

实用 无机化工工艺学

主 编 符德学



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主编 符德学

副主编 刘长春 田京城 王龙道 成战胜

编委(按姓氏笔划) 石香玉 行春丽 李存红

刘咏 苏永祥 祝天林

徐绍红 黄艳芹 霍丽

本书共分九章。河南焦作大学符德学参加其中第1、4、5、8章的编写,刘长春参加第2章的编写,田京城参加第3、6章的编写,王龙道参加第9章的编写,成战胜参加第6章的编写,石香玉参加第3、7章的编写,行春丽参加第6、7章的编写,李存红参加第5、8章的编写,祝天林参加第3、8章的编写,刘咏参加第3、4章的编写,苏永祥参加第2、3章的编写,霍丽参加第3、5章的编写,徐绍红参加第6、7章的编写,黄艳芹参加第2、8章的编写,全书由符德学审定。

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内容提要

本书本着具备基本理论、突出实用性、全面性和易操作性的原则进行编写。内容涉及硫酸工业、氯碱工业、纯碱工业、合成氨、硝酸工业、化肥工业等基础化学工业、及氟化盐、铬盐、磷酸盐、铝盐、亚铵、过碳酸钠、双氧水、泡花碱等无机盐工业,着重对产品的性能、生产原料、工艺流程及生产设备和后续产品等进行了详细介绍。本书适合职业大学无机化工专业作教材使用,也可供科研人员、工厂技术人员参考。

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职业性
立一种和普
节的教育体
大学应进行
实践能力培
心,原来使
《实用无机
面加大等特
的理论推
员及工厂
全书
的编写,日
香玉参加
参加第 3
5 章的编
符德学审
由于

前言

职业性大学作为另一种高等教育形式已受到国务院及教育部的重视和大力提倡,旨在建立一种和普通高等教育并举的高教体系,是对我国普通高校重理论轻实践,教学和生产实践脱节的教育体系的一项重大改革。目前,教育部重点扶持4所全国示范性职业大学,并提出职业大学应进行相应的教材改革、教学方式改革、实验改革及考试方式改革,目的在于加强学生的实践能力培养,以弥补普通高等教育的不足。其中,教材改革是职业高等教育教学改革的核心,原来使用的普通高校教材已远不能适应职业大学教学改革的要求。为此,我们决定编写《实用无机化工工艺学》。本教材具有理论够用、着重实际、突出工艺、便于操作以及内容覆盖面加大等特点,以突出能力培养和工艺训练;缩短书本知识与生产实际的差距,对一些不必要的理论推导作了删除,增加了最新发展起来的新产品、新工艺。对职业大学、成人教育、科研人员及工厂技术人员都有较高的参考价值。

全书共分九章。河南焦作大学符德学参加其中第1、4、5、9章的编写,刘长春参加第2章的编写,田京城参加第5、6章的编写,王龙道参加第9章的编写,成战胜参加第6章的编写,石香玉参加第3、7章的编写,行春丽参加第6、7章的编写,李存红参加第5、8章的编写,祝天林参加第3、8章的编写,刘咏参加第3、4章的编写,霍丽参加第2、8章的编写,苏永祥参加第2、5章的编写,河南平原大学黄艳芹参加第6、7章的编写,徐绍红参加第2、8章的编写,全书由符德学审定。

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7.1.4 中国纯碱工业概况

1949年前,全国仅在天津塘沽、大连有两家氨碱法制纯碱工厂,最高产量为101 kt(1940年)。新中国成立后,为了满足工业发展需要,纯碱生产有了较大发展,除了恢复与扩建原来两家碱厂外,还有四川自贡、青岛、湖北应城、杭州龙山等地设计和建设了中小型碱厂几十座,产量由1949年的88 kt发展到1987年的2.37 Mt(不包括台湾省),居世界第三位。主要原料消耗也有所降低,工艺和设备有了不少改进。我国自己开发的联合制碱生产,虽然在投产时间上比日本晚,但技术水平差距不大,目前主要以海盐为原料。而在内地还有一定数量的天然碱,多年来对内蒙古察千里门诺尔碱矿、吉林大布苏天然碱湖和河南吴城天然碱矿加工利用的科学研究上取得了一定成绩。近年还在沿海各省发现20多处地下岩盐资源,例如江苏淮安地区的岩盐储量相当可观,如采用这种卤水制碱,将会降低生产成本,改善制碱生产面貌。

虽然40多年我国各方面取得了显著成绩,但从国民经济对纯碱工业的需要,和赶上世界平均每人纯碱7.5 kg水平,仍有很大差距。因为我国1987年生产的纯碱按每人平均只有2.2 kg,所以自产纯碱不能满足消耗需要,仍需从国外进口相当数量纯碱。为了迅速改变纯碱供应紧张,部分依赖进口的局面,我国已在山东潍坊、河北唐山、江苏连云港各新建年产0.6 Mt的大型碱厂。此外,我国与先进国家纯碱工业技术的主要差距是能耗高,同一工艺的单位产品能耗约高25%~33%。先进国家氨碱法生产1t纯碱能耗指标为13 GJ,联合制碱法为9 GJ。

7.1.5 制碱的主要原料—原盐

原盐为制碱的主要原料,其主要来源为海盐、岩盐和天然盐水。

1. 海盐 海水溶有各种盐类,其中以NaCl为主。将海水引入盐田,可晒得海盐,其成分因地、因晒制条件而异。下面为某地的海盐化学成分(重量%):

NaCl	89.93	MgBr ₂	0.01
CaSO ₄	0.48	KCl	0.22
MgSO ₄	0.57	水分	6.48
MgCl ₂	0.52	其他	0.27

2. 岩盐 天然氯化钠尚有以矿床形式存在于地层中的称为岩盐。常用注入溶化的方法予以开采,所得盐卤成分各不相同。现举出一种为例:

NaCl 297.84 kg/m³; CaSO₄ 4.77 kg/m³; MgCl₂ 1.68 kg/m³;
MgSO₄ 0.76 kg/m³; 相对密度 1.199(23℃)

3. 天然盐水 一般含NaCl 12%以上,并含有KCl、NH₄Cl、CaSO₄、MgCl₂等杂质。

目前,我国海盐产量最大,因交通便利,靠近碱厂,故成本最低,为原盐的重要来源。

7.2 氨碱法制纯碱

7.2.1 氨碱法生产程序概述

1. 生产流程 纯碱由98%~99%(重量)的Na₂CO₃组成。用食盐(有效组分NaCl)和石灰石按下列制成纯碱:

但是它不
实现。比较贵

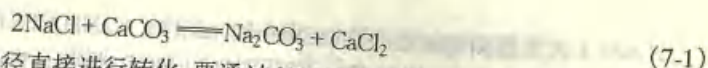
由于NH₃
复杂。要保持
虑,必须尽力维

图7-1是

2. 纯碱的
采用天然盐水。
为了避免设
出。

盐水进入吸

这两个放热
低碳化度的



但是它不能依照这条途径直接进行转化,要通过 NH_4HCO_3 和 NaHCO_3 的中间产品才能实现。比较贵的氨 NH_3 , 在这里只起媒介作用, 在生产过程中没有消耗, 可不断循环使用。

由于 NH_3 循环系统参予主要生产过, 使碱的生产过程无论在设备方面或操作方面更为复杂。要保持原有生产环节平衡作业, 务必细心操作并具有丰富的生产经验。从经济效果考虑, 必须尽力维持最低的氨耗。

图 7-1 是氨碱法生产纯碱示意流程。

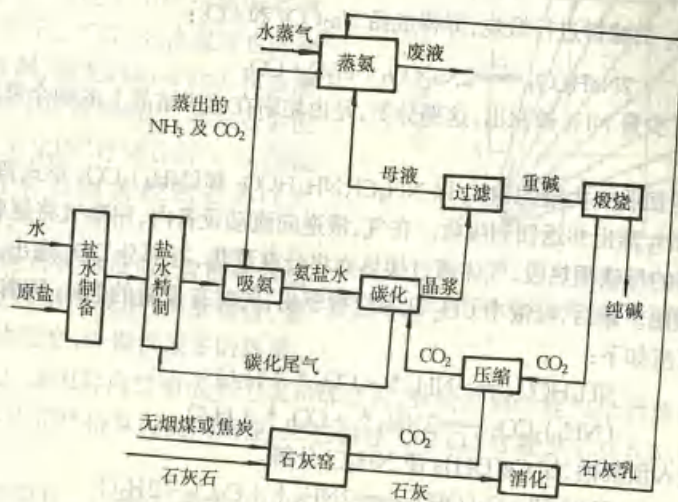
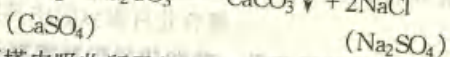
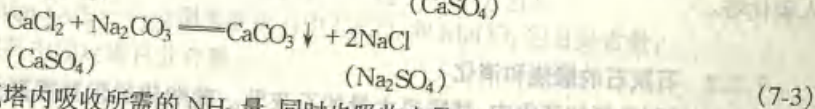
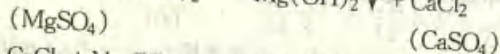
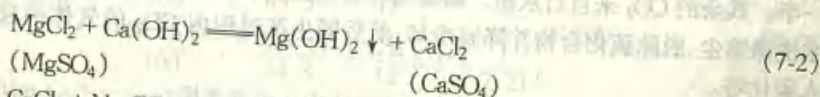


