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力使带电尘粒捕集在集尘板上。目前多使用管式或管式-板式相结合的集尘器。

(1) 用管式高压静电除尘器治理石灰粉尘和碱尘 青岛碱厂在煅烧车间采用 GZD 100kV/20mA 单管式静电除尘器, 安装在碱筛之上, 尾气经除尘后进入小屋, 进一步除去碱尘后, 由屋顶排入大气。石灰车间采用 CGB 100kV/0.02A 静电除尘器, 安装在石灰吊灰机顶端。

使用后, 煅烧碱筛尾气碱尘由 6000mg/m³, 降至 300mg/m³; 石灰吊灰机灰尘由 3097mg/m³ 降至 150mg/m³, 回收率 95%。

(2) 用卧式除尘器治理石灰窑顶排放的石灰粉尘 大连化学工业公司碱厂使用 BG-30m² 卧式电除尘器处理放空窑气, 除下的粉尘由摇臂锤振荡清灰、海水增湿、汽车外运出厂、除尘后窑气由风机抽吸经烟囱排入大气。使用后粉尘含量由 500~5000mg/m³ 降至 10mg/m³, 除尘效率 99.5%。

第三节 废物综合利用生产化工产品

氨碱厂废液废渣的处理, 在投入资金采取有效措施, 固然可以解决环境污染问题。但未解决资源流失问题, 而且程度不同地增加产品成本, 降低了企业的经济效益。如上节所述, 大化公司碱厂等氨碱厂治理废液废渣增加产品成本达 6.3~13.2 元/吨纯碱。因此它并非治本之道。治理废液废渣的根本出路, 在于开展废物的综合利用, 变废为宝、造福人民。现将中国一些氨碱厂的综合利用的情况, 分述于下。

一、废液制氯化钙和再制盐

从蒸馏废液制取氯化钙, 可以同时副产再制盐。

1. 氯化钙的物理化学性质和用途

氯化钙的一般性质和用途见第一章第一节。氯化钙在空气中强烈吸湿而潮解。CaCl₂·2H₂O 上方空气平衡相对湿度, 在 20℃ 时为 22%, 50℃ 时为 17%; CaCl₂·6H₂O 上方空气平衡相对湿度, 在 20℃ 时为 32.3%, 在 24.5℃ 时为 31%。用颗粒状氯化钙在 25℃ 干燥气体时, 可使气体中水分降到 0.14~0.25g/m³。氯化钙在 25℃ 时实际持水量 (表面层) 为

气体相对湿度/%	36	60	70	80	85	90	95
持水量/(kg/kg)	1.0	1.6	2.2	2.8	3.5	5.0	8.4

氯化钙有无水物和四种水合物形态, 它们的性质列于表 16-2。

CaCl₂ 溶于水可形成浓度很高的溶液, 在一定温度下析出水合物。CaCl₂ 浓度与温度关系列于表 16-3 并示于图 16-3。

表 16-2 纯氯化钙及其水合物的性质

性 质	CaCl ₂	CaCl ₂ ·H ₂ O	CaCl ₂ ·2H ₂ O	CaCl ₂ ·4H ₂ O	CaCl ₂ ·6H ₂ O
ωCaCl ₂ /%	100.00	86.03	75.49	60.63	50.66
相对分子质量, M _r	110.99	129.01	147.02	183.05	219.08
熔点 mp/℃	772	260	176	45	30
沸点 bp/℃	1670	—	—	—	—
ρ(25℃)/(g/cm ³)	2.22	2.24	1.85	1.83	1.72
生成热(18℃)/(kJ/kg)	-7190	-8610	-9490	-10980	-11911
熔化热/(kJ/kg)	256(772℃)	—	—	—	170(30℃)
水合热(无水盐)/(kJ/kg)	—	-240	-295	-600	-840
溶解热 ^① /(kJ/kg)	-680	-380	-290	-50	80
比热容/[J/(kg·K)]	670	840	1170	1340	1420

