ANALYSIS ON INFLUENTIAL FACTORS OF THE CRUDE SALT QUALITY

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Abstract: The source and formation of impurities in crude salt as well as the method of decreasing the content of impurities were analyzed. The author pointed out the influence of salt pan biology on the impurities in the crude salt and provided corresponding measures. Considering the single characteristic of the users of our company, the way to remove impurities by combining salt with alkali was put forward.

Key words: Quality of crude salt; water-soluble impurity; water-insoluble impurity.

PREFACE

With the development of China's chlorinealkali industry, the demand of crude salt is increased, and this demand has accounted for around 70% of the whole crude salt market. On the other hand, more and more advanced production technology has been adopted to improve production efficiency in chlorine-alkali industry, but it need more better quality of crude salt. Therefore, crude salt production enterprises should improve and ensure their product quality. Only in this way, can they survive and develop continuously in market competitiveness.

ANALYSIS OF CRUDE SALT COMPONENTS

The components of crude salt are mainly sodium chloride, water-soluble impurities, water-insoluble impurities and moisture. Little moisture in crude salt has little effect on production of chlorine-alkali industry, which reduces the active ingredients only; however, the other two types of impurities not only reduce the active ingredients, but also affect chlorine-alkali production, increasing the difficulty and cost of pretreatment. When the crude salt quality is too bad, it may result in production interruption, off production, etc, make the production not go on continuously and cause large losses. At the production of crude salt, moisture sometimes is related with more water-soluble impurity, especially fine NaCl crystals and NaCl crystals containing mother liquor.

Table 1 below is the quality standard of China's crude salt, and table 2 is the average quality of crude salt at home and abroad.

Table1: Chinese National Standards of Industrial Salt GB/T5462-2003

Item	Index		
	Top-class	First-class	Second-class
NaCl % ≥	96.00	94.50	92.00
Moisture % ≤	3.00	4.10	6.00
Water-solubility material % ≤	0.20	0.30	0.40
Ca^{++}, Mg^{++} % ≤	0.30	0.40	0.60
SO_4^{2-} % ≤	0.50	0.70	1.00

Table2: Average quality of crude salt in china and in other foreign countries

Year	Origin	Water-insoluble impurity, %	Water-soluble impurity, %				Moisture, %	NaCl %
			KCl	$MgCl_2$	$CaSO_4$	$MgSO_4$		
1975	China	0.45	0.06	0.32	0.58	0.10	2.88	95.20
	Mexico	0.02	0.04	0.04	0.17	0.04	1.84	97.60
	Australia	0.03	0.04	0.04	0.17	0.03	2.54	96.70
	DaQingHe	0.31		0.14	0.43	0.10	2.17	96.84
1980	China	0.25	0.04	0.40	0.31	0.26	3.40	95.00
	Mexico	0.03	0.04	0.12	0.10	0.14	2.43	97.00
	Australia	0.02	0.02	0.12	0.07	0.11	2.31	97.10
	DaQingHe	0.24		0.24	0.51	0.10	2.70	96.21
1994	Mexico	0.03	0.47				2.37	97.14
	Australia	0.02	0.54				2.54	96.91
	DaQingHe	0.09	0.70				1.92	97.15

From table 1 and Table 2, it can be seen that the quality of crude salt produced in China was significantly lower than other foreign countries; and the quality of crude salt produced by Daqinghe Company was better than other Chinese companies.

The more moisture and impurities the crude salt contains, the less sodium chloride the crude salt contains.

THE SOURCE OF IMPURITIES AND METHOD OF REDUCING IMPURITIES

The source of water-soluble impurities and method of reducing impurities

1) The source of water-soluble impurities and its formation

Crude salt production is carried out in complex solution brine, which contains a variety of ions, including sodium ion, chlorine ion, calcium ion, magnesium ion, sulfate ion etc. When NaCl is crystallized and separated from the brine, some brine will remain on the surface or the crannies of NaCl crystal particles. The smaller or finer the crystal particles are, the more brine will remain on the surface area of NaCl crystal particles, and there will be more water-soluble impurities in crude salt.

At the crystallization process, if the crystallization speed is too fast, part of brine will sealed in the NaCl crystals, resulting in more water- soluble impurities.

The higher the brine concentration is, the higher the impurity concentration is, and the impurities will lower the quality of crude salt.