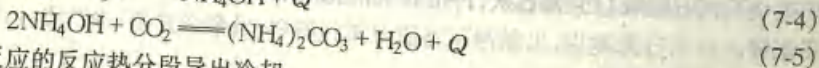
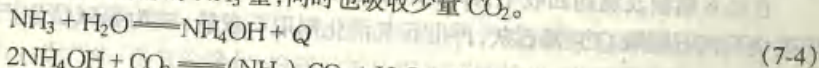
图 7-1 氨碱法示意流程

2. 纯碱的生成 NaCl 以水溶液形式进入生产过程。可以用固体 NaCl 制备成盐水或者采用天然盐水。

为了避免设备和管道结垢, 常将 Na_2CO_3 和 $\text{Ca}(\text{OH})_2$ 加到盐水精制设备里, 使钙和镁析出。

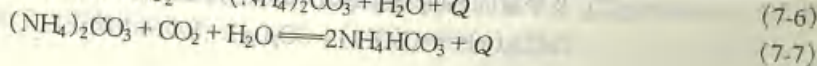
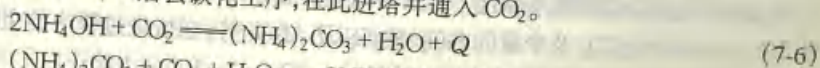


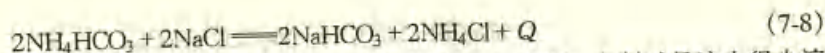
盐水进入吸氨塔内吸收所需的 NH_3 量, 同时也吸收少量 CO_2 。



这两个放热反应的反应热分段导出冷却。

低碳化度的氨盐水冷却以后去碳化工序, 在此进塔并通入 CO_2 。





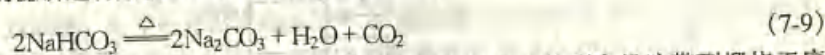
CO_2 有一部分来自石灰窑;有一部分来自 NaHCO_3 煅烧。 NaHCO_3 在制碱母液中很少溶解,所以以结晶形式析出。在实际生产中, NaHCO_3 析出量相当于 NaCl 带入的 Na 量的 70%~75%,其余的 Na 仍留在溶液中,在后面的过程中也不能利用。

吸收 CO_2 和生成 NaHCO_3 也是放热过程,所以碳化塔要进行充分冷却。

碳化塔取出液中悬浮的 NaHCO_3 结晶,用回转真空过滤机进行固、液分离。

从过滤机吸入的空气同母液接触,使空气带出 NH_3 。含氨空气在净氨塔内用水洗涤,将氨回收系统中。

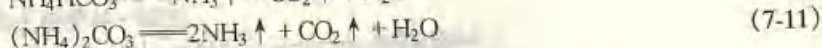
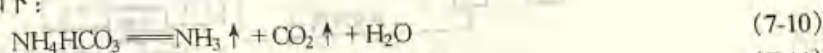
含 NaHCO_3 的滤饼进行煅烧,即得成品 Na_2CO_3 和 CO_2 :



与此同时,并有少量 NH_3 被驱出,这部分氨,是由粘附在滤饼结晶上的剩余母液带到煅烧工序的。

3. NH_3 的回收 大量的 NH_3 以 NH_4Cl 、 NH_4HCO_3 和 $(\text{NH}_4)_2\text{CO}_3$ 形式留在母液里。必须将母液中的 NH_3 蒸出并返回到吸收。在气、液逆向流动设备内,用蒸气将氨驱出。

在蒸氨塔的母液预热段,气体通过换热面将母液预热,有部分 CO_2 逸出。在预热段,气体同液体直接接触。最后,母液中 CO_2 几乎全被驱出,同时有少量的 NH_3 随着 CO_2 从液体转变成气体。其反应如下:



然后,进入预灰桶,加 $\text{Ca}(\text{OH})_2$ 使 NH_4Cl 分解。



最后,在蒸馏段,用蒸气驱出 NH_3 ,直至溶液中只剩微量的 NH_3 ,蒸馏段出来的终点溶液进入闪蒸器,稍降温后排出。

从蒸氨塔出来的含 NH_3 和 CO_2 很浓的气体,经冷凝器去吸收工序。

4. 二氧化碳

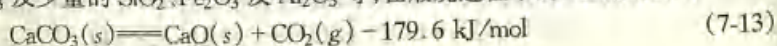
从煅烧和吸收来的,经过洗涤的气体,所含的 CO_2 量约少于形成 NaHCO_3 所需 CO_2 量的一半。其余的 CO_2 来自石灰窑。碳酸钙在石灰窑内分解为 CO_2 和 CaO 。窑气在洗涤塔内用水洗涤除尘、脱除硫化物并降温冷却,然后同生产过程内 CO_2 的气体一起由气体压缩机送入碳化塔。

7.2.2 石灰石的煅烧和消化

在盐水精制及氨的回收中,都需要大量的石灰乳。碳酸化过程又需要大量的 CO_2 气,因而煅烧石灰石制取 CO_2 及石灰,再由石灰消化制取石灰乳,成为氨碱法生产中不可缺少的准备工序。

1. 石灰石的煅烧

(1) 石灰石煅烧的基本原理 石灰石的主要成分为 CaCO_3 ,较优者含量 95%左右,此外尚有 2%~4% 的 MgCO_3 及少量的 SiO_2 、 Fe_2O_3 及 Al_2O_3 等,在煅烧过程中的主要反应是:



(7-8)
母液中很少溶
Na 量的 70%

用水洗涤,将

(7-9)
带到煅烧工序

母液里。必须

预热段,气体
从液体转变

(7-10)

(7-11)

(7-12)
来的终点溶液

所需 CO₂ 量的
在洗涤塔内用
气体压缩机送

的 CO₂ 气,因
不可缺少的准

左右,此外尚
反应是:

(7-13)

根据热力学数据可求出理论上 CO₂ 分压达 0.1 MPa 时石灰石的分解温度为 1180 K。
实际操作温度要比上述为高,因为 1180 K 时石灰石分解速度缓慢。矿石分解速度以反
应面(已生成的 CaO 与其内部 CaCO₃ 的分界面)向内部前进的速度(R)表示,该速度与矿石块
的大小无关,与温度 t(°C)的关系为:

$$\lg R = 0.003145t - 3.3085 \text{ cm/h} \quad (7-14)$$

由式(7-14)可见,采用高温可以缩短煅烧
时间。

在一定温度下,不同大小矿石块所需煅
烧时间如图 7-2 所示。但是,提高温度也受到
一系列因素的限制,温度过高可能出现熔融
或半熔融状态,发生挂壁或结瘤,而且还会使
石变成坚实不易消化的“过烧石灰”。实践证
明,一般燃烧石灰石温度控制在 940 ~
1200°C 范围之内。

石灰石的煅烧是吸热反应,通常靠燃烧
焦炭或无烟煤(也可用气或油)供给热量,要
求燃料在窑中燃烧完全,以提供最多的热量。

但有时因氧气不足,或因窑内结瘤成块造成局部缺氧,致使燃料不能完全燃烧,而产生少量
CO。因此,在操作中要严格控制空气用量,以控制窑气中 CO 含量少于 0.6%,O₂ 含量少于
0.3%。

窑气中 CO₂ 来源有二:一是 CaCO₃ 的分解;一是燃料燃烧的产物。前者为纯 CO₂ 气;后者
为 CO₂ 与 N₂ 的混合气。理论上燃烧纯碳时,气体中 CO₂ 可达 21%,氧过剩或 CO 的产生都将
降低 CO₂ 浓度。由此可见,燃烧石灰石少用燃料,不仅可节约燃料;而且可以提高窑气中 CO₂
浓度,但必须提供足够分解反应所需的热量。现将 100 kg 石灰石所配的燃料 kg 数称为“配焦
率”并以符号 F 表示,则

$$\text{窑气中 CO}_2 \text{ 浓度} = \left[\frac{\text{CaCO}_3 \%}{100} + \frac{\text{MgCO}_3 \%}{84.3} + \frac{\text{C} \%}{12} \times F \right] \times 100 \quad (7-15)$$

$$\left[\frac{\text{CaCO}_3 \%}{100} + \frac{\text{MgCO}_3 \%}{84.3} + \frac{\text{C} \%}{12} \times F \times \frac{1}{0.21} \right] \times 100$$

式中 CaCO₃ %, MgCO₃ %——分别为石灰石中 CaCO₃ 和 MgCO₃ 的百分含量;

C%——燃料中固定碳百分含量;

0.21——空气中氧的摩尔分率。

理论上,窑气中 CO₂ 浓度为 44.2%,但一般在 40%左右,产生的窑气必须及时导出,否则
将影响反应的进行。生产中,窑气经净化、冷却后被压缩机不断抽出,以实现石灰石的持续分
解。