① 除一水物是用 300mol 水之外, 其余都是 1mol 溶质用 400 mol 水。

表 16-3 CaCl_2 在水中的溶解度

温度/℃	$\omega\text{CaCl}_2/\%$	固 相	温度/℃	$\omega\text{CaCl}_2/\%$	固 相
-49.8	30.5	冰 + $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	50	56.9	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$
-25	33.4	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	75	59.1	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$
0	37.3	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	100	61.3	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$
20	42.7	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	125	63.7	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$
30	50.0	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O} + \alpha\text{-CaCl}_2 \cdot 4\text{H}_2\text{O}$	150	67.2	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$
29.5	52.4	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O} + \beta\text{-CaCl}_2 \cdot 4\text{H}_2\text{O}$ (介稳)	175.5	74.9	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O} + \text{CaCl}_2 \cdot \text{H}_2\text{O}$
29.2	53.0	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O} + \gamma\text{-CaCl}_2 \cdot 4\text{H}_2\text{O}$ (介稳)	200	75.7	$\text{CaCl}_2 \cdot \text{H}_2\text{O}$
40	53.6	$\alpha\text{-CaCl}_2 \cdot 4\text{H}_2\text{O}$	260	77.7	$\text{CaCl}_2 \cdot \text{H}_2\text{O} + \text{CaCl}_2$
45.3	56.5	$\alpha\text{-CaCl}_2 \cdot 4\text{H}_2\text{O} + \text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	300	80	CaCl_2

表 16-4 商品氯化钙溶液的相对密度 (15℃) 与冰点

$\text{CaCl}_2/\%$	相对密度(15℃)	冰点/℃	$\text{CaCl}_2/\%$	相对密度(15℃)	冰点/℃
0	1.000	0	16	1.145	-11.56
2	1.018	-0.89	18	1.165	-14.50
4	1.034	-1.89	20	1.186	-18.00
6	1.052	-2.89	25	1.239	-29.44
8	1.069	-4.11	30	1.295	-46.00
10	1.087	-5.39	32	1.317	-28.61
12	1.105	-7.06	33	1.328	-21.61
14	1.125	-9.16	34	1.340	-15.39

高浓度氯化钙溶液有较低的结晶温度, 利用这一性质, 氯化钙浓溶液 (卤水) 常用做低温冷冻介质。表 16-4 列出氯化钙溶液浓度与相对密度和冰点的数据。

从蒸馏废液回收氯化钙和食盐, 遵循 $\text{CaCl}_2\text{-NaCl}$ 两元体系相图。 $\text{NaCl-CaCl}_2\text{-H}_2\text{O}$ 体系溶解度列于表 16-5 和示于图 16-4。

2. 产品规格及消耗定额

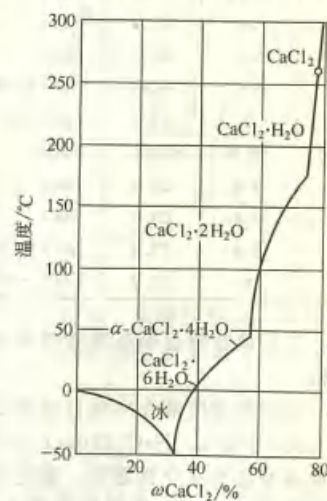
按现行企业标准, 氯化钙 (二水) 质量指标: $\text{CaCl}_2 \geq 70\%$, $\text{NaCl} \leq 2.5\%$ 。再制盐质量指标: $\text{NaCl} \geq 99\%$, $\text{Ca}^{2+} \leq 0.8\%$, $\text{SO}_4^{2-} \leq 0.02\%$, 水不溶物 $\leq 0.03\%$ 。

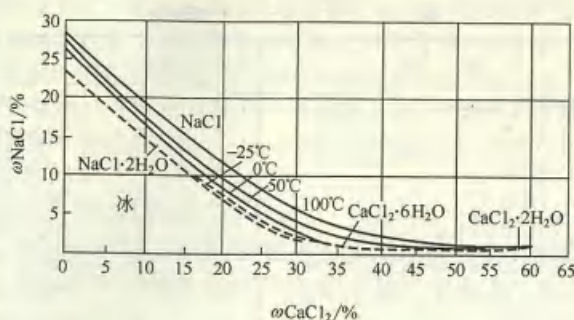
消耗定额, 每吨二水氯化钙消耗定额: 废液 7.5m^3 , 蒸汽 3.2t , 电 $19.3\text{kW} \cdot \text{h}$, 河水 120m^3 。每吨再制盐 (生产 1t 二水氯化钙生产 1.2t 再制盐) 消耗定额: 粗盐 $0.8 \sim 0.85\text{t}$, 蒸汽 2.7t , 电 $31.1\text{kW} \cdot \text{h}$, 河水 56m^3 。