2) Method of reducing water-soluble impurities

(1) Strictly control the coefficient of Na+/Mg++, and implement the technology of new brine, deep brine and long-term crystallization. Prevent "used brine" from being added into the new brine. Because this harmful operation will not only increase the impurities concentration of SO_4^{2-} and Mg++, etc, but also increase brine viscosity, resulting in low-speed evaporation, "crystal skeleton", more fine salt particles, finally leading to poor crude salt quality.

Na+/Mg++ ratio is important technical parameter to control crystallization process and to ensure the crude salt quality. With NaCl coming out from brine, Na+/Mg++ ratio goes lower and lower, and It indicates that impurities concentration in brine and brine viscosity get higher and higher, resulting in spontaneous nucleation on the brine surface, forming fine salt or flake salt, leading to poor crude salt quality. Therefore it is necessary to strictly control the technical parameters.

Table 3 is the measurement results of the relationship between brine quality and crude salt quality.

Table3: The relationship between crude salt quality and brine quality

Test number	Brine quality when starting crystallization		Brine quality when finishing crystallization		NaCl content in crude salt, dry base(%)
	Na^+/Mg^{2+}	$^oBe'$	Na^+/Mg^{2+}	$^oBe'$	
1	7.40	25.58	1.80	28.16	97.49
	4.90	26.20	1.70	28.30	97.26
	2.70	27.27	1.60	28.40	96.86
2	7.40	25.58	1.35	28.70	97.26
	4.90	26.20	1.40	28.60	96.85
	2.70	27.27	1.40	28.63	94.80

From table 3, it can be seen: At the starting of crystallization, Na^+/Mg^{2+} ration is higher, and crude salt quality is better; at the end of crystallization, Na^+/Mg^{2+} ration is lower, and the crude salt quality is poor.

Brine with small depth and long-term crystallization should be applied in actual production. This is because under similar working conditions, if the brine depth is small, the brine's temperature varies significantly during one day, so do the evaporation speed and supersaturation degree, leading to fine salt, flake salt and more mother liquor remaining on or in the salt, and they further cause bad crude salt quality; Instead, If the brine depth is big, brine's temperature varies slightly during one day, so does its evaporation speed and supersaturation degree, and crystal growth speed is small and uniform. It is advantageous to reduce vacuole in salt, form big, neat crystal grains and finally form good crude salt quality.

Theoretically speaking, the growth speed of NaCl crystals had better be lower than the critical crystallization speed (2×10-6mm3/s). Under this condition, it can make NaCl crystal neat and transparent; otherwise, the crystal is anomalous and not transparent, having vacuole inside the crystals. But in reality, it is very difficult to realize the fine control. According to meteorological condition in DaQingHe company as well as many-year practices, it is feasible and operational to control the crystal growth speed by adjusting brine's depth considering different temperatures and evaporation values in different months. In March and September, brine depth is 6-8 cm; in April and October 10-14 cm, in May 15-19cm; from June to August more than 20 cm.

(2) Using physical methods to remove impurity ions of the brine

There are several chemical methods to remove calcium and magnesium ions, sulfate ions in the brine effectively, but it is difficult to apply physical methods. Because of high content of impurity ions in the brine as well as huge brine volume, chemical treatment methods are not economic. In addition, it is difficult to achieve in production.

However, if there are some neighboring factories which adopt ammonia-alkali method to produce Sodium Carbonate, mixing Sodium Carbonate mother liquor with saturated brine can reduce the content of SO_4^{2-} in the saturated brine and increase the content of Cl- in the saturated brine. NaCl

crystals from this treated brine are transparent and solid, with no or few Vacuole. Therefore, the crude salt quality can be improved simultaneously. Because crude salt production area is very large, effective mixing and low cost are the key point to remove impurities in the brine by chemical methods.

(3) Making use of low temperature to reduce the content of SO_4^{2-} in the brine.

According to meteorological data in DaQingHe Company, the minimum temperature in winter is around -15 ℃ or lower. At low temperature, the solubility of Na_2SO_4 gets lower, and Na+ combines SO_4^{2-} and H2O to form Glauber's salt Na_2SO_4•10-H_2O, which crystallizes from the brine. According to this characteristic, a large number of SO_4^{2-} can be removed.

