INDUSTRIALIZATION AND APPLICATION OF REMOVING TRACE ORGANIC MATTER IN EDIBLE SALT

Hong-bin LOU

Haolong Salt Chemical Co., Ltd., CNSG, Pingdingshan, Henan 467001

Abstract: The paper introduces the research results of removing trace organic matter in edible salt for Haolong Salt Chemical Co, Ltd. Meanwhile, it presents the components and formation mechanism of offensive odor and taste matters in edible salt together with its removal and the results of industrialization application.

Key words: edible salt; removal; micro-organic matter; research achievements;

PREFACE

Pingdingshan salt mine is located in Ye County and Wuyang County in Henan Province, with the ore-bearing area of 400 square kilometers and reserve of 230 billion tons. Sine it started to be developed in 1987, this mine area has had four sets of 600,000 tons / year vacuum salt-making devices and one set of 300,000 tons / year vacuum salt-making device which are putting into operation with the annual output of refined salt of more than 300 million tons. Haolong Salt Chemical Co., Ltd, CNSG are a leading enterprise for salt ore development, where the production of salt in 2007 was up to 1,800,000 tons, including 400,000 tons iodized salt, which is responsible for the iodized salt supply of more than 9000 million people in Henan Province. In the early stage of production, the chemical and physical targets of salt quality in each salt plant all meet the requirement of GB5461-2000—Excellent Grade standard of edible salt. However, as the production continues, products of each Salt Plant has emerged the offensive odor and taste on after another; at beginning it is lighter, appearing intermittently, and then it is more and more frequently and more and more serious; with the bad impact becoming increasingly large, users constantly ask for claims and salt factories have paid a heavy and enormous cost. In this case, Haolong Salt Chemical Co., Ltd, CNSG cooperates closely and actively with the Fudan University, Tianjin University and relevant scientific research institutes to research how to remove the offensive odor and taste of edible salt.

THE COMPONENTS AND FORMATION MECHANISM OF THE OFFENSIVE ODOR AND TASTE MATTERS

Determination of Components

After a great deal of analysis and survey, it is believed that the offensive odor may be related to the geological structure of mine. In 2001, Haolong Salt Chemical Co., Ltd, CNSG commissioned Fudan University to analyze the offensive odor and taste matters, and then Fudan University carried out the field research according to the information provided by our company and did sampling analysis detection in respect of materials in each stage, such as: The original brine, four-effect feed liquid, mother liquor, salt slurry and wet salt, etc. Through a lot of detection and analysis of testing data, it is determined that offensive odor and taste are caused mainly by lower fatty acids with small molecule, including propionic acid, butyric acid, iso-butyrate acid, valerate acid and isovalerate acid, with the content in edible salt of below 1ppm. In addition, there are still some organic acids with long carbon chain like Kwai acid as well as some alkanes and heterocyclic substances. The matters which causes offensive odor are mainly lower fatty acids with small molecule, including propionic acid, butyric acid, isobutyrate acid, valerate acid and isovalerate acid; therefore, in order to eliminate its impact on human olfactory sense, its content must be reduced below the threshold of human olfactory sensation. The contents of offensive odor and taste matters in various feed materials are shown in Table 1; the contents of offensive odor and taste matters in edible salt and the olfactory sensation threshold are in Table 2.

Table 1

Odor matters / Samples	Acetic acid	Propionic acid	Butyric acid	Iso-butyrate acid	Valerate acid	Iso-valerate acid	Sum
The original brine (mg/l)	0.8	0.6	0.2	0.6	0.4	3.5	6.1
Four-effect feed liquid (mg/l)	4.9	3.0	0.7	2.0	0.7	12.2	23.5
Edible salt (mg/kg)	0.049	0.034	0.031	0.057	0.007	0.306	0.313

Table 2

	Propionic acid	Butyric acid	Iso-butyrate acid	Valerate acid	Iso-valerate acid
The content in edible salt（ppm）	0.034	0.031	0.057	0.007	0.306
Olfactory sensation threshold（ppm）	0.00057	0.00019	0.0015	0.00062	0.000078