3. 生产方法

中国氯化钙产品主要有二水氯化钙和无水氯化钙二种。生产方法可分为氨碱废液回收法、氯酸钾废液回收法和盐酸石粉法三种。这里只论述氨碱废液回收法。

(1) 工艺流程和工艺条件 从氨碱厂蒸馏废液回收氯化钙并副产再制盐 (氯化钠), 又称盐钙联产法。工艺流程示于图 16-5 和图 16-6。

图 16-3 $\text{CaCl}_2\text{-H}_2\text{O}$ 体系的溶解度

图 16-4 NaCl 和 CaCl_2 在水中共溶度表 16-5 NaCl- CaCl_2 - H_2O 系统溶解度

$t/^\circ\text{C}$	液 相		固 相	$t/^\circ\text{C}$	液 相		固 相
	$\omega\text{NaCl}/\%$	$\omega\text{CaCl}_2/\%$			$\omega\text{NaCl}/\%$	$\omega\text{CaCl}_2/\%$	
-25	13.8	11.2	$\text{NaCl} \cdot 2\text{H}_2\text{O} + \text{冰}$	75	27.45	0	NaCl
	7.4	20.0	$\text{NaCl} \cdot 2\text{H}_2\text{O}$		1.7	40.0	NaCl
	1.3	32.8	$\text{NaCl} \cdot 2\text{H}_2\text{O} + \text{CaCl}_2 \cdot 6\text{H}_2\text{O}$		1.0	50.0	NaCl
	0	33.5	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$		0.9	55.0	NaCl
0	26.3	0	NaCl	100	0.8	58.4	$\text{NaCl} + \text{CaCl}_2 \cdot 2\text{H}_2\text{O}$
	8.4	20.0	NaCl		0	58.8	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$
	0.9	35.0	NaCl		28.2	0	NaCl
	0.6	36.9	$\text{NaCl} + \text{CaCl}_2 \cdot 6\text{H}_2\text{O}$		11.4	20.0	NaCl
25	0	37.2	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	125	2.2	40.0	NaCl
	26.45	0	NaCl		1.2	55.0	NaCl
	8.9	20.0	NaCl		1.1	60.2	$\text{NaCl} + \text{CaCl}_2 \cdot 2\text{H}_2\text{O}$
	0.7	40.0	NaCl		0	60.9	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$
50	0.5	44.65	$\text{NaCl} + \text{CaCl}_2 \cdot 6\text{H}_2\text{O}$		29.0	0	NaCl
	0	44.9	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$		12.3	20.0	NaCl
	26.8	0	NaCl		2.9	40.0	NaCl
	9.6	20.0	NaCl		1.7	55.0	NaCl
	0.6	55.0	NaCl		1.6	60.0	NaCl
	0.6	56.6	$\text{NaCl} + \text{CaCl}_2 \cdot 2\text{H}_2\text{O}$		1.5	62.8	$\text{NaCl} + \text{CaCl}_2 \cdot 2\text{H}_2\text{O}$
	0	56.9	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$		0	63.8	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$

工艺流程特点是在制盐时充分除钙 (CaCl_2)，在制氯化钙时充分除盐，以保证两种产品质量合格。

利用蒸馏废液在滩地自然蒸发，浓缩至含 CaCl_2 120g/L，送入化盐桶，加入部分原盐，制成含 CaCl_2 90g/L、NaCl 220g/L 的盐钙卤。盐钙卤经预热器预热后送入双效蒸发器逆流蒸发，以制取再制盐和氯化钙溶液。氯化钙溶液再经升膜器、降膜器制成二水氯化钙产品。

双效蒸发生产再制盐的工艺条件：一效温度为 125°C ，蒸发器压力为 $(0.196 \sim 0.392) \times 10^5 \text{ Pa}$ ，加热蒸汽压力为 $(4.9 \sim 5.39) \times 10^5 \text{ Pa}$ 。二效温度为 74°C ，蒸发器压力为 $-0.80 \times 10^5 \text{ Pa}$ 。

双效蒸发后，钙卤浓度浓缩至含 CaCl_2 450g/L，同时析出 NaCl 结晶，进入盐浆桶，然后送入离心机分离，并喷入纯碱溶液以防止结块。再进入沸腾炉干燥，获得含 NaCl 99.0%~99.6% 的高质量再制盐。