2. 石灰窑及其操作 目前,煅烧石灰石大多数采用混料竖式窑,其优点是生产能力大,上
料下灰完全机械化、窑气浓度高、热利用率高、石灰质量好。

石灰窑的结构示意图如图 7-3 所示。

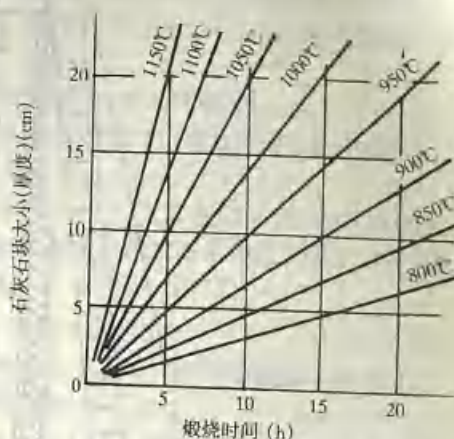


图 7-2 石灰石块大小与煅烧温度及煅烧时间的关系

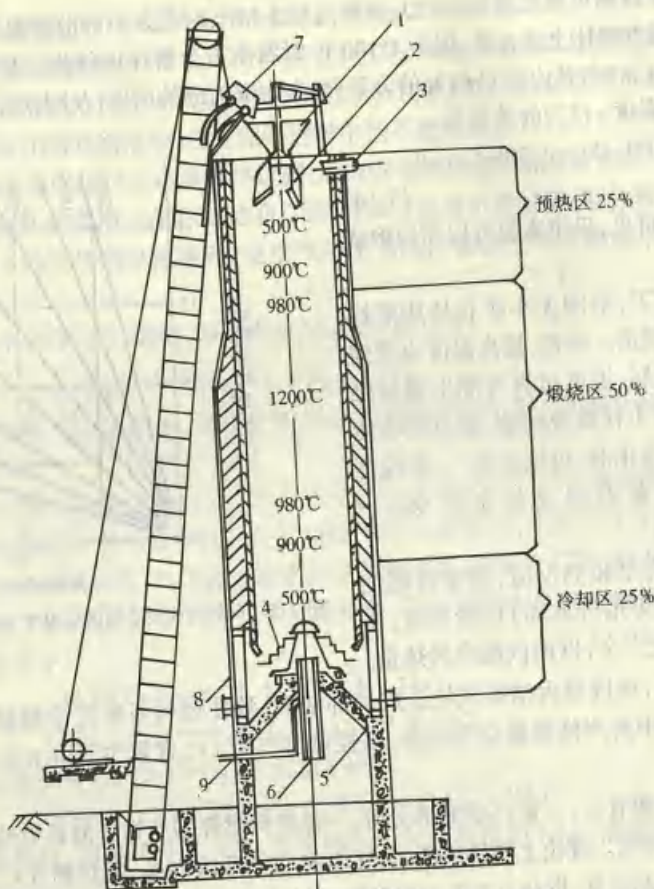


图 7-3 石灰窑简图

1—漏斗；2—分石器；3—出气口；4—出灰转盘；5—四周风道；6—中央风道；7—吊石罐；8—出灰口；9—风压表接管

窑身用普通砖或钢板制成，内砌耐火砖，两层之间填装绝热材料。以减少热量损失。从窑顶往下可划分三个区域：预热区、煅烧区和冷却区。预热区位于窑的上部，约占总高的四分之一，其作用是利用从煅烧区上升的热窑气将石灰石及燃料预热并干燥，以回收窑气余热，提高热效率。煅烧区位于窑的中部，经预热后的混料在此进行煅烧，完成石灰石的分解过程。为避免过烧结瘤，该区温度不应超过 1350°C 。冷却区位于窑的下部，约占窑有效高度的四分之一，其主要作用是预热进窑的空气，使热石灰冷却，这样，既回收了热量又可起到保持窑篦的作用。

配料比例、块度大小、风压风量及加料出料速度等，都是保持石灰窑正常操作的主要条件。窑内平衡状态易受操作失误或操作中断的干扰，必须采取措施尽快恢复正常。在石灰石和焦炭量的比例得当的前提下，应采取下列措施：

如果燃烧区过低，可由石灰温度过高得知。可以通过加大空气吹入量来提高燃烧区的位置。

如果燃烧区过高，可由出气温度过高得知。措施要复杂些，必须在尽量减少空气量的同时

加强出灰，直

燃烧区传

并加料将窑衬

调节空气量来

最重要的

从下部送入窑

石灰易产

如灰尘指

2. 石灰

盐水精

$\text{Ca}(\text{OH})_2$ ，但

生产中采用

石灰乳

一般使用的

石灰乳

用。影响悬

使石灰乳质

采用 $65\sim 80$

石灰消

1—灰仓

9—杂水

① 纯碱

加强出灰,直到燃烧区被机械地恢复到正常位置。然后快速加料将窑装满,恢复正常风量。

燃烧区伸长(上下温度都高),则首先通过进风使燃烧区的下界限向上移动,接着加强出灰并加料将窑补满,促使燃烧区向中部收缩。在焦石比已经调整好的反应区正常情况下,只采取调节空气量来保持窑的正常状态。在正常状态下,控制窑内气体为中性或轻微还原性气体。

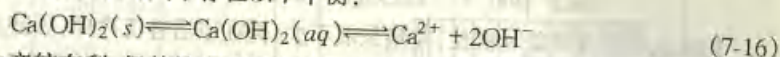
最重要的是细心调节空气量。为避免漏入空气,全窑需维持正压,正压是由送风机将空气从下部送入窑内而形成的。

石灰易产生粉尘,所以必须注意所有石灰处理装置的防尘,并经常维护。

如灰尘扬起不可避免时,可将其抽出,用水洗涤抽出的含尘空气,洗水可用于消化石灰。

2. 石灰的消化

盐水精制及蒸氨所用的不是 CaO 而是 $\text{Ca}(\text{OH})_2$ 。使用适量水即可使 CaO 消化成 $\text{Ca}(\text{OH})_2$,但 $\text{Ca}(\text{OH})_2$ 溶解度很小且随温度升高而降低,粉末状的消石灰使用又很不方便,故生产中采用其悬浮液,又称石灰乳,其中存在以下平衡:



石灰乳较稠,对生产较有利,但其粘度随厚度而增加,太稠则将沉降而堵塞管道及设备,一般使用的石灰乳含活性 CaO 约 160~220 tt^①,相对密度约为 1.27。

石灰乳中悬浮粒子的分散度很重要,粒小易制成均匀不易下沉的乳状物,便于运输和使用。影响悬浮粒子大小的因素有石灰的纯度、水量、水温及搅拌强度。石灰中杂质多或过烧会使石灰乳质量降低。消化用水的温度高可以加速消化并呈悬浮粒度较细的粉末,生产上一般采用 65~80℃ 的温水为宜。

石灰消化系统的示意流程见图 7-4。

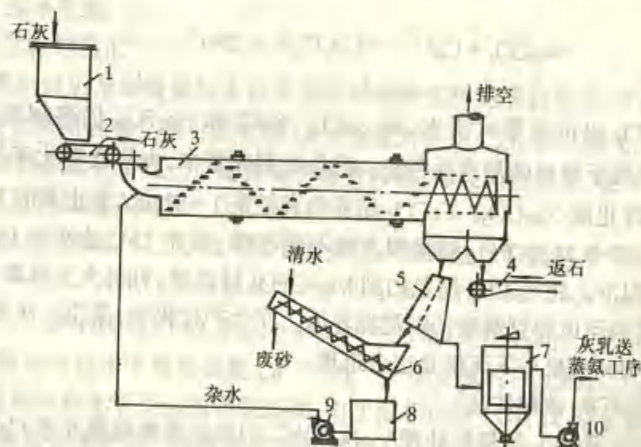


图 7-4 石灰消化流程及化灰机示意图

1—灰仓;2—链板机;3—化灰机;4—返石皮带;5—振动筛;6—螺旋洗砂机;7—灰乳桶;8—杂水桶;
9—杂水泵;10—灰乳泵

① 纯碱工厂常用的一种浓度单位,称为“滴度”。符号可用 tt 或 ti。1tt = $\frac{1}{20}$ mol/L,本章以后遇“tt”即为此意。

化灰机(消化机)为一卧式回转圆筒,稍向出口一端倾斜(约0.5度),石灰与水从一端加入,互相混合反应。圆筒内装有许多螺旋形式排列的抄板,在转动时将固体混合物和另一端推动。尾部有孔径不同的两层筛子,完成的石灰乳从筛孔中流出,经振动筛进入灰乳桶,剩下的生烧或过烧石灰则由筛子内流出,大块生烧者可以再入窑重使用,称为返石。而从振动筛出来的小块称为废砂,予以排弃。

7.2.3 盐水的精制

1. 盐水精制的任务

纯碱生产中的转化Na是由食盐提供的。接近饱和的NaCl水溶液作为粗盐水导入系统。自然界中常有这种天然盐水,由钻井深处用泵抽出。也可用水溶解固体盐制成粗盐水。如用海盐制得的饱和粗盐水。其大致组成(kg/m³)如下:

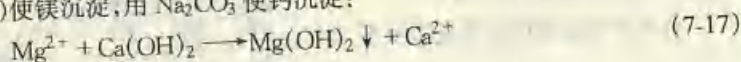
NaCl 300.4; CuSO₄ 4.81; CaCl₂ 0.8; MgCl₂ 0.35

粗盐水中所含钙盐和镁盐,其量虽然不大,但在以后各工序中,因能与NH₃与CO₂作用形成沉淀复盐,引起设备管道结垢甚至堵塞,而且会增加原盐和氨的损失。这些杂质还会混入重碱中,最终将影响纯碱的质量。因此,生产中都采用预先精制的措施,以除去这些杂质。一般要求除去钙、镁的精度在99%以上。

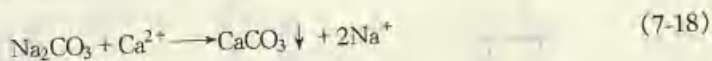
2. 盐水精制的方法

(1) 石灰纯碱法

用Ca(OH)₂(石灰乳)使镁沉淀,用Na₂CO₃使钙沉淀:



得一次盐水及一次泥。

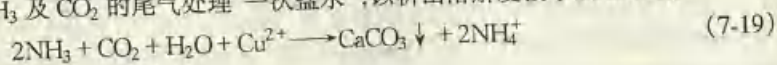


得二次盐水及二次泥。

Mg(OH)₂和CaCO₃以沉淀形式析出,而CaCl₂、NaCl和Na₂SO₄仍溶解在盐水中。随CaCO₃带入的Na⁺,也用于制碱的形式而存在。但是在制碱塔中,由于受转化率的限制,所以这种Na⁺只有一部分转化成Na₂CO₃。CaCO₃结晶的直径是1-10μm,而生成的Mg(OH)₂结晶的直径只有几μm。单个Mg(OH)₂结晶根本就不能沉降,而在15℃盐水中CaCO₃结晶的沉降速度在0.1m/h以下。将CuCO₃结晶加到Mg(OH)₂结晶里,可长大变成聚合体,其沉降速度很快,在澄清设备内可以得到清晰的沉淀泥界面。在生产过程中,采用二次泥返回一次精制设备中来加速沉出物的凝聚与下沉就是这个道理。

(2) 石灰-塔气法(石灰-碳酸铵法)

以碳化塔顶含NH₃及CO₂的尾气处理“一次盐水”,以析出溶解度极小的CaCO₃。



除Mg²⁺与上法相同。

此外,也可采用聚丙烯酰胺(PAM),因其分子大且具有极性基团,易于吸附沉淀粒子,在颗粒之间能够“架桥”而形成空间网状结构的絮状物,这对缩短沉降时间、提高设备生产能力颇有成效。生产厂制备的二次盐水中总氯离子浓度(以符号T_{Cl}表示)一般达105tt左右。

石灰-塔气法的盐水精制流程见图7-5。

水从一端加
和另一端推
乳桶,剩下的
、振动筛出来

水导入系统。
盐水。如用

CO₂ 作用形
还会混入重
杂质。一般

(7-17)

(7-18)

盐水中。随
的限制,所以
Mg(OH)₂ 结
CaCO₃ 结晶的
合体,其沉降
尼返回一次精

CO₃。
(7-19)

沉淀粒子,在
备生产能力颇
左右。

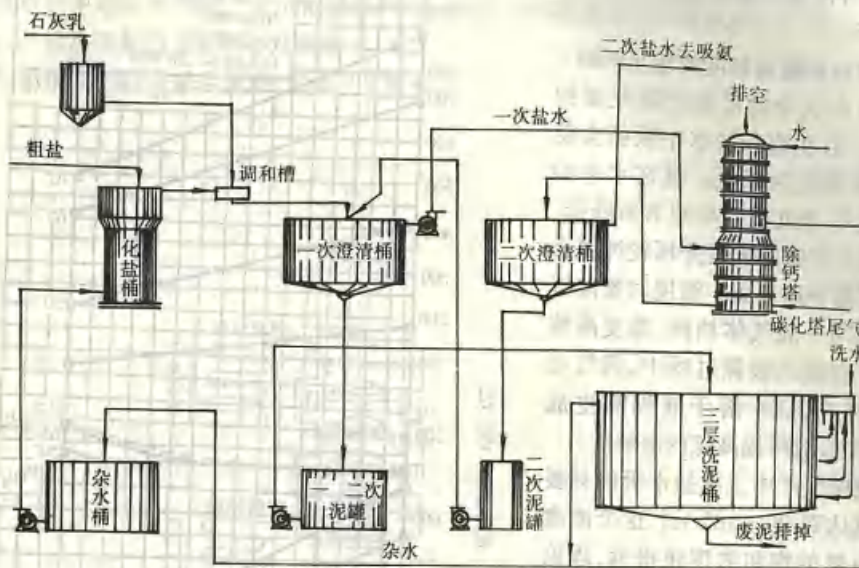


图 7-5 盐水精制流程图

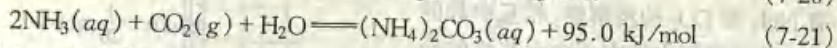
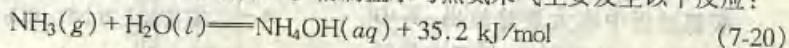
7.2.4 盐水吸氨

1. 吸收过程的理论

盐水吸氨的目的是制备氨盐水并使其达到碳酸化所要求的浓度 (T_{Cl} 89~94 tt, F_{NH_3} ①99~102tt)。吸氨所用的氨气来自蒸氨塔,其中除氨外还有 CO₂ 和水蒸气。此外,过滤器所抽入空气(称滤气)以及碳化塔尾气中都含有一定量的氨,都应回收利用,使之进入盐水中。

(1) 吸氨过程的基本原理

① 吸氨反应及氨盐水上方的气体平衡分压。精制盐水与蒸氨来气主要发生以下反应:



此外,气体还与盐水中残余微量 Ca²⁺、Mg²⁺ 产生少量的沉淀物。

盐水吸氨是伴有化学反应的吸收过程,由于液相中含 NH₃ 及 CO₂ 量逐渐增加,且化合生成碳酸铵,致使氨分压较同一浓度氨水的氨平衡分压有所降低;溶液中 CO₂ 越多则溶液上方氨的平衡分压就越低,在 65℃ 以下,温度对 CO₂ 分压的增加影响不大。尤其在氨浓度高时,温度对 CO₂ 分压影响更小,但温度对水蒸汽及氨的分压影响却很大。温度升高, NH₃ 分压明显上升。在温度较高时,溶液中 CO₂ 含量增加,会使氨分压很快下降,而水蒸汽分压下降不多。

上述规律对氨碱法生产中的吸氨、碳化及蒸氨等过程都很重要。曾有人对含 85.5tt NaCl

① F_{NH_3} 表示游离氨

和溶有不同数量的 NH_3 及 CO_2 溶液上方平衡分压进行研究测定,结果如图 7-6 所示。

② 原盐和氨溶解度的相互影响

NaCl 在水中的溶解度随温度的变化不大,但在饱和盐水中吸氨会使 NaCl 溶解度稍为降低。氨在水中的溶解度很大,但在盐水中也有所降低,即氨盐水上方的氨的平衡分压较纯氨水上氨的平衡分压为大。温度对氨溶解度的影响与一般气体相同,温度高溶解度小。在盐水吸氨过程中,因气相有 CO_2 存在, CO_2 溶于液相能生成 $(\text{NH}_4)_2\text{CO}_3$,故可提高氨的溶解度。

在纯碱生产中二次盐水吸氨只要要求游离氨达到 99~102 tt。这个浓度距常温下氨的饱和浓度还很远,理论上似应多吸一些为好,这虽对碳化反应有利,但 NaCl 在液相中的溶解度将随氨增浓而下降,这对制碱中钠的利用率及产率将会引起不良后果。因此,氨盐水中氨与盐的相对浓度必须兼顾两个方面,按理论反应 $F_{\text{NH}_3}/T_{\text{Cl}}$ 值应为 1,但考虑到氨的逸散损失等,一般取 1.08~1.12,故按经验多取 $F_{\text{NH}_3}=99\sim102\text{ tt}$, $T_{\text{Cl}}=89\sim94\text{ tt}$ 。

③ 吸氨过程的热效应

吸氨过程中有大量热放出,其中有 NH_3 和 CO_2 的溶解热,相互中和的反应热及蒸氨来气中所含水蒸气的冷凝热。在正常生产条件下,每制 1t 纯碱,约放出热量 $2.16 \times 10^6\text{ kJ}$ 。此热量如不引出系统,将足以使溶液温度上升高达约 120°C ,致使吸氨塔完全失去作用,所以,冷却问题是吸氨过程的关键。