(4) Using settlement method to reduce the calcium sulfate in brine

Calcium sulfate crystallizes from the brine in brine's evaporation and concentration process, the easiest way to remove Calcium sulfate is settlement. If extending the storage time at adjustment pool, sulfate ion can be reduced in the brine.

(5) Expanding the size of crystallization pool

Because of the influence of natural conditions and sodium chloride crystals, in crystallization pool, all the crude salt quality are poor at corner or sideline zone. They are irregular powder salt and have to be re-crystallized, leading to some waste. If crystallization pool is expanded, the corner and sideline area is relatively decreased, and the quantity of poor crude salt is relatively decreased, too.

(6) Using plastic film to cover all crystallization pool

Plastic film not only helps to increase output of crude salt, but also can avoid forming poor quality of crude salt because precipitation damages the normal crystal growth. In addition, it can also reach the purpose of long-term crystallization, limiting production ability of market.

(7)Using over-saturated brine for crystallization

When the brine reaches saturation point of NaCl, 81.08% of calcium sulfate will be crystallized. When brine is concentrated to 26.25 °Be, 94.35% of calcium sulfate will be crystallized; only 10.98% of sodium chloride is crystallized at this phase. Therefore, it is helpful for improving crude salt quality to control the brine concentration at more than 25.5 °Be '.

(8) Using brine to wash crude salt

Domestic crude salt is washed in the following ways: small pipes, big pipes, washing machine, pulverizer+ washing machine. They help to improve the crude salt quality. At present, all crude salt makers use saturated brine to transport and wash crude salt. If using lower-concentration brine for washing, it can improve the quality, but also result in some loss of salt.

Australia's salt makers use spraying washing way. Crude salt is conveyed on the mobile steel net conveyor belt. Some spraying device is installed above the conveyor belt. There are three washing zones in whole convey belt.

The source of water-insoluble impurity and method of reducing impurities

1) The resource of water-insoluble impurity and method of reducing impurities in production process

Crude salt production is carried out on the clay board under open-air condition. Farming crystal (one time per 10mm evaporation) and harvesting operation can damage clay board inevitably, stirring mud and sand, which possibly goes into the crystallization pool, causing poor crude salt quality, so do the precipitation, strong wind and atmospheric falling dusts. Mud and sand caused by harvesting and precipitation can be controlled by careful processing, but mud and sand caused by farming crystal operation, strong wind and falling dusts can not be controlled in real practice.

Water-insoluble impurities exist mainly on the surface or gaps between crystals, about 90%; while the others exist inside the crystals, accounting for around 10%.

After animals and plants living in the brine die, their remaining can increase the water-insoluble impurities in crude salt. The size of Some environment garbage is big enough for worker to easily find and remove them, such as plastic sheets, paper scraps, cigarette remains, small stones, mud pies, etc.

Repairing production pool is an important operation to reduce water-insoluble impurities. Operating rules and regulations should be carried out strictly; for example, soaking brine's concentration should be chose carefully to soak the crystallization board thoroughly, and insure that different layers of crystallization board contain the same salt; crystallization pool should be solid, neat and

smooth; in this way, insoluble substance in the board is not easy to enter into the crude salt product. In addition, crude salt harvesting operation, farming crystal operation, clarifying operation should be carried out carefully and strictly to reduce water-insoluble impurities.

Adopting solid, durable, anti-wind, anti-the sunlight, anti-brine material to protect slope, ditch bottom, preventing impurity from entering crude salt. At the top of slope, some gradient should be made to prevent falling water from entering crystallization pool.

Roller compaction and spraying operation should be carried out on the bank of pool or ground near pool, in order to keep moist and avoid dust from flying upward and falling into pool.

After the rain, there is more mud on the ground, so strict management should be taken to avoid workers, mechanical devices or equipments from taking mud into crystallization pool.

Fully making use of clarifying function of the adjustment pool, pouring high clear brine into crystallization pool or using highlyclear brine to wash crude salt can raise the crude salt quality.

2) Adopting dead salt layer, farming crystal techniques

In order to reduce water-insoluble impurity significantly, it is a good way to adopt dead salt board and farming crystal techniques. In this way, farming operating and harvesting operation is carried out on the dead salt layer, they don't contact mud board directly, and so water-insoluble impurity can be reduced.

DaQingHe Company did the experiment from January 25th, 1993 to June 7, 1994, with the result in the following table.