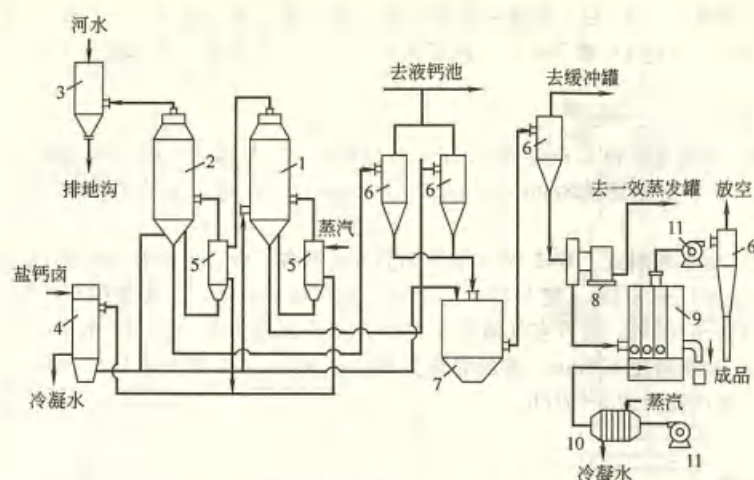


图 16-5 再制盐生产流程

1—效蒸发罐；2—二效蒸发罐；3—水喷射器；4—预热器；5—加热器；6—旋风分离器；
7—盐浆罐；8—离心机；9—沸腾干燥炉；10—预热器；11—鼓风机

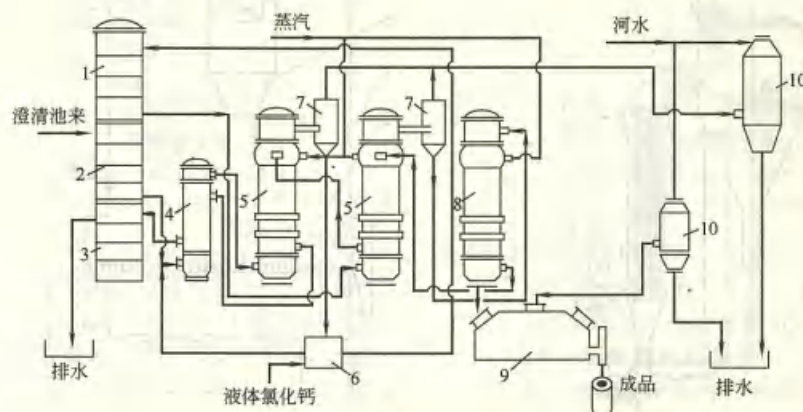


图 16-6 氯化钙生产流程

1—钙液罐；2—高卤罐；3—热水罐；4—预热器；5—升膜蒸发器；6—液钙池；
7—分离器；8—降膜蒸发器；9—储槽；10—水喷射器

用膜式蒸发器生产氯化钙，其工艺条件为：由双效蒸发器浓缩之钙卤，经澄清析盐，析出的盐含 CaCl_2 高，作为原料盐送回化盐桶再次利用。澄清后钙液先经升膜蒸发器浓缩至含 CaCl_2 600g/L，经澄清除 NaCl 后，送入降膜蒸发器，蒸发至含 CaCl_2 70%~72%，然后装桶，冷却后即成固体二水氯化钙产品。

产品品种除桶装的二水氯化钙外，还可生产片状二水氯化钙产品。片状产品生产方法是：将降膜蒸发器蒸发出来的含 CaCl_2 70%~72% 的液体氯化钙放入蒸汽保温的储槽内，自流进入滚筒式制片机，滚筒内表面喷以冷却水，使滚筒外表面的液体氯化钙凝固成 1~2mm 厚度的固体氯化钙，经刮刀刮下即为片状氯化钙，冷却到 60~70℃，用聚乙烯编织袋包装（两层编织袋之间夹一层塑料薄膜）。

在制取高质量 CaCl_2 产品时，要在澄清时进一步除去杂质。其法是将蒸发到浓度为 40% 的

VERIFICATION

I, Wenli,Zhang of 601, Building B-2, Northern Territory, Dongsheng Technology Park, Haidian District, Beijing 100192, China, hereby declare that I am conversant with the Chinese and English languages and am a competent translator thereof. I declare further that to the best of my knowledge and belief the following 纯碱工学(第二版) Soda Technology (2nd Edition) is a true and correct translation.

All statements made herein of my own knowledge are true and all statements made on information and belief are believed to be true. I further understand that willful false statements and the like are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the United States Code. I declare under penalty of perjury that the foregoing is true and correct.

Dated this 11 day of Nov. 2022.

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Wenli Zhang

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charged dust particles are trapped on the dust collecting plate. At present, tube-type or tube-plate dust collectors are widely used.

(1) Treatment of lime dust and alkali dust by tube-type high-pressure electrostatic precipitators. A GZD 100 kV/20 mA single-tube electrostatic precipitator is used in the calcination workshop of Qingdao Soda Plant, which is installed above the alkali screen. After dust removal, the exit gas enters the cabin for further removal of alkali dust, and then is discharged into the atmosphere from the roof. A CGB 100 kV/0.02 A electrostatic precipitator is used in the lime workshop, which is installed at the top of the lime hoist.