④ 吸氨过程的体积变化

盐水吸氨后,相对密度减小、体积增大;又因气体带来的水气冷凝而稀释了饱和盐水,使体积更加增大,一般情况下,经过吸氨,体积增加约 13.5%。

⑤ 吸氨过程的实质

由于蒸氨来气中含 NH_3 与 CO_2 分子比约 4:1~5:1,因此,盐水吸氨过程,实质上为液相同时

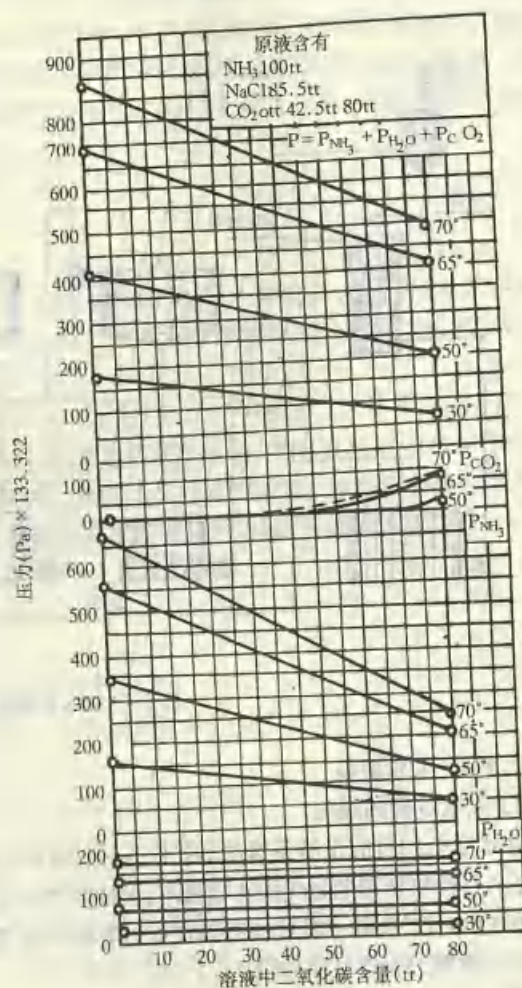
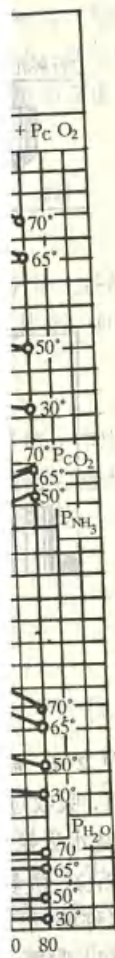


图 7-6 氨盐水上方的 NH_3 、 CO_2 和 H_2O 的分压

注: 1tt = $\frac{1}{20}\text{ mol/L}$

吸收 NH_3 及
在液相的结
同高度液相
(2) 盐
吸氨的

它是一
逐渐由塔顶
部、中部两



的分压

达约 120℃,致

饱和盐水,使体

质上为液相同时

吸收 NH_3 及 CO_2 气的过程。吸收包括物理吸收和化学吸收,其中化学吸收为部分 NH_3 与 CO_2 在液相的结合,且该化学吸收的速度是正比例于游离氨浓度的。据近年生产查定数据,沿塔的不同高度液相中 CO_2 与 NH_3 二者的浓度经约为一常数,故知盐水对两者吸收成正比例。

(2) 盐水吸氨的主要设备及流程

吸氨的主要设备是吸氨塔,如图 7-7 所示。

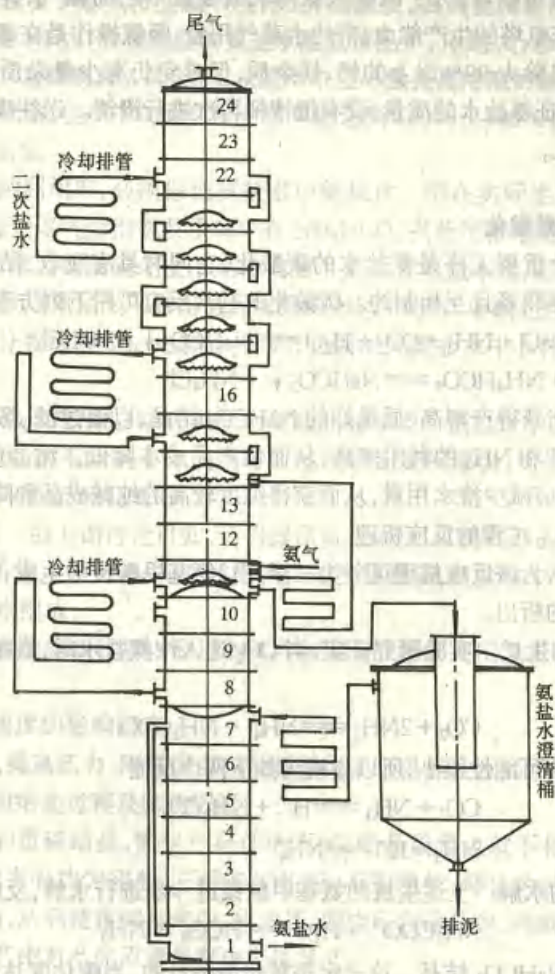


图 7-7 吸氨塔的结构及流程

它是一个多段铸铁单泡罩塔。其流程也以吸氨塔为中心。精制盐水由泵送入塔顶,靠自重逐渐由塔顶流下,每圈中安装单菌帽以利吸收,因该过程是放热过程,为保证吸收良好,在塔的上部、中部两次引出到冷却排管(或板式换热器)进行冷却,然后回到其下一圈继续吸氨,第二次冷

却后进入氨气入口圈,这里氨浓度最高,放热最强烈,为保证吸氨效果好和达到一定的浓度要求,故将盐水循环冷却吸收,并可随时引出部分氨盐水,经澄清桶排泥并经冷却后送入氨盐水罐(位于塔底下7圈)气液在塔中逆流接触,盐水自上而下其含氨量越来越多,氨气浓度自下而上越来越小。出塔尾气中所含微量氨再送入净氨塔以水吸收,得到的稀氨水可送去化盐。

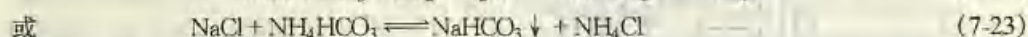
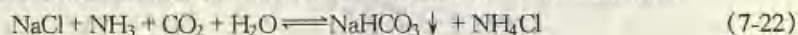
为了节约动力,在引出塔外冷却时,必须保证液体有足够的静压头,使其能克服管道阻力而返回塔内。为此,需要仔细确定塔体上的进出口位置,必要时要加空圈。

由于吸收的氨来自蒸氨塔,为了减少吸氨系统因装置不严而漏气、并加快蒸氨塔内 CO_2 及 NH_3 的蒸出、提高蒸氨塔的生产能力、节约水蒸气用量,吸氨操作是在部分真空下进行的。

精制后的盐水虽已除去 99% 以上的钙、镁杂质,但难免仍有少量杂质进入吸氨塔形成碳酸盐和复盐沉淀,为保证氨盐水的质量,设有澄清桶再次进行澄清。送往碳化的氨盐水中所含沉淀不应多于 0.1 g/L。

7.2.5 氨盐水的碳化

氨碱法制碱的一个重要工序是氨盐水的碳化,它同时具有吸收、结晶和传热等单元过程。这些单元过程互相联系且互相制约。碳酸化的基本反应可用下列方程式概括:



碳酸化的目的在于获得产率高、质量好的 NaHCO_3 结晶,以便过滤、煅烧得到成品。结晶的产率高,标志着 NaCl 和 NH_3 的利用率高,从而使产品成本降低。结晶质量好即粒大均匀,便于和母液分离,可相应减少洗水用量,从而获得纯度较高的纯碱成品和降低蒸氨负荷。

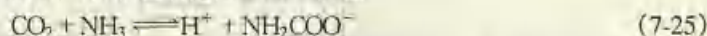
1. 氨盐水吸收 CO_2 过程的反应机理

比较多的研究者认为该反应机理可分为三步:(1)氨基甲酸铵的生成;(2)氨基甲酸铵的水解;(3)碳酸氢钠结晶的析出。

(1) 氨基甲酸铵的生成 实验研究证实,当 CO_2 通入浓氨盐水时,最初总是出现氨基甲酸铵



这一三分子反应的可能性很小,所以应视为如下两个反应



(2) 氨基甲酸氨的水解 上述生成的氨基甲酸铵进一步进行水解,反应为:



(3) 复分解析出 NaHCO_3 结晶 这一步是碳化最终目的,当碳化度达到一定高度,溶液中 HCO_3^- 浓度积累相当高以后, HCO_3^- 与 Na^+ 浓度相乘积超过了该温度下的 NaHCO_3 溶度积,则产生沉淀,完成了复分解反应:



在碳化液中氨浓度一直是较高的,且比 OH^- 浓度大好多倍,所以吸收的 CO_2 绝大部分消耗到生成氨基甲酸铵的反应中去,这已为实验所证实。

沉
的水解
2.
(1)

碳
是 NH_4F
完全,Na
但因受种
(2)