Formation Mechanism

According to the phenomenon that each salt plant in the same mining area all has the same problem, the formation of offensive odor and taste may be caused by the mine's geological structure. According to data introduction, rock salt is formed in the process of constant evaporation of seawater that is mingled in the process of crustal movement; this constitution style provides us with the facts of offensive odor and taste formation. Because

the water elements are relevantly complicated, containing a variety of substances, including human, animal droppings, dead bodies and other vegetations, in the process of crustal movement, a large number of animal and plant residues decomposed into humic acid; In addition, there exists many oil fields and coal

fields around the salt fields, and when forming the coal, oil and salt together a large number of organic compounds were also formed. Because the water-solubility of organic matters is poor and they are lighter than salt water, they accumulated at the same layer; with the evaporation of moisture, they were concentrated between the salt and salt layer, and then the interlayer between the salt layers was formed---- oil shale layer, due to mutual infiltration.

When it was time to exploit the oil shale layer, oil shale layer is eroded by water; low-carbon-chain organic acids have a weak water-solubility, so brine has a small amount of dissolved organic matters, and also because the boiling point of such organic compounds is at 140 ℃ ~ 250 ℃, they can not be evaporated out of the system by salt-making system from evaporation to drying. Throughout the whole evaporation process, the organic matters are constantly concentrated from Ⅰ-effect to Ⅳ-effect, and the concentration is always increasing; while the salt slurry is discharged from Ⅳ-effect, so the offensive smell of salt slurry is the biggest.

At the mining process, if the exploitation has not yet reached the oil shale layer, the brine has no offensive odor; that is the main reason why in the early production stage there is no offensive odor and taste.

RESEARCH AND TESTING ABOUT THE WAYS TO REMOVE TRACE ORGANIC MATTERS

Through looking up related literatures at home and abroad, according to the characteristics of such kind of organisms, the extraction method, heating method, masking method and adsorption method were made use of to make experiments to remove trace organic matters.

Extraction

Extraction method aims to add an organic solvent (extractant) to the original brine, but the solvent should be basically immiscible with original brine; and then make use of the dissolving capacity difference (the distribution relations) of organic matters in the original brine and extractant to extract the organic matters from the original brine. A lot of experiments were done in the lab, making the following conclusions:

(1) the main components of organic matters in the original brine are low-carbon organic acids, which are not only soluble in organic solvents, but also soluble in water. Therefore, the removal of organic matters from the original brine requires more extraction series and complex equipment, and fixed investment is large.

(2) Generally organic extractant has certain solubility in the brine; taking 0.05% for example, only because of the dissolving consumption of extractant in the original brine, the cost of salt product will increase by more than 10 Yuan / ton salt. In addition to the extractant consumption and alkali consumption when renewing the extractants, the comprehensive cost of products would be increased by more than 30 Yuan / ton salt. It is not economic.

(3) The solubility of organic extractant in the original brine is far larger than the total concentration of organic matters in original brine, so brine after extraction treatment will contain a large number of organic extractants; if the original salt brine containing organic extractant is used for vacuum salt production, some unpredictable problems maybe occur.

Therefore, considering the economics, security, it is not suitable to use extraction method to remove the trace organic matters in the industrial production.

Heating

Heating is an effective way to eliminate organic matters; taking into account the fact that the boiling points of offensive odor substances are all below 200 ℃, such as propionic acid 141 ℃, butyric acid 163.5 ℃, iso-butyrate acid 153 ℃, valerate acid 187 ℃ and isovalerate acid 176.5 ℃; and then acidize the salt slurry to PH value ≤ 3, and next bake to remove these offensive odor matters with

the baking high temperature of more than 200 ℃. A lot of testing have been made in the lab; at the same time, through the cooperated research with relevant institutions the pilot test is carried out. As for the heating method for removing of trace organic matters, the following conclusions are as follows:

(1) heating can remove organic matters well and eliminate the offensive smell.

(2) the effect of eliminating the offensive odor of edible salt improves with the temperature increasing; when the temperature rose to 180 ℃ effect begins to become obvious, and bad odor can be completely eliminated at 220℃.