By using the electrostatic precipitator, the alkali dust in the exit gas of the alkali screen in the calcination workshop is reduced from 6000 mg/m³ to 300 mg/m³; the dust of the lime hoist is reduced from 3097 mg/m³ to 150 mg/m³, with a recovery of 95%.

(2) Treatment of lime dust discharged from the top of the lime kiln by a horizontal dust collector. The soda plant of Dalian Chemical Industry Company uses a BG-30m² horizontal electrostatic precipitator to treat the vented kiln gas. The removed dust is subjected to vibration dust cleaning by a rocker hammer, humidified by seawater, and transported out of the factory by truck, and the de-dusted kiln gas is sucked by a draught fan and discharged into the atmosphere through a chimney. By using the collector, the dust content is reduced from 300-5000 mg/m³ to 10 mg/m³, with a dust removal efficiency of 99.5%.

Section III Comprehensive Utilization of Wastes to Produce Chemical Products

The treatment of waste liquors and residues from ammonia alkali plants at the cost of investments for effective measures can certainly solve the problem of environmental pollution. However, it does not solve the problem of resource loss, and moreover, it increases the costs of products to varying degrees, thereby reducing the economic benefits of enterprises. As mentioned in the forgoing section, the treatment of waste liquors and waste residues in some ammonia alkali plants, such as the alkali plant of Dahua Company, increases the product cost by 6.3 - 13.2 yuan/ton of soda ash (sodium carbonate). Therefore, it is not a fundamental solution. The fundamental way to treat waste liquors and waste residues is to comprehensively utilize the wastes so as to turn the wastes into treasure for benefiting the people. The comprehensive utilization in some ammonia-alkali plants in China is described below.

I. II. Preparation of Calcium Chloride and Refined Salt from Waste Liquors

When calcium chloride is prepared from distillation waste liquor, refined salt can be produced as a by-product.

1. Physical and chemical properties and uses of calcium chloride

The general properties and uses of calcium chloride are shown in Section I of Chapter I. Calcium chloride absorbs moisture strongly in the air and deliquesces. The relative humidity of the air above CaCl₂•2H₂O is 22% at 20°C and 17% at 50°C. The equilibrium relative humidity of the air above CaCl₂•6H₂O is 32.3% at 20°C and 31% at 24.5°C. When the gas is dried with granular calcium chloride at 25°C, the moisture in the gas can be reduced to 0.14 -0.25 g/m³. The actual water holding capacity (surface layer) of calcium chloride at 25°C is:

Relative humidity of gas/% 36 60 70 80 85 90 95

Water holding capacity/(kg/kg) 1.0 1.6 2.2 2.8 3.5 5.0 8.1

Calcium chloride has anhydrate and four hydrate forms, and their properties are listed in Table 16-2.

CaCl₂ dissolved in water can form a high concentration solution, and hydrate can be precipitated at a certain temperature. The relationship between the concentration and temperature of CaCl₂ is shown in Table 16-3 and Figure 163.

Table 16-2 Properties of Pure Calcium Chloride and Its Hydrate

Property	CaCl ₂	CaCl ₂ •H ₂ O	CaCl ₂ •2H ₂ O	CaCl ₂ •4H ₂ O	CaCl ₂ •6H ₂ O
ω CaCl ₂ /%	100.00	86.03	75.49	60 ± 63	50.66
Relative molecular mass, M_r	110.99	129.01	147.02	183.05	219.08
Melting point mp/°C	772	260	176	45	30
Boiling point bp/°C	1670	-	-	-	--
Density (25°C)/g/cm ³	2.22	2.24	1.85	1.83	1.72
Heat generated (18 °C)/(kJ/kg)	-7190	-8610	-9490	-10980	-11911
Heat of melting/(kJ/kg)	256(772°C)	-	-	-	170(30°C)
Heat of hydration (anhydrous salt)/(kJ/kg)	-	-240	-295	-600	-840
Heat of dissolution ^① /(kJ/kg)	-680	-380	-290	-50	80
Specific heat capacity/[J/(kJ • K)]	670	840	1170	1310	1420

① Except for monohydrate, a case where 300mol of water is used, for other hydrates, 400mol water is used for 1mol solute.