为获
不足外,
① 碳

碳化度 R
出氨量占
氨的不足

② 重
算的氨盐
常以共晶

③ 最
中每吸收
偏离最适

氨盐
1.14。

(3) 碳
对于

(4) 碳
碳化

度、形状等
好,有利于
结晶在整个

NaHC
液中析出

但结晶粒度
根据结

所以,在结
有 50% 的

总体质量就

定的浓度要求,
入氨盐水罐(位
自下而上越来越

克服管道阻力

蒸氨塔内 CO_2
空下进行的。
吸氨塔形成碳
氨盐水中所含

传热等单元过
括:

(7-22)

(7-23)

到成品。结晶
F即粒大均匀,
氨负荷。

基甲酸铵的水

出现氨基甲酸

(7-24)

(7-25)

(7-26)

(7-27)

高度,溶液中
 HCO_3^- 溶度积,

(7-28)

(7-29)

H_2O 绝大部分消

沉出 NaHCO_3 的反应将影响一系列复杂离子反应的平衡,其中最重要的是使氨基甲酸铵的水解反应向右移动,致使溶液中溶态氨积累,从而对于吸收过程产生显著影响。

2. 工艺条件

(1) 碳化度及其对钠利用率的影响

$$\text{碳化度 } R = \frac{\text{全部 } \text{CO}_2 \text{ 摩尔数}}{\text{总 } \text{NH}_3 \text{ 摩尔数}} \times 100\% \quad (7-30)$$

碳化度的大小表明了总氨转变成 NH_4HCO_3 的程度,因为直接影响 NaHCO_3 平衡产率的是 NH_4HCO_3 而不是 NH_3 。故在适宜的氨盐水组成情况下, R 越大,总氨转变成 NH_4HCO_3 越完全, NaCl 利用率 U_{Na} 就越高。为此,工业生产中应尽量提高溶液的碳化度以提高钠利用率。但因受种种条件的限制,生产中的碳化度一般只能达到 180%~190%。

(2) 氨盐水的组成

为获得最高的钠利用率,必须保证氨盐水中氨盐比。但在实际生产过程中,除碳化度 R 不足外,还必须考虑到尾气带出氨及重碱中有 NH_4HCO_3 共析所带来的影响。

① 碳化塔尾气带出氨及碳化度不足的问题 最适宜氨盐水组成是以碳化塔取出晶浆的碳化度 $R=200\%$,且塔顶尾气不带出氨为前提的,但实际生产中碳化度常小于 200%,尾气带出氨量占总氨的百分数约为 6%~12%。因此,必须加大氨盐水中 NH_3/NaCl 的比值,以弥补氨的不足。

② 重碱(NaHCO_3)中 NH_4HCO_3 共析对氨盐比的影响 氨盐水中的氨盐比应当比理论计算的氨盐比更高一些,这不但是由于上述塔顶尾气带走氨的原因,而还因为 NaHCO_3 沉淀中常以共晶形式带走一部分 NH_4HCO_3 。

③ 最佳吸氨量 由上面讨论可知,适当提高氨盐比,可以提高钠的利用率,但在吸氨过程中每吸收 1 mol 氨将带入约 0.4 mol 的水蒸汽。故吸氨越多,氨盐水中 NaCl 浓度必然越低,越偏离最适宜的氨盐水组成。

氨盐水中最适宜的氨盐比可以利用 $\text{NH}_3\text{-NaCl-H}_2\text{O}$ 溶解度图进行计算,一般采用 1.12~1.14。

(3) 碳化吸收速度的影响因素

对于碳化过程,提高压力、降低温度以及低碳化度阶段都是有利于增大吸收速度的。

(4) 碳酸氢钠的结晶过程及影响因素

碳化塔中产生的重碱结晶,随生产条件的不同,结晶质量也就不相同。结晶质量包括粒度、形状等因素。粒大而均匀完整、三维长度相近、不为须状,即认为结晶质量好。结晶质量好,有利于过滤洗涤,从而使重碱含水少、收率高、煅烧后含盐分少,纯碱质量可以提高。所以,结晶在整个纯碱生产中对产品质量具有决定性意义。

NaHCO_3 在水中的溶解度随温度降低而减少,但它极易形成过饱和溶液。由于过饱和溶液中析出 NaHCO_3 结晶的情况,与一般结晶过程类似,即过饱和度愈大,则结晶速度也愈快;但结晶粒度小、质量差、对过滤煅烧操作不利。

根据结晶动力学可知,在同样的过饱和情况下,高温时晶粒生长速度大于晶核生成速度。所以,在结晶初期维持较高一些的温度($\approx 60^\circ\text{C}$)就不致于形成过多的细小结晶。实验证明,如有 50% 的 NaHCO_3 在适宜的温度下结晶出来,那么结晶的后半期中,由于已有良好的基础,对总体质量就有了保证。塔的中部温度较高是依靠反应热来维持的。从中部温度降到出塔温度

25℃左右的冷却过程应该逐渐进行,因为此时虽已有良好的基础,但过快的冷却也仍会造成过大的过饱和度,可能产生新的细小的晶体。

碳化塔的良好操作应当是析出大粒而完整的重碱结晶,以满足下一步母液分离的要求。否则,不但影响产品质量,而且会使蒸氨工序的负荷加大。

结晶的质量可用沉降时间和沉降率表示。沉降时间是以量筒取塔下晶浆 100 ml,静置到液、固两相分层所需要的时间测定的。一般要求 150~200 s 为合格。而所谓沉降率是:在分层后固相层的体积占总体积的百分率,一般要求 40%~50%。

碳化过程中放出大量的热,将使进塔液温度升高。但温度高时,重碱的溶解度大。所以在结晶析出后应当逐渐降温,不仅使反应趋于完善,析出尽可能多的结晶;并在继续析出时可使晶体长大,质量得到保证。此刻应特别注意控制冷却的速度,在较高温度下(一般为中部温度)应适当维持一段时间,以期有足够晶核生成。若冷却时间太短,晶核尚未形成,会导致过饱和度的增大,最后将出现大量细小结晶,这些细小结晶甚至在取出时还未能长大,形成“细晶浆”(又称“浮碱”)。但若冷却时间过长,将降低设备利用率。塔的下部降温也不可过快,以免形成细晶。一般液体在塔内停留时间约为 1.5~2 h,取出温度约为 25℃左右。

为使过饱和度保持一个恒定值而不致增大太快,开始降温时速度要慢。而在最终出塔前降温可以稍快,因此时碳化度已高,反应速度减慢,不易形成大的过饱和度,适当的加速冷却也不致生成细晶,反而可提高产率。由保证结晶质量的观点出发,要求塔内各层温度分布如图 7-8 所示。由图可见,最高反应温度约在塔高的 2/3 处,约为 65℃左右,然后逐渐冷却达到取出温度 22~28℃或稍高些。

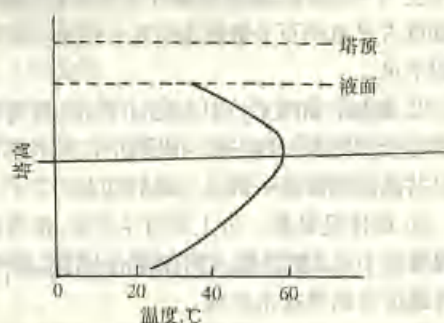


图 7-8 碳化塔不同高度的温度分布

3. 碳化流程与碳化塔

(1) 碳酸化的典型流程如图 7-9 所示。

将氨盐水注入清洗塔(又称预碳化塔和中和塔)中,鼓入窑气,溶解塔中的疤垢并初步提高碳化度后再送入制碱塔,窑气和煅烧重碱所得的炉气经压缩机(往复式或离心式)升压后送入塔内。出塔晶浆靠液位而自压到碱液槽,送往过滤工序。制碱塔生产一段时间后,塔内结疤垢较厚,传热不良,不利析晶,而清洗塔则已清洗完毕,此时可互相倒换使用,谓之“倒塔”。两塔尾气中含有少量氨及二氧化碳,经气液分离后尾气送往盐水车间供精制盐水用。在实际生产过程中,常由数塔组成一组,其中一塔清洗,其它塔制碱。

2. 碳化塔的结构及性能

碳化塔是氨碱法制碱的主要设备之一,它是由许多铸铁塔圈组装而成,结构上大致可分上下两部分:上部为 CO_2 吸收塔段,每圈之间装有笠帽形板及略向下倾的漏液板,板及笠帽边缘都有分散气泡的牙齿以增加气、液接触面积促进吸收。塔的下部有十个左右的冷却水箱,用以冷却碳化液以析出结晶,水箱中间也没有笠帽。碳化塔的底部都有晶浆取出口和浓 CO_2 气(下段气)入口,冷却段中部又有稀 CO_2 气(中段气)入口(此为两段进气)。塔顶有进液口及尾气出口,塔高约 22~25 m,目的是为保持一定的液柱和停留时间。液柱过高也无必要,因为静