(3) As for the salt produced with gypsum crystal seed anti-scaling method, because of the existence of the trace gypsum, in the heating process, the salt will easily become yellow, reducing salt whiteness affecting the appearance and quality of salt.

(4) For industrial applications, the salt as a block of primary products should be heated to 200 ℃ to remove the offensive odor. At the same time, it should as be cooled to about 60 ℃ for salt conveyor, and the material and operation of dry bed are both provided high requirements. According to our preliminary estimation, utilizing heating method to remove organic matters, eliminate the salt offensive smell, the cost every tons salt will be increased by 50 Yuan; from the point of economical benefit, this method is not feasible.

Masking method

It is known that offensive odor and taste is mainly caused by small molecules low-grade fatty acids like propionic acid, butyric acid, iso-butyrate acid, valerate acid and iso-valerate acid. Considering the acid's characteristics, it can be considered to add alkalis, transforming these acids into strong-alkali weak-acid salt; according to the relevant literatures, such substances have no offensive smell, and also such substances are contained in the human body, which are not harmful to human body. So the offensive odor and taste can be removed by masking these matters causing offensive odor and taste.

In 1999, this method was applied to the 300,000 tons / year vacuum salt production line in my company, with good results initially; this method only increased the cost per ton salt by 0.2 Yuan, and is easy to operate. But with the passing of time, the drawbacks of this method are shown: the salt that was just produced from the production line have not offensive odor; but when the salt was then delivered to the salt vault of various companies all over the cities, especially after the rainy season, the offensive odor and taste becomes very obvious. This is mainly because the salt in the process of storage absorbs a lot of moisture and carbon dioxide in the air, forming carbonic acid, so that the trace organic matters masked are dissociated once again. This method was forced to put an end in 2001.

Adsorption

Absorption method is to utilize solid adsorbent with specific surface features to adsorb the organic matters in the original brine, making organic matters accumulated and fixed at the surface of solid adsorbent; with the separation of adsorbent and the original brine, the organic matters in the original brine is also be removed. Absorption method, as an industrial production method, has simple process, high applicability and high reliability; in industrialization amplification process, the amplification effect is relevant small, and it is easy to industrialized; if the adsorbents can be recycled well, adsorption method is also very economical; and also adsorbent is generally non-toxic and tasteless, and has a higher security degree for the production of food.

1. Determination of adsorbents

1.1. Molecular sieve, activated alumina and other inorganic adsorbents

The experimental results show that the saturation adsorption amount is small, and treatment effect is not prominent. Although the hydrophobic molecular sieve has certain

adsorption amount, yet its regeneration is more difficult.

1.2. Activated Carbon

With large surface areas, activated carbon is a kind of broad-spectrum adsorbent, that is, the selectivity of absorption is poor. Experiments found that: activated carbon has a large adsorption capacity of original brine, but its regeneration condition is strict, and the regeneration effects are not good; Without regeneration, activated carbon consumption will be large, and with high cost of treatment, the cost for treating $1m^3$ original brine is more than 10 Yuan; simultaneously a large number of abandoned activated carbon will also bring about the environmental issues.

1.3. Alkaline ion exchange resin

Whether it is strongly basic or weakly basic ion exchange resins, because of the interference of chloride ions in original brine, organic acid group can not effectively exchange with resins; so there is almost no effect of the removal of organic matters in original brine.

1.4.Non-polar organic synthesis adsorbent

It is a new type of adsorbent with a lot of surface areas, compared with activated carbon, which has not only a large absorption amount, but also high selectivity, but the production cost of adsorbent is very high. Experiments revealed that this kind of adsorbent has a large handling capacity of original brine, but the effective regeneration needs organic solvents, with high regeneration costs.