Table 16-3 CaCl_2 Solubility in Water

Temperature °C	$\omega\text{CaCl}_2/\%$	Solid phase	Temperature °C	$\omega\text{CaCl}_2/\%$	Solid phase
-49.8	30.5	$\text{Ice} + \text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	50	56.9	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$
-25	33.4	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	75	59.1	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$
0	37.3	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	100	61.3	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$
20	12.7	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	125	63.7	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$
30	50.0	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O} + \alpha\text{-CaCl}_2 \cdot 4\text{H}_2\text{O}$	150	67.2	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$
29.5	52.4	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O} + \beta\text{-CaCl}_2 \cdot 4\text{H}_2\text{O}$ (metastable)	175.5	74.9	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O} + \text{CaCl}_2 \cdot \text{H}_2\text{O}$
29.2	53.0	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O} + \gamma\text{-CaCl}_2 \cdot 4\text{H}_2\text{O}$ (metastable)	200	75.7	$\text{CaCl}_2 \cdot \text{H}_2\text{O}$
40	53.6	$\alpha\text{-CaCl}_2 \cdot 4\text{H}_2\text{O}$	260	77.7	$\text{CaCl}_2 \cdot \text{H}_2\text{O} + \text{CaCl}_2$
45.3	56.5	$\alpha\text{-CaCl}_2 \cdot 4\text{H}_2\text{O} + \text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	300	80	CaCl_2

Table 16-4 Relative Density (15°C) and Freezing Point of Commercial Calcium Chloride Solution

$\text{CaCl}_2/\%$	Relative density (15°C)	Freezing point/°C	$\text{CaCl}_2/\%$	Relative density (15°C)	Freezing point/°C
0	1.000	0	16	1.145	-11.56
2	1.018	-0.89	18	1.165	-14.50
4	1.034	-1.89	20	1.386	-18.00
6	1.052	-2.89	25	1.239	-29.44
8	1.069	-4.11	30	1.295	-46.00
10	1.087	-5.39	32	1.317	-28.61
12	1.105	-7.06	33	1.328	-21.61
14	1.125	-9.16	34	1.340	-15.39

High concentration calcium chloride solution has a lower crystallization temperature. By using this property, a concentrated calcium chloride solution (brine) is often used as a low-temperature freezing medium. Table 16-4 lists the data of concentration, relative density and freezing point of calcium chloride solutions.

The recovery of calcium chloride and salt from distillation waste liquor follows the phase diagram of CaCl_2 and NaCl binary system. The solubilities of NaCl - CaCl_2 - H_2O systems are listed in Table 16-5 and shown in Figure 16-4.

2. Product Specification and Consumption Quota

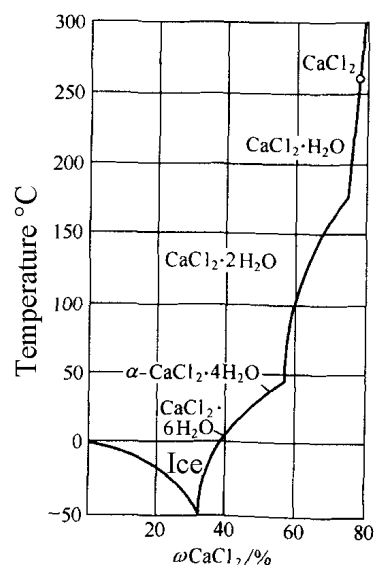
According to the current enterprise standard, the quality indexes of calcium chloride (dihydrate) are: $\text{CaCl}_2 \geq 70\%$, $\text{NaCl} \leq 2.5\%$. The quality indexes of refined salt: $\text{NaCl} \geq 99\%$, $\text{Ca}^{2+} \leq 0.8\%$, $\text{SO}_4^{2-} \leq 0.02\%$, water insoluble $\leq 0.03\%$.

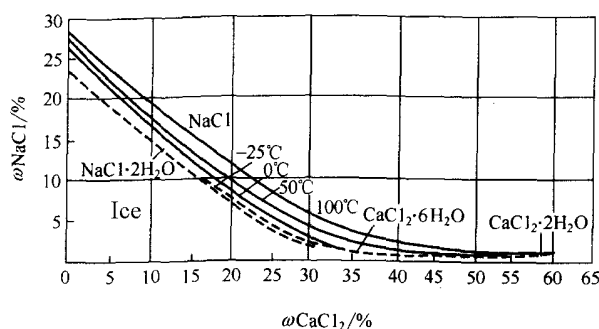
Consumption Quotas Consumption quota for per ton of calcium chloride dehydrate: waste liquor: 7.5m^3 ; steam: 3.2t; electricity: $19.3\text{kW}\cdot\text{h}$; river water: 120m^3 . Consumption quota for per ton of refined salt (1.2 t refined salt is produced from production of 1t calcium chloride dehydrate): crude salt: 0.8 - 0.85 t; steam: 2.7 t; electricity: $31.1\text{kW}\cdot\text{h}$; river water: 56m^3

3. Production Methods

Calcium chloride products in China mainly include calcium chloride dihydrate and anhydrous calcium chloride. The production methods can be divided into: ammonia alkali waste liquor recovery method, potassium chlorate waste liquor recovery method and hydrochloric acid-limestone method. Only the recovery of ammonia alkali waste liquid is described here.