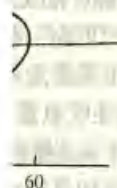
冷却也仍会造成过

母液分离的要求。

晶浆 100 ml, 静置到
所谓沉降率是: 在分

溶解度大。所以在
在继续析出时可使
(一般为中部温度)
形成, 会导致过饱和
长大, 形成“细晶浆”
不可过快, 以免形成

--- 塔顶
--- 液面



的温度分布

的疤垢并初步提高
离心式) 升压后送入
时间后, 塔内结疤垢
谓之“倒塔”。两塔
水用。在实际生产

结构上大致可分上
液板, 板及笠帽边缘
右的冷却水箱, 用以
取出口和浓 CO_2 气
塔顶有进液口及尾
高也无必要, 因为静

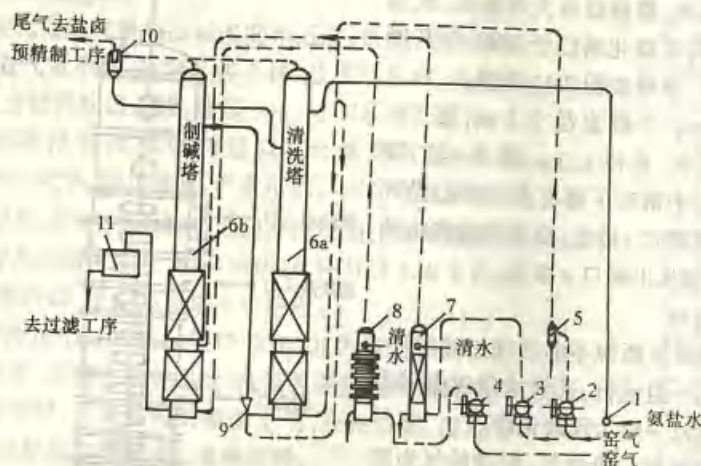


图 7-9 碳酸化示意流程图

1—氨盐水泵; 2—清洗气压缩机; 3—中段气压缩机; 4—下段气压缩机; 5—分离器; 6a、6b—碳化塔;
7—中段气冷却塔; 8—下段气冷却塔; 9—气升输鹼器; 10—尾气分离器; 11—碱液槽

压过高会造成压缩机功率浪费。而出塔晶浆的碳化度也不会增加多少。

碳化塔直径一般为 1.98~3.2 m, 目前有向大型化发展的趋势。

冷却水箱的前后花板上设有隔板, 可使冷却水走向成为“之”字或“田”字等, 以利用传热。冷却水箱多采用铸铁制作, 传热系数初期为 $186 \sim 233 \text{ W/m}^2 \cdot \text{K}$ 。后期降到 $105 \sim 140 \text{ W/m}^2 \cdot \text{K}$ 左右。经验认为, 日产每吨纯碱需冷却面积 $6 \sim 8 \text{ m}^2$ 。

我国各碱厂仍以传统型设备为主, 其主要性能见表 7-4。

表 7-4 不同尺寸碳化塔结构及主要工艺性能表

塔径(mm)	1 200	1 600	1 980	2 500	3 200
塔高(mm)	22 542	18 200	25 069	25 117	26 650
笠帽 上段	16	16	21	21	29
个数 下段	0	0	11	10	
塔圈高度(mm)	600	450	375, 506	420	540, 800
隔板开孔率(%)	11.3	9.55	9.0	8.4	9.8
上盖开孔率(%)	33.7	23.4	33.5	31.5	—
水箱数, 个	10	10	11	9	12
冷却面积(m^2)	128	200	内 459 外 533	内 737 外 912	1 921
操作压力(MPa)	1.3	0.7	0.4	0.4	0.3
生产能力(t/d)	21	35.6	74	122	220~240
空塔气速(m/s)	0.0355	0.038	—	—	—
生产强度($\text{t/m}^3 \cdot \text{d}$)	0.843	0.554	0.716	0.98~1.15	1.22~1.33

由于水箱笠帽式碳化塔存在冷却表面结疤、生产周期短、结构复杂、建设投资大等缺点,我国开发的自然循环外冷式碳化塔已于 1985 年开展了工业规模的试验。该塔如图 7-11 所示。

上段直径 2.5m, 下段直径 2.8 m, 高 26.5m。外部冷却器 2 台, 直径 1.3m、高 7.4m。塔上部为筛板和泡罩, 中部和下部有多个中心循环管, 塔内悬浮液经循环口 j 排出, 冷却后液体由循环口 m 返回塔内, 而从出碱口 a 取出。

3. 碳化塔的作业

为了保证出碱晶浆源源不断送往过滤工序, 把几座碳化塔联成一组运行, 通常采用四座塔为一组, 三座为制碱塔; 一座为预碳化塔。

过去碳化塔曾采用一段进气, 所进的气为窑气与炉气(燃烧来 CO_2 气)的混合气, 浓度很难超过 60%。以后改为两段进气, 即从塔底送入浓度高的炉气, 冷却段中部送入窑气(浓度约为 36%~40%, 这就更符合逆流原理, 强化了吸收, 提高碳化程度, 因而提高了钠利用率。至于清洗塔, 主要目的在于洗疤, 要求鼓动促溶并适当提高温度, 因此, 以窑气从塔底通入并关闭冷却水及中段气入口。碳化塔在操作中, 一般要掌握好下段气的量与浓度。实践指出, 部分窑气送往下段, 使下段气浓度由 90% 降至 82%~84%, 可使碳化周期增大, 转化率可达到高而稳。这主要是由于下段气量增大提高了效率的结果。但如果下段气量过大, 反应区将下移, 会使冷却水管结疤增多, 反而缩短碳化周期。经验证明, 适当提高下段气量, 维持 CO_2 浓度达到 84% 左右, 产量不会下降, 转化率却有所提高。

碳化塔的适宜控制条件如下:

(1) 碳化塔液面的高度应控制在距塔顶 0.8~1.5 m 间, 液面过高, 尾气带液现象严重并会造成出气总管堵塞。液面过低, 则出气含氨及 CO_2 量大, 使其损失增加并降低塔的生产能力。

(2) 严格控制塔的中部温度较高为好, 且在高度方向上分布的温热区域应较宽, 以保证结晶质量。这是因为维持中部温度高不但转化率高,

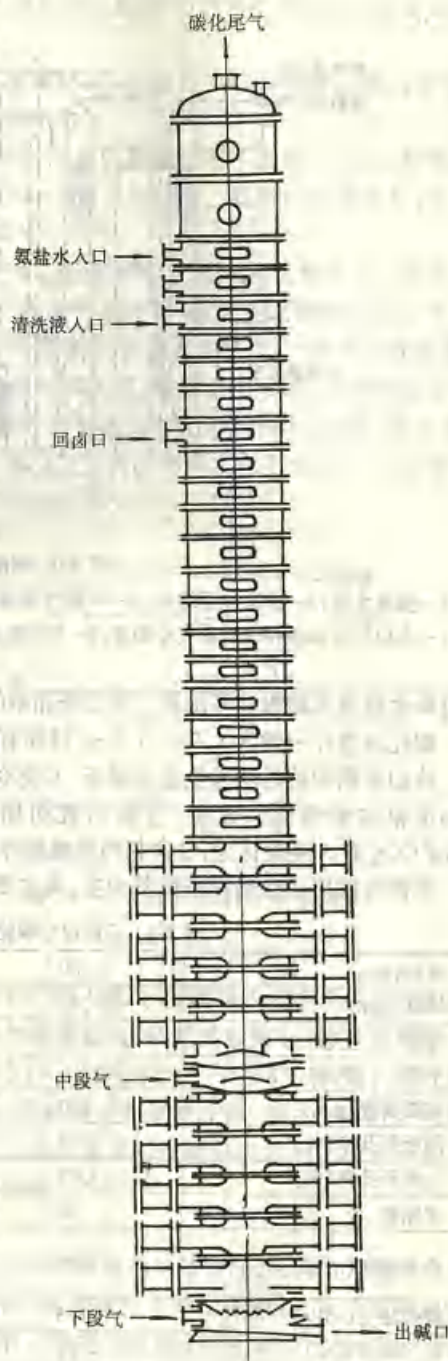


图 7-10 碳化塔

并且可使 NaHCO_3 结晶粒大而均匀。中部温度最高的区域约在塔高 $3/5$ 处左右。

(3) 碳化塔进气量与出碱速度相适应, 否则, 如出碱速度过快而进气量不足, 反应区将下移, 造成结晶细, 产量下降。反之, 会使反应区上移, 塔顶 NH_3 与 CO_2 损失过大。

(4) 出碱液温度要保持适宜。出碱温度低, 会使 NaHCO_3 析出较多, 转化率高, 产量增加。但温度过低会过多消耗冷却水, 并能引起堵塔, 缩短操作周期。出碱温度主要靠调节冷却水量来实现, 但必须注意, 调节时不可变化过快, 以免突然冷却, 造成结晶细小而堵塔。

(5) 要按规定时间进行换塔并在 2h 内恢复正常。在碳化塔操作中, 应尽力避免温度、流量等条件的剧烈波动变化。正常操作时, 不同塔高的截面上气、液相组成、温度等均不相同, 但要求在该截面上是稳定的。