1.5. Polar organic synthetic adsorbent

It is the new adsorbent with large specific surface area, large saturated adsorption amount and high selectivity; generally, ordinary regenerant can be used for its regeneration, but the production cost is high. Comparing to the weak polarity, moderate polarity and strong polarity organic synthesis adsorbent such conclusions can be made: the more intense the surface polarity of adsorbent is, the less adsorption capacity it has, and the worse treatment effect it has, but with the help of dilute alkali liquid the regeneration effect will become better; as for strong-polar adsorbent, with dilute alkali complete regeneration can be basically achieved; for weak-polar adsorbents, the amount of saturated adsorption is the largest and treatment effect is also very good, but with dilute alkali for regeneration, non-polarity organic matters in the original brine will accumulate in the adsorbent's surface; after regeneration for certain times certain number, organic solvents must be used for the adsorbent processing.

From the above experimental results, the organic synthesis adsorbent has an excellent adsorption properties and regeneration performance, which should be the preferred adsorbent. Besides, the weak polarity organic synthesis absorption is between non-polarity adsorbent and strong polarity absorption and has both of their characteristics. Taking into account the composition characteristic of organic matters in the original brine and the cost performance of adsorbent, the weakpolarity organic synthetic adsorbent is finally selected as adsorbent.

TECHNOLOGICAL RESEARCH OF ABSORPTION AND REGENERATION

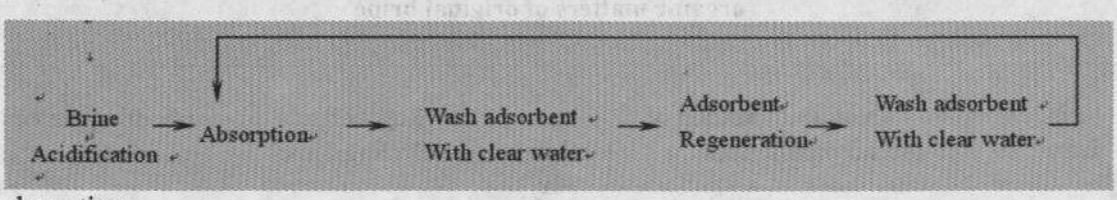
When determining the type of adsorbent, the next key task is to establish the conditions of adsorption and regeneration process.

Results of indoor small-scale tests

From experiments it is found: When the PH of original brine > 6, the adsorbent basically doesn't work, so the organic matters in the original brine can not be effectively removed; when pH <4, if the acidity of original brine is increased again, the effectiveness of absorption can not be improved; when pH <5, the organic matters in the brine can be effectively removed by absorption. When the adsorption velocity < 2mm/s, then reducing the flow rate, the handling capacity of the original brine has not be significantly improved; when the flow rate > 4mm / s, then improve the flow rate, the handling capacity of the original brine is significantly reduced. For liquid regenerant

like methanol, ethanol, acetone and caustic soda, all of them can be used for the effective regeneration of adsorbents after the saturation absorption.

According to the experimental results, the following adsorption regeneration cycle program is determined:



By the experimental results, the initial adsorption conditions can be determined as follows: acid pH = 4.0 ~ 5.0, the original brine flow rate of 2 ~ 4mm / s;

By the experimental results, the initial regeneration conditions are determined as follows: washing flow rate of clear water is 5 ~ 15 mm/s; regenerative liquid is caustic soda of 2% ~ 6%; regenerative liquid flow rate is 0.1 ~ 0.4mm / s; regenerative liquid dosage is 10 ~ 15ml; regeneration temperature is room temperature.

Under the above-mentioned cycle program and absorption regeneration conditions, the adsorbent was made a 10-cycle assessment, which showed that: This adsorbent has a large saturation adsorption capacity, and the volume ratio of original brine and adsorbent is more than 800; regeneration effect is so good that after absorption regeneration ten times, the saturation adsorption capacity wasn't significantly reduced; Absorption regeneration conditions that are determined are feasible.

Whether adsorbent dosage or the inner-diameter of adsorption column, they are relatively small. It is necessary to make the scaling-up experiments in order to determine the conditions for industrial-scale absorption.

