Study on Comprehensive Utilization of Residues in Salt Making Area

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Subject: Category Ⅰ Salt Making: Application and byproduct

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Abstract: Waste residues produced from salt making include gypsum residue and the primary and secondary residue from brine purification. The residues in large volume and with complicated composition are mainly piled up in the plant, which has a large impact on environment. Waste residues from Zigong Shuping salt making area are studied in this paper. Based on analysis of residue compositions and in accordance with residue characteristics, the authors investigated the downstream application market and carried out experimental studies on indoor desalination and comprehensive utilization in accordance with the investigation. The idea of downstream application is proposed, thus comprehensive utilization of residues can be achieved. With its obvious environmental protection benefits, it can be popularized and applied in various salt making enterprises.

Key words: Residues from salt making; gypsum; desalination; comprehensive utilization

Introduction

At present, brine purification technology is adopted in most of salt making enterprises, from which a large quantity of residues is also produced. In a 600,600 t/a vacuum salt making facility of Zigong Shuping salt making area, the technology of brine purification with flue gas has been adopted for 8 years with stable and normal operation. As the brine treatment volume is large, a large amount of primary and secondary residues is produced from brine purification with calcium sulfate and calcium carbonate as the major components. With salt making capacity expansion, waste residues from the salt making area keep on increasing and the built-up volume is large, making their treatment more and more difficult. In order to solve the problem of residue treatment, the authors have conducted a special study on comprehensive utilization of residues from salt making with the aim of making waste profitable.

Investigation on salt making area and downstream enterprises

The research group first collects first-hand data and then carries out investigation on salt making area and downstream market.

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2.1 Site investigation

Residues sample from Shuping salt aking area are taken for analysis and inspection. Residue composition is analyzed to lay a foundation for subsequent application. The results of analysis and inspection are shown in the following Table 1.

Table 1 Composition of various residues (wet residues)

Sample	$Mg(OH)_2$	$CaSO_4$	$CaCO_3$	$Ca(OH)_2$	$MgSO_4$	NaOH	NaCl
	%	%	%	%	%	%	%
Primary residues from brine purification	7.6	40.9	26.2	2.0	-	2.4	10.9
Secondary residues from brine purification	3.7	9.0	58.0	6.2	-	2.0	15.1

As can be seen from the above table, there is mainly $CaSO_4$, $CaCO_3$ retained in the mother liquor and a portion of Mg $(OH)_2$ residues in the primary residues. In secondary residues, $CaCO_3$ is the main component. Gypsum residues mainly contain $CaSO_4$. In the above residues, sodium chloride content is relatively high, having a certain impact on residue utilization.

Meanwhile, condensate water from Shuping is analyzed for subsequent desalination experiment, with results as follows.

Table 2 Condensate water composition

Sample	Cl^-	pH
	g/L	
Condensate water from Effect II-IV	0.07	9.53

2.2 Downstream application field

In accordance with characteristics of residues from salt making, we learn that their major applications are in following fields.

(1) Gypsum residues and primary residue (magnesium residue for short): Major component is calcium sulfate.

1. Building material: It is dehydrated to calcium sulfate hemihydrate which can be used to produce gypsum board, building blocks, painting gypsum, building gypsum, cement additives etc. as well as gypsum - based conductive material.
2. Agriculture: There is much calcium in salt gypsum, which can be used as

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feedstock in calcium fertilizer production. Salt gypsum containing a certain amount of salt and alkali can be used to improve acid soil. Salt gypsum can be used in the production of such fertilizers as ammonium sulfate, potassium ammonium sulfate and potassium sulfate.

3. Industry: Industrial waste gypsum and cement are used together to consolidate foundations. The technical results which cannot be achieved with only cement can be achieved in special soft soil. Cement consumption is saved. It can also be used to produce gypsum whisker. Gypsum can also be used to co-produce cement, making sulfur in salt gypsum to form sulfur acid and other component to form cement clinker.

(2) Secondary residues (calcium residues): It mainly contains calcium carbonate and a small amount of gypsum.

Calcium carbonate, a widely-applied inorganic salt mineral, is divided into precipitated calcium carbonate (PCC) and ground calcium carbonate(GCC). Its application is in rubber, plastics, paper making, painting, glass, ceramics and water treatment etc. with key points as follows.

1. Plastic polymer: Ground calcium carbonate is added to plastics as an important filler. It can increase capacity and quantity, cut cost and improve process ability, wear resistance, tensile strength, impact strength and stability of plastic products.
2. Paint and coating: As important filler in paint production, calcium carbonate is characteristic of good wear resistance, low content of electrolyte, improved corrosion resistance and coating rheological property.
3. Rubber: A large amount of calcium carbonate is filled in rubber, so product volume can be increased, thus saving expensive natural rubber and cutting cost. Its tensile strength and wear resistance is higher than pure vulcanized rubber. It also has obvious reinforcement effect in synthetic rubber.

2.3 Market survey

Based on the composition of primary and secondary residues, the research group has conducted a detailed survey on building material and cement industry. The overall idea and orientation of residue utilization in the cement industry is determined through comparison and analysis. In combination with data collection and investigation results, we worked out the experimental scheme and carried out the desalination experiments.