(1) **Process flow and process conditions** Calcium chloride is recovered from the distillation waste liquor of ammonia alkali plants and refined salt (sodium chloride) is produced as a byproduct, which is also called salt and calcium co-production method. The process flow is shown in Figure 16-5 and Figure 16-6.

Table 16-3 Solubility of CaCl_2 - H_2O System

Fig. 16-4 Co-solubility of NaCl and CaCl₂ in waterTable 16-5 Solubility of NaCl-CaCl₂-H₂O System

$t/^{\circ}\text{C}$	Liquid phase		Solid phase	$t/^{\circ}\text{C}$	Liquid phase		Solid phase
	$\omega\text{NaCl}/\%$	$\omega\text{CaCl}_2/\%$			$\omega\text{NaCl}/\%$	$\omega\text{CaCl}_2/\%$	
-25	13.8	11.2	NaCl · 2H ₂ O + ice	75	27.45	0	NaCl
	7.4	20.0	NaCl · 2H ₂ O		1.7	40.0	NaCl
	1.3	32.8	NaCl · 2H ₂ O + CaCl ₂ · 6H ₂ O		1.0	50.0	NaCl
	0	33.5	CaCl ₂ · 6H ₂ O		0.9	55.0	NaCl
0	26.3	0	NaCl	100	0.8	58.4	NaCl + CaCl ₂ · 2H ₂ O
	8.4	20.0	NaCl		0	58.8	CaCl ₂ · 2H ₂ O
	0.9	35.0	NaCl		28.2	0	NaCl
	0.6	36.9	NaCl + CaCl ₂ · 6H ₂ O		11.4	20.0	NaCl
25	0	37.2	CaCl ₂ · 6H ₂ O	125	2.2	40.0	NaCl
	26.45	0	NaCl		1.2	55.0	NaCl
	8.9	20.0	NaCl		1.1	60.2	NaCl + CaCl ₂ · 2H ₂ O
	0.7	40.0	NaCl		0	60.9	CaCl ₂ · 2H ₂ O
50	0.5	44.65	NaCl + CaCl ₂ · 6H ₂ O	125	29.0	0	NaCl
	0	44.9	CaCl ₂ · 6H ₂ O		12.3	20.0	NaCl
	26.8	0	NaCl		2.9	40.0	NaCl
	9.6	20.0	NaCl		1.7	55.0	NaCl
	0.6	55.0	NaCl		1.6	60.0	NaCl
	0.6	56.6	NaCl + CaCl ₂ · 2H ₂ O		1.5	62.8	NaCl + CaCl ₂ · 2H ₂ O
	0	56.9	CaCl ₂ · 2H ₂ O		0	63.8	CaCl ₂ · 2H ₂ O

The technological process is characterized by fully removing calcium (CaCl₂) in salt making and fully removing salt during calcium chloride making to ensure the quality of both products.

The distillation waste liquor is naturally evaporated on the beach to concentrate to contain 120 g/L CaCl₂, sent into a salt dissolving barrel, and added with some crude salt to make a calcium brine containing 90 g/L CaCl₂ and 220g/L NaCl. After being preheated by a preheater, the calcium brine is sent to a double-effect evaporator for counter-current evaporation, so as to prepare refined salt and calcium chloride solution. The calcium chloride solution is then made into a calcium chloride dihydrate product via a climbing film device and a falling-film device.

The technological conditions of double-effect evaporation for refined salt production are as follows: the first-effect temperature is 125°C, the evaporator pressure is $(0.196 - 0.392) \times 10^5 \text{ Pa}$, and the heating steam pressure is $(4.9 - 5.39) \times 10^5 \text{ Pa}$; the secondary effect temperature is 74°C, and the evaporator pressure is $0.80 \times 10^5 \text{ Pa}$. The two-effect temperature is 74°C and the evaporator pressure is $0.80 \times 10^5 \text{ Pa}$.