Indoor scaling-up lab test results

Indoor scaling-up lab test requires adsorbent dosage of 200ml, and adsorption column diameter of 20mm. First, the original brine is acidified with 5% hydrochloric acid to pH = 4 ~ 4.5, then flows through adsorption column loaded with 200ml adsorbents, with the flow rate controlled at 30 liters / day. From the beginning of 80 liters, 1000ml brine sample is taken after treatment every 20 liters, and then use breaker to perform the indoor open evaporation-crystallization salt production; obtained salt crystals are taken samples for assessment after vacuum filtration and drying. Regenerative liquid is 600m 15% caustic soda solution, with regeneration time of 3 hours. In the above-mentioned conditions, a total of 10 recycling Absorption experiments were carried out, and the results are shown in table 1.

Table1. The results of indoor scaling-up lab test with absorption method to remove the trace organic matters of original brine

Items / Time	Treatment situation of adsorption column	Flow rate (Liter /day)	Regeneration Cycling Times	Handling amount of brine / liter
March 23 ~ April 6	——	30	1	280
April 6-April 22	600ml 5%NaOH 200ml HCl	30	2	260
April 22 ~ May 15	600ml 5%NaOH 200ml HCl	30	3	180
May 15 ~ June 1	600ml 5%NaOH 200ml HCl	30	4	200
June 1 ~ June 11	600ml 5%NaOH 200ml HCl	30	5	120※
June 11 ~ June 19	600ml CH_3OH 50min	30	6	120※
June 19 ~ June 24	600ml CH_3OH 200ml HCl	30	7	80※※
June 24 ~ July 2	600ml 5%NaOH 600ml CH_3OH 200ml HCl	30	8	180
July 2 ~ July 9	600ml 5%NaOH 200ml HCl	30	9	180
July 10 ~ July 18	600ml 5%NaOH 200ml HCl	30	10	160

※: Adsorbent bed had a lot of sediments and colloidal particles, which lead to the increase of bed pressure and the decline of flow rate.

※ ※: Brine used in the experiments contained the mother liquor from the evaporation system, so that the treatment ability

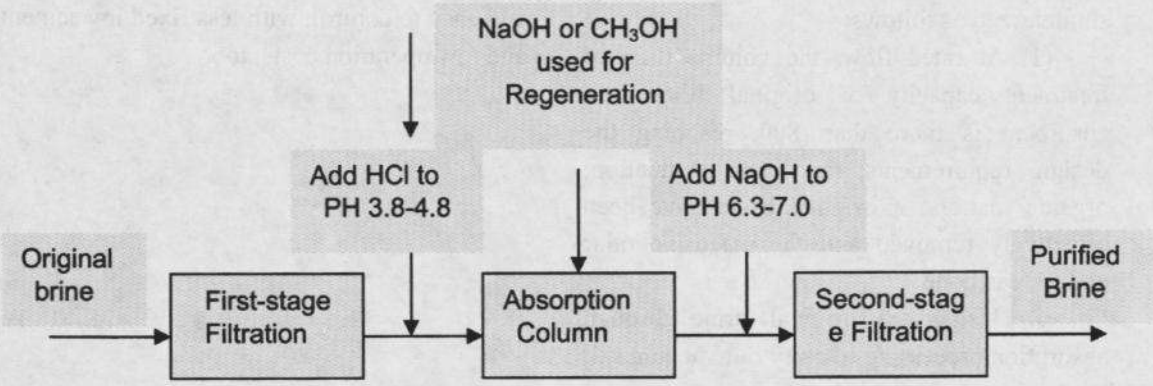
Tests prove that through lab test the determined absorption regeneration procedures and conditions are feasible. Under the normal circumstances, adsorbent treatment capacity of each round is between 160 and 260 liters, with an average of 186.6 liters / round, and the volume ratio of saturation absorption capacity is 900 m^3 brine / m^3 adsorbent. The treated original brine has no offensive smell; and using it for salt production in the laboratory, the salt products have also no offensive odor, which have reached the GB5461-2000 national standard of edible salt.

Pilot-scale test results

In order to ensure the success of the Industrialization, minimizing the risk of technological innovation, the pilot teats were carried out at the 30,000 tons / year production line in Ye County.