After communicating with technical personnel from the downstream corporation, we learned the application situation of residues in cement production and their requirement for residue composition.

(1) During cement production, primary and secondary residues can be added in. Cement proportioning experiment need to be made prior to production. Calcium and magnesium residue addition volume is determined on the basis of experimental results.

(2) Sodium chloride-containing calcium and magnesium residues are added in during cement production. The index requirement from the cement plant is $Cl^{-}\leq0.35$ and $H_2O\leq12\%$.

(3) *General Standard Specification for Portland Cement GB175-2007* is implemented, in which major requirement for compound is shown in the table.

Table 3 Requirement in cement standard

(In mass percentage)

Substance	SO_3	Cl^-	MgO
Content requirement	<3.5%	<0.06%	<5.0%

In order to reach the requirement for the cement plant, the desalination treatment must be carried out to make sodium chloride and the moisture content reach the required value. The research group used condensate water from salt making to carry out the desalination washing experiment to remove salt in calcium and magnesium residues. Comparison is made with different washing schemes.

3 Experimental studies

3.1 Determination of experiment route and scheme

The salt content in the residue is high, so it cannot be decreased to the required value in primary washing and washing water cannot be recycled. In order to minimize salt content, reduce environmental pollution, increase washing water concentration and make it be comprehensively utilized, multiple washing is adopted to conduct the desalination experiment. The experimental scheme is shown in the following figure (Figure1).

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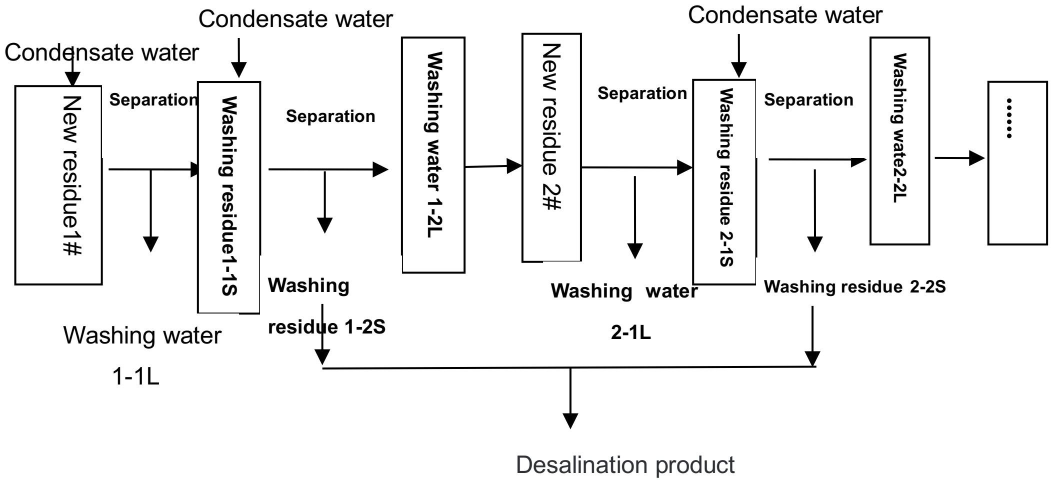

Figure 1 Experiment scheme

3.2 Desalination exploration experiment

Calcium and magnesium residue is washed with water in different proportions. Gypsum residue is similar to the primary residue, so no separate experiments are carried out.

1 kg primary residue and washing water in different proportions are stirred for 30 minutes. Washing liquid and residue samples are taken respectively for salinity content measurement after filtration and separation, as shown in Table 4.

Table 4 Analysis results for primary desalted residue and water

Experiment No.	Washing water ratio （residue：water）	Sample	Cl^-（g/L）
TS-1-1	1：1	desalinated water	54.2
		desalinated residue	2.2
TS-1-2	1：2	desalinated water	32.1
		desalinated residue	1.8
TS-1-3	1：3	desalinated water	24.7
		desalinated residue	1.6

It can be seen from Table 4 that chloride ion content in the residue and washing liquids gradually decrease as the volume of washing water increases. Based on comprehensive consideration, we think that volume of washing water is too high and washing liquid is difficult to treat, so the ratio of 1:2 is selected. A circular desalination experiment is conducted in the next step.

3.3 Circular washing desalination

1kg primary residue and 1 kg secondary residue is taken and stirred for 30 minutes.

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Three circular washing schemes are selected to conduct the experiment respectively.

(1) Experiment scheme 1: 1kg primary residue and 1 kg secondary residue is taken respectively and washed with condensate water for two times.

(2) Experiment scheme 2: The 2nd time washing water from Experiment 1 is used as the 1st time washing water for new residue (After-washing water is reutilized.) And then it is washed with condensate water for the 2nd time.

(3) Experiment scheme 3: After the washing water of two times from Experiment 1 is used as the 1st and 2nd washing water for the new reissue. The 3rd washing is carried out with condensate water.