After double-effect evaporation, the calcium brine was concentrated to contain 450 g/L CaCl₂; at the same time, the NaCl crystals are precipitated, and the calcium brine is then sent to a salt slurry barrel, and further to a centrifuge for separation; sodium carbonate solution is sprayed to prevent agglomeration; then, the solution is dried in a fluidized bed furnace to obtain a high-quality refined salt containing 99.0% -99.6% NaCl.

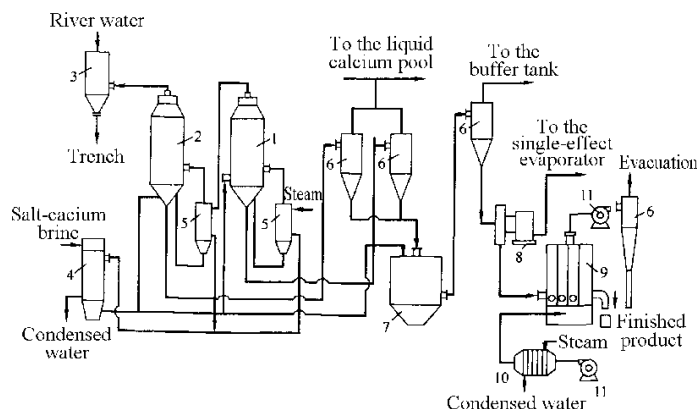


FIG. 16-5 Refined Salt Production Flow

1-One-effect evaporation tank; 2-Two-effect evaporation tank; 3-Water ejector; 4-Preheater; 5-Heater; 6-Separator; 7-Salt slurry tank; 8-Centrifuge; 9-Fluidized bed drying furnace; 10-Preheater; 11-Air blower;

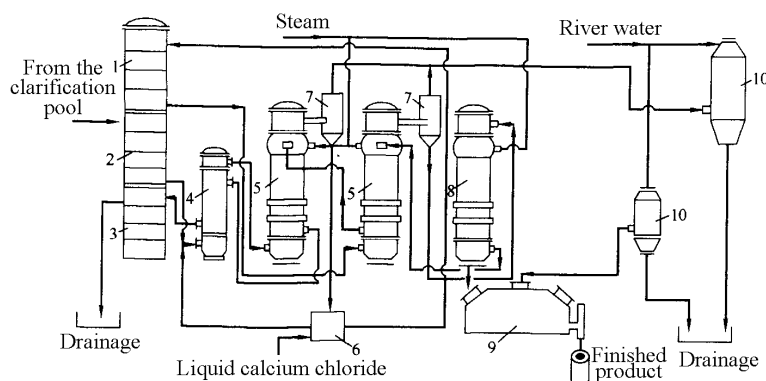


FIG.16-6 Process Flow for Liquid Calcium Chloride Production

1-Calcium liquid tank; 2-High brine tank; 3-Hot water tank; 4-Preheater; 5-Climbing film evaporator; 6-Liquid calcium pool; 7-Separator; 8-Falling film evaporator; 9-Storage tank; 10-Water ejector

The technological conditions for calcium chloride production by film evaporation method are as follows: the calcium brine concentrated by the double-effect evaporator is clarified for salt precipitation; the precipitated salt having a high CaCl_2 content is sent back, as a raw material salt, to the salt dissolving barrel for reuse; the clarified calcium solution is concentrated to contain 600g/LCaCl_2 by a climbing-film evaporator; after clarifying and removing NaCl , the solution is sent to a falling-film evaporator to be evaporated to contain 70% - 72% CaCl_2 ; then the product is packed with barrel, which becomes a solid calcium chloride dihydrate product when becoming cooled.

In addition to barreled calcium chloride dihydrate, it can also produce flaky calcium chloride dihydrate products. The process for producing flaky calcium chloride dihydrate product is: the solution evaporated by a falling film evaporator to contain 70% - 72% liquid calcium chloride is put into a storage tank that is thermally insulated with steam, and flows by gravity into a drum-type flaking machine; the inner surface of the drum is sprayed with cooling water, so that the liquid calcium chloride on the outer surface of the drum solidifies into solid calcium fluoride with a thickness of 1 - 2mm, which is scrapped by a scraper as flaky calcium chloride; the flaky calcium chloride is cooled to 60-70°C and packed in polyethylene woven bags (a new film is sandwiched between two layers of woven bags).

In preparing high-quality CaCl_2 , impurities should be further removed during clarification. The method comprises the following steps: removing NaCl from the waste CaCl_2 solution evaporated to 40% concentration,