quality of well brine is easy to control, and to get high quality of brine steadily. This process is very effective to resolve the problems such as the block of pipe and equipment by dirty in the product system of sodium chloride, anhydrous sodium sulfate. This process also improves work efficiency of the equipment in production, increase product ability of the equipment.

3.1 Application of the filtration technology by HVM membrane

3.1.1 Configuration and filtration principle of HVM membrane

Through a special surface treatment, polytetrafluoroethylene (PTFE) form a porous configuration and has pore size between $0.1 \sim 0.2\mu\text{m}$, which can separate solid particles with size greater than $0.02\mu\text{m}$. Over 80 percent of the porosity of the membrane can guarantee its maximum flux while effectively intercept all the solids in the liquid, and only $0.1 \sim 0.3\text{Mpa}$ pressure is required during filtration. The suspended solids are completely intercepted on membrane surface during filtration and can be release by back pulse easily because the membrane material has excellent non-stick property and very low friction coefficient. Therefore, the HVM membrane will not easily get plugged.

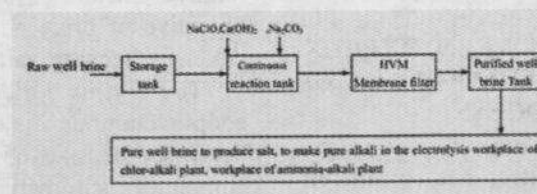


HVM™ membrane

HVM(TM) membrane is an integral tubular membrane, which is completely made of PTFE. The membrane is produced by Hyflux in Singapore and is adopt the similar technology used in artificial blood vessel to make porous filtration membrane. This tubular membrane has smaller pore size on exterior surface and larger pore size in interior membrane and also combines with special surface treatment to make it HVM(TM) membrane suitable for liquid filtration application. The membrane has good chemical and physical character as PTFE and its pore size is between $0.2 \sim 0.5\mu\text{m}$. The membrane has unique integral tubular structure, which cannot be easily tore, delaminated and corroded, which can last 3 years membrane life without question.

3.1.2 Introduction of HVM membrane well brine purification process

The quality of raw brine in China is very unstable. It contains very high concentration of the organics, water-insoluble solids, and calcium & magnesium ion. The Hyflux well brine purification technology process clear up the organics by dosing the oxidant and continuous reaction, and this process also balance the quality of raw brine, and obtain high quality brine filtrate by HVM membrane. The process is described as below:



3.2 Characteristics of this Process

- (1) The well brine with suspended solid concentration as high as 500mg/l can be reduced to below 1mg/l
- (2) Add hypochlorite sodium in continuous reaction tank to remove organic contain in raw brine, also add $\text{Ca}(\text{OH})_2$ react with Mg^{2+} to form $\text{Mg}(\text{OH})_2$ and add Na_2CO_3 and Ca^{2+} to form CaCO_3
- (3) After the reaction tank, the brine is pumped into HVM membrane filter, the CaCO_3 & residual $\text{Mg}(\text{OH})_2$ will be intercepted at the membrane surface and form cake. The filter will automatically back wash through slight negative pressure when the cake accumulated enough. The salt sludge will be released from membrane surface because of the non-stick property and very low friction coefficient of the smooth membrane surface. Finally the filter will automatically discharge the salt sludge. The purified brine will go through the membrane and flow out the filter from the top of filter.
- (4) The purify process is to force the brine through the filter to get the high quality purified brine. After removing the organics ($\text{NH}_3\text{-N}$, humic acid, microbe etc.), magnesium, calcium, clay, oil, the quality of purified brine will have $\text{SS} < 1\text{mg/l}$, $\text{Ca}^{2+} + \text{Mg}^{2+} < 1\text{mg/l}$. This brine can improve the efficiency of evaporate, reduce energy and consume, and assure the continuous operation. The routine production will not be affected by brine in unstable quality of raw brine. The purified well-brine not only can be used to produce high quality salt, but also to make soda in the electrolysis workshop of chloro-alkali plant and workshop of soda plant.
- (5) This process occupy small footprint, is continuous operation and is convenient to operate for its highly automation design. Because of its advanced technology, we can adjust the technology basing on different raw materials. This advanced technology has been accepted by the field of chloro-alkali industry. We have obtained more than eighty projects during about one year.

4. COMPARISON BETWEEN HYFLUX FILTECH'S TECHNOLOGY AND CONVENTIONAL PROCESS

The design of Hyflux Filtech has considered to remove the all the impurities, which is not just to remove Ca^{2+} , Mg^{2+} , but also to

remove nitride and ammoniate, humic acid, which is very high-technology oriented, and according to different raw material quality and objective brine quality. According to our systematic analyzing work, the materials that affect vacuum salt production is not just Ca, Mg, SS but also the organic substance as well. Hyflux Filtech designed this process include all these factors to reach completely brine purification.

(1) The Influence of Organic

Organic is one of the main factors to scale the evaporation equipment, its screen-like structure is very easy to adhere to the surface of evaporator, and also to attract other particles to form scale fast. The conventional process uses accelerated sedimentation, which is to add organic flocculants in the sedimentation tank, which tends to leave organic residues in the liquid. The process designed by Hyflux Filtech has its own step to remove the organics so it will not need to add organic flocculants, which improve the quality of liquid.

(2) Banishing Ca, Mg

The HVM membrane has small pore size, which has great efficiency to the interception of the precipitate formed by Ca, Mg, so it has no requirement for the raw material, which makes much easier for plants to choose raw material. The membrane filtration uses forced filtration and the filtrate quality is not influenced by the raw material quality.

(3) Simple Flow Process

In the conventional process, the reaction and sedimentation take place in a huge tank as batch operation. Therefore, it will need several batch reactors to make the continuous production. A 300'000 ton per year salt production plant will require three reactors with 2000 m³, according to this, a 600'000 ton per year salt production need to use even larger reactor or more ones. The separation efficiency from this reaction and sedimentation process is very unstable. In additional, the conventional process can not remove nitride or ammoniate to meet the objective of brine purification, which brings adverse effects on salt production.

The Hyflux Filtech designed process to adopt continuous operating process, to decrease the size of reaction tank, and the completely automatic filtration also reduces the labor intensity greatly, and makes simple process with small footprint.

(4) Economical Investment

In the membrane filtration system, the huge reactors should not be demanded. Comparing the other separation technology, the porous HVM membrane supplies high flow rate of brine, so lead to the lower investment. For example, a filter with 100m² filtration area can produce 40m³ purified saturated brine per hour. Its market price is 89,1000RMB/set. The guarantee of membrane element use life is 3 years.

5. SUMMARY

According to statement above, the brine purification process from Hyflux Filtech can achieve high brine quality, high automation operation, high operating stability and occupy small footprint, and has been applied to brine purification process broadly in chloro-alkali industry in China; The high quality purified brine can eliminate the potential production problems from high Ca/Mg concentration in raw brine, and at the same time, improves the quality of product and bring distinct economic benefit and environment benefit to the chloro-alkali companies.