The experimental results show that: (1) Applying the operating parameters according to the indoor absorption tests to industrial production, there is no obvious scaling-up effect, and the volume ratio of original brine amounts and adsorbent amounts is more than 800. (2) Absorption of the original brine basically has no bad effect to the evaporation system. (3) Various indicators of salt products have been able to meet the national standards.

Process flow diagram



Process outline

(1) Filtration process: first, 1500 m^3 original brine from large brine pool is pumped to the filting material filter group for filtration, aiming to remove the suspended sand and jelly and other mechanical impurities in original brine, in order to reduce the effects of mechanical impurities on the adsorbents. Filter group is constituted by the three filters, with one for washing and two for operation by turns.

(2) Absorption process: after filtration, the original brine is acidified with hydrochloric acid to pH = 3.8 ~ 4.8, then enter the Floating Bed Absorption Tower Group for filtration treatment, which comprises of seven Absorption Towers, with one for regeneration and six for running operation by turns. after removal of organic matters by absorption the original brine is sent into the middle brine pool, with caustic liquid to adjust pH value to 6.3 ~ 7.0; meanwhile, it is easy to produce sediments like $Ca(OH)_2$ and $Mg(OH)_2$, if they are directly sent into the evaporation system, sediment scaling at the heating pipes and transporting pipes will have the adverse effect on evaporation system. Therefore, after adding alkali, the original brine should be treated by filting material filter, the final clear brine is sent directly to the pool for temporary storage or evaporation salt-producing system.

(3) Regeneration process: Washing adsorbent with water in absorption tower, until without precipitation when adding alkali. Inject regenerative liquid with regulated flow rate for regeneration treatment, and send the regeneration of waste water containing organic matters to the recovery slot; after using regenerative liquid up, wash absorbent with water to pH = 7; then repeat back-washing and washing to mix up adsorbent bed, until it can be put into use for the brine absorption again. Because the components of organic matters contained are very complex, and some adsorbed species are difficult to regenerate with alkali and accumulate on the surface of adsorbents, the system must be treated with methanol after long-time running (about 3 months).

Results of Industrialized Device

This technology has been used in the 300,000 tons / year vacuum salt production device in our company. In December 20th, 2002, it was started up and production run debugged and directly put into operation. After absorption treatment, the original brine is sent to salt evaporation system to produce salt; this device has been continuous in operation for nearly six years, with more than 200 million tons salt produced. In January 2007, this technology was successfully applied

to a newly-built 600,000 tons / year vacuum salt-producing device, and operation results were very good. The research results are also identified by the experts in Henan Province Science and Technology Department. Its industrialization characteristics can be summarized as follows:

(1) At rated flow, the volume ratio of treatment capacity of original brine and adsorbent is more than 800, reaching the design requirements, and no attenuation; organic matters of original brine have been effectively removed and the offensive odor and taste is gone.

(2) Using the original brine through absorption processing to carry out vacuum salt production, the salt products have no offensive odor, meeting the requirements of national edible salt standard GB5461-2000.

(3) Processing system is running smoothly, safely, reliably and is easy to operate, the process flow and operations parameters are reasonable.

(4) The processing cost per ton salt was 6.5 Yuan, relevantly economical.

(5) The adsorption of original brine has no bad influence on the following evaporation system is not adversely. In contrast, the effective removal of organic matters reduces the boiling point, improves the production environment of evaporation workshop, and weakens the foaming of evaporation can liquid as well as reduces the consumption of defamers.

CONCLUSIONS

Selecting weak-polarity organic synthesis adsorbent with large pore size and high-surface area, the adsorption method achieved industrialization successfully at 300,000 tons / year and 600,000 ton / year vacuum salt-making devices in order to remove micro-organic matters contained salt brine with low-carbon-chain organic acids as representative. As a result, the trace organic matters with offensive odor and taste have been effectively removed, and using the adsorbed original brine for vacuum salt production, the edible salt obtained has no offensive odor. Absorption processing system of original brine is simple, stable, safe, reliable and easy to control, with less fixed investment and low operation costs, too.