Meanwhile, dewatering ways for washing residue is compared in order to reduce moisture in it. Finally, moisture in washing residue is reduced to around 10%. After washing, residue and water is filtered and separated and then sent to sample analysis and inspection with results shown in Table 5.

(1) Experiment scheme 1

1kg primary residue and 1 kg secondary residue is taken respectively and twice-washed with condensate water. The experimental results are in the following table.

Table 5 Analysis results for residue and water in circular desalination - Experiment scheme 1

Residue	Sample	Liquid phase Cl^-（g/l）	Solid phase Cl^-（%）	Solid phase water content（%）
Primary residue	XD-1-1	28.5	1.0	-
	XD-1-2	4.3	0.3	10.2
Secondary residue	XD-2-1	33.1	1.4	-
	XD-2-2	5.7	0.3	1.6

(2) Experiment scheme 2

Double washing: The second washing water from Experiment 1 is used as the first time washing water for the new residue. And the second time washing is done with condensate water. The experimental results are in the following table.

Table 6 Analysis results for residue and water in circular desalination in Experiment scheme 2

Residue	Sample	Liquid phase Cl^-（g/l）	Solid phase Cl^-（%）	Solid phase water content （%）
Primary residue	XD-1-3	31.5	1.1	-
	XD-1-4	4.6	0.2	9.6
Secondary residue	XD-2-3	39.6	2.2	-
	XD-2-4	7.4	0.2	1.5

(3) Experiment scheme 3

Triple washing: The post secondary washing water from Experiment 1 is used as the first and second washing water for the new residues. The third washing water is condensate water. The experimental results are in the following table.

Table 7 Analysis results for residue and water in circular desalination in Experiment scheme 3

Residue	Sample	Liquid phase Cl^-（g/l）	Solid phase Cl^-（%）	Solid phase water content （%）
Primary residue	XD-1-5	49.8	1.5	-
	XD-1-6	10.7	0.3	-
	XD-1-7	1.5	0.1	10.7
Secondary residue	XD-2-5	62.6	3.0	-
	XD-2-6	14.6	0.6	-
	XD-2-7	2.02	0.1	1.9

Data in Table 5~7 indicate that:

(1) The salt content in residue and washing liquid gradually decrease as the washing time increase.

(2) Through circulating washing, Cl^- content in calcium and magnesium residue after final washing is less than 0.35%.

(3) Moisture content of dewatered residue is less than 12%.

3.4 Comparison and selection of desalination methods

Based on experimental results, three desalination methods are compared and recommended, as shown in Table 8.

Table 8 Comparison and recommendation of desalination methods

Experimental scheme	Specific method	Experimental results	Features	Recommended
Scheme 1	New residues are washed with fresh condensate water for two times.	Washing residues are qualified and Cl^- concentration in after-washing water is 28-35 g/l.	After-washing water is not reutilized and water consumption is high.	No
Scheme 2	New residues are washed with the first time after-washing water and the second time condensate water.	Washing residues are qualified and Cl^- concentration in after-washing water is 30-40 g/l.	Process flow and running time is short, and operation is simple. The first time washing water is reutilized and water consumption is the lowest.	Yes
Scheme 3	New residues are washed with the second time after-washing water and condensate water for three times.	Washing residues are qualified and Cl^- concentration in after-washing water is 50-63 g/l.	Cl^- concentration in after-washing water is two times higher than that in Scheme 2. The second time washing water can be reutilized, but process flow and running time is long, and operation is complicated.	No

Based on above comparison, it is recommended that Scheme 2 is adopted. It means that the first time after-washing water and condensate water is used to wash new residues. The Cl^- content in the obtained residue is qualified and the volume of washing water is low.

3.5 Desalination amplification experiment

Based on experiment results, Scheme 2 is adopted. 10 kg primary residues and 10kg secondary residues are taken to conduct indoor amplification experiment with results as follows.

Table 9 Amplification experiment on primary and secondary residues

Residue	Washing	Liquid phase Cl^-（g/l）	Solid phase Cl^-（%）	Solid phase water content（%）
Primary residues	FDXD-1-1	34.4	1.2	-
	FDXD-1-2	5.0	0.2	10.5
Secondary residues	FDXD-2-1	40.9	1.3	-
	FDXD-2-2	7.5	0.2	1.8

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It can be seen from above table that after the second time washing of primary residues and secondary residues in amplification experiment, Cl- content in the finally -washed residues is less than 0.35% and moisture content is also less than 12%. In this way, Experimental scheme 2 is proven feasible and can be applied in the subsequent engineering.

4 Conclusion and discussion

4.1 Calcium and magnesium residues are washed with condensate water for two times. After dewatering and drying, the desalinized residue contains Cl^-<0.35% and H_2O<12%. Product quality can completely meet the requirement from downstream enterprises, so the technology can be popularized and applied in the similar plants.

4.2 After washing and desalination of calcium and magnesium residues, washing water concentration is not yet saturated and cannot meet the requirement for the brine tank. If residue washing and desalination is conducted within the salt making area, washing water and other saline waste water in the area can be mixed together for further comprehensive treatment. For example, part of the water can be used to dissolve residual salt so as to realize zero discharging of waste water in the salt making area.

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