From the table, it can be seen, compared to mud board layer and farming crystal techniques, dead salt layer and farming crystal techniques made the amount of water-insoluble impurities reduce by 67%.

Composition / Crystallization Techniques	NaCl	Water-insoluble substance	Water-soluble substance	moisture
Dead salt layer and farming crystal techniques	97.13%	0.03%	0.69%	1.88%
Mud board layer and farming crystal techniques	97.15%	0.09%	0.70%	1.92%

Table 4 Influence of different crystallization techniques on water-insoluble substance content in crude salt

The source of impurities in transportation and warehousing process and method of reducing them

Because the transportation quantity of crude salt is large while its price is low, in practice it is usually not packaged, and it is easily polluted. Many factors can pollute crude salt to increase water-insoluble impurities such as dirty vehicle, atmosphere falling dust, strong wind and air-open storage, etc. Therefore, it is necessary to strengthen transportation management and improve the transportation conditions. It is the best to have special vehicle equipped; without special vehicle, it is necessary to clean the transportation vehicles before loading, keep loading equipment clean and cover crude salt at storage.

STRENGTHENING THE SALT FIELD BIOLOGY MANAGEMENT, REDUCING EACH KIND OF IMPURITY

The domestic salt field mostly belongs to the type of salt field with rich nutrition, where P

and N content is high, causing high content of organics. Especially in middle-grade and highgrade salt pools, high content of organics causes halophytica to breed massively, and also halophytica excretes amylase to causes high viscosity and low transparence of brine.

High viscosity and thick brine have following disadvantageous effects

Excessive inorganic and organic particles floating in brine make the crystal nucleus increase and fine crystals be formed, and the quality of fine crystal is quite poor.

NaCl crystal's settling speed is slow, and is not easily to form the ripple in the surface of brine, resulting in forming salt of sheep shape, which has poor quality.

High viscosity and thick brine make $CaSO_4$ supersaturated and crystallized in crystallization pool in advance, resulting in the poor quality of crude salt.

High viscosity of brine causes the crude salt to stick to more inorganic and organic particles, resulting in more water-soluble impurity and water-insoluble in crude salt.

Measures to reduce the brine viscosity and increase transparency

Measures mainly aim to control the quantity of halophytica and prevent them breed massively in order to form the balanced living system of salt field. The following measures can be taken:

When pumping sea water, not only sea water density should be considered, but nutrient content should also be considered. Generally if phosphate is more than 0.05mg/l, this sea water belongs to the nutrient salt brine. In practical production, the influence of sea water density and nutrient salt brine influence on salt production should be evaluated roundly.

Manpower removing impurities

This measure includes installing filtration net with 0.18 mm-aperture water gap, collecting halophytica and inorganic particles adhered, then burning or burying them, preventing them from diffusing to other salt pools.

Let animals in brine eat halophytica

Main measure is to put artemia into the brine and maintaining sufficient artemia quantity.

Although artemia cannot digest halophytica well, it is a kind of animal with filter eating and rectum. Whether their food is organic or inorganic particles, only if the diameter is between a few microns and 50 microns, can they be eaten by artemia, and so long as the diameter has several microns to 50 microns, it is possible to filter the food.

COMBINING SALT AND ALKALOID, ERADICATING IMPURITIES

Because Daqing River is far away from the Tangshan Sanyou Alkali Factory approximately is 60 km, that the transporting the crude salt by pipeline may be considered, namely, changing the transportation of solid crude salt into the transportation of liquid crude salt: Dissolves after the crude salt and precipitate, then uses the chemical process again to remove impurities further, then with pipeline directly transport to alkali factory; moreover, because the transportation is carried on under the sealing condition, reducing the possibility of secondary pollution. Because the DaQingHe company has become the subordinated company of Sanyou Group the, the crude salt basically supplies the demand of Sanyou Group, and the goal is single, therefore we must judge the special pipeline transportation from the quality and technical angle. But comparing to auto transportation, whether transportation cost is worthy should be considered. When the transportation quantity is big, the pipeline transportation is better.

EPILOGUE

In sum, the origin of the crude salt impurities is complexity, with many varieties, so each link must be controlled because of the possible tangible effects. The union between salt and alkaloid and moving the alkali factory of impurity pretreatment process to the salt field are also the plan which can be considered.