7.2.6 重碱的过滤

纯碱生产中, 过滤过程是用来分离来自碳化塔悬浮液中的 NaHCO_3 结晶。得到的结晶送入煅烧工段, 而母液则和洗涤水一起(称为滤液)送往蒸氨工段回收氨。

纯碱过滤工段的主要任务是使送入煅烧工段的 NaHCO_3 形成连续物料流, 其工艺指标为: 湿 NaHCO_3 含水量 $13\% \sim 18\%$, NaCl 含量 $< 0.4\%$, 总氮含量 $< .8\%$ 。因此, 过滤时必须对滤饼洗涤, 将重碱中残留的母液洗去, 使纯碱中含有的 NaCl 降到最低, 洗水宜用软水, 以免水中所含 Ca^{2+} 、 Mg^{2+} 形成沉淀而堵塞滤布。

(一) 过滤机

过滤工段的主要设备是连续式转鼓真空过滤机。

真空过滤是由于过滤机滤鼓内被真空机抽成负压, 形成滤布两边的压力差, 致使母液通过滤布而被抽走, 重碱则截留在滤布表面上, 再由刮刀将重碱刮下, 送至煅烧工序煅烧成纯碱。它的优点是能连续操作, 生产能力大, 自动化程度高, 适合于大规模生产。但它过滤出来的重碱含水量较高, 最低也在 15% 左右, 有时高达 20% 以上。

如图 7-12 所示。

根据进行的过程, 过滤机转鼓可以有条件地划分成以下各区:

过滤区: 在真空下, 母液吸入转鼓, 而 NaHCO_3 结晶则滞留在滤布表面上, 形成滤饼;



图 7-11 自然循环外冷式碳化塔
a—出碱口; b—下段气入口; c—中段气入口; d—氨母液入口; e—尾气出口; j—外循环出口; m1, 2—外循环入口

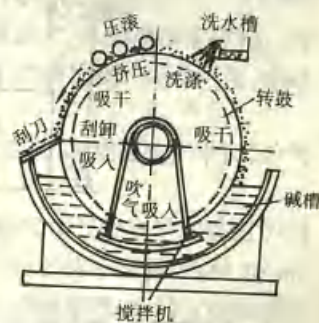


图 7-12 真空过滤机转鼓旋转一周过程中的作用示意图

预干燥区:此时转鼓表面处在悬浮上方,由滤饼往转鼓内抽吸母液;

滤饼洗涤区:往转鼓表面供给洗涤水,洗涤水穿过滤饼进入转鼓,同时由滤饼的晶际空间逐出母液;

主要干燥区:往其中供给空气,空气通过 NaHCO_3 滤饼层并由滤饼的晶际空间排出洗水,从而降低滤饼的水分含量;

闭合区:利用刮刀将 NaHCO_3 滤饼由转鼓表面刮下,同时防止空气在刮刀与母液吸入区之间的间隙处吸入转鼓;

母液吸入区:即所谓滤布“湿”吹洗,在吹压缩空气前进行,这是延长滤布使用期限所必须进行的作业;

吹气区:往小室中送入压缩空气,用以在与气液混合物(真空而进入转鼓)运动相反的方向上恢复滤布,压缩空气首先经过滤布由小室逐出已进入母液吸入区的母液。穿过滤布后,母液不仅由滤布孔隙驱出 NaHCO_3 结晶,而且能溶解这些结晶,从而使滤布再生过程加快。然后用压缩空气吹洗滤布;

过渡区:用于防止送入吹洗的压缩空气进入真空腔室。

转鼓转动一周,完成整个过程循环,而转鼓每一小室均通过各区。

国内碱厂采用的真空过滤机生产能力多在 300~350 t 纯碱/d,大型化的日产能力为 500~600 t。

(二) 真空过滤的流程及控制要求

真空过滤的简要流程如图 7-13 所示:

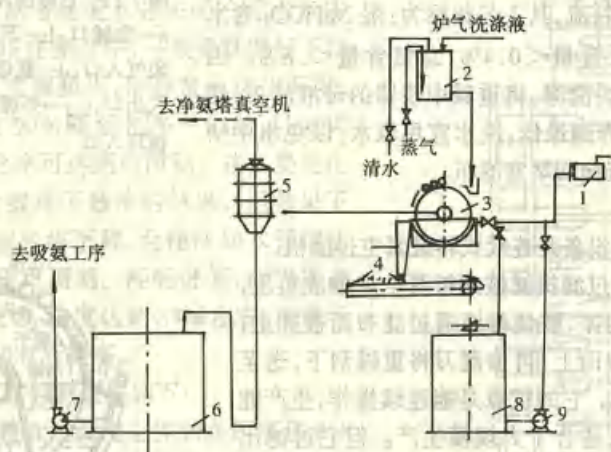


图 7-13 重碱过滤流程图

1—出碱液槽;2—洗水槽;3—过滤机;4—皮带输送机;5—分离器;6—母液 I 桶;7—母液 I 泵;8—碱液桶;9—碱液泵

由碳化塔底部出来的碱液晶浆,经过碱液槽流入真空过滤机的碱槽内,槽内有搅拌器以免重碱在碱槽内沉积。正常操作时,滤鼓的下部约五分之二浸于碱槽内,由于真空系统作用,液

自滤饼的晶隙空间

隙空间排出洗水,

刮刀与母液吸入区

卡使用期限所必须

运动相反的方向

穿过滤布后,母液
上过程加快。然后

的日产能力为 500

母液 I 泵; 8—碱

曹内有搅拌器以免
真空系统作用,液

体通过滤布的孔隙被抽入转鼓内,而重碱结晶则被截留在滤布上。随着转鼓的转动,滤布上的重碱经过洗涤、吸干后转到刮刀处刮下,由重碱皮带输送机送往煅烧工序。重碱被刮刀刮下后,滤布上尚有 3~4 mm 厚的重碱,需用压缩空气吹下,使滤布复原以便继续使用。

液体被吸入转鼓时,同时吸收部分空气,这部分滤液及气体经气液分离器分开。气体中除空气外,还含有少量的 NH_3 及 CO_2 ,需经净氨塔后再由真空机排出。母液则送往蒸氨工序。

真空过滤机使用一段时间后,由于滤布堵塞,需停下来用温水洗涤。

真空过滤机的操作主要是真空度的调节。真空度的大小(26.7~33.3 kPa),决定过滤机的生产能力、重碱中水分及成品质量。其次是滤饼的洗涤问题。洗水温度太高, NaHCO_3 溶解损失大;太低则不易洗净,通常应接近晶浆温度。洗水用量过多,会使母液体积增加,除加大 NaHCO_3 损失以外还会增加蒸氨负荷;洗水用量过少,又会洗不净盐分。洗水用量的多少,依重碱结晶质量而定,以保持最高所得成品纯碱中含 NaCl 不大于 1% 为准。

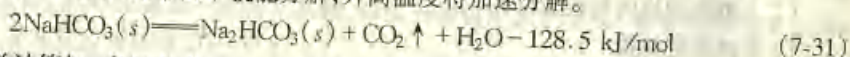
若过滤机采用金属滤网代替毛布或人造纤维,其运转周期较长,可以提高设备的利用率。

7.2.7 重碱的煅烧

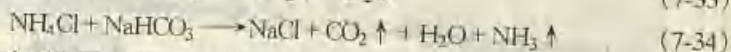
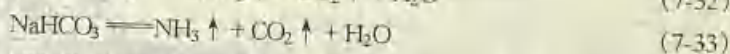
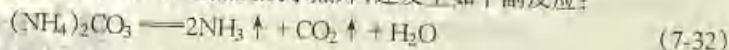
重碱经煅烧分解得到纯碱产品。生产上对煅烧的要求是成品中含盐分少,不含未分解的 NaHCO_3 ;产生的炉气含 CO_2 浓度高且损失少;耗用燃料少。

(一) 重碱煅烧的原理及设备

重碱为不稳定的化合物,常温下就能分解,升高温度将加速分解。



通过热力学计算知,当温度在 100~101℃ 时,分解压力已达到 0.1MPa,即可使 NaHCO_3 分解完全。但实际上在此温度下反应进行很慢。温度越高,则反应越快,在 190℃ 条件下,半小时内即可使 NaHCO_3 完全分解。因此,实际上煅烧的出碱温度多控制在 165~190℃。在煅烧过程中,除以上反应和重碱中的游离水分受热变成水蒸外,还发生如下副反应:



这些副反应的发生,不仅消耗了热量,而且使系统中循环氨量加大,从而增加了氨耗。同时由于最后一个反应是复分解反应,使产品中留下了 NaCl ,影响了产品质量。由此可见,在过滤工序中,重碱洗涤是很重要的。

重碱煅烧过程中,可以得到浓度很高的 CO_2 ,即所谓“炉气”。目前,就我国生产来说,炉气中 CO_2 可达 90% 左右,而重碱的烧成率约 51%。

煅烧重碱的设备称为煅烧炉。目前生产中使用的主要是内热式蒸气煅烧炉。如图 7-14 所示。其炉体为卧式圆筒形。其规格为 $\phi 2.5 \text{ m}$,长 27 m,炉体上设有两个滚圈,相距 16 m。炉体与物料的重量通过滚圈而传给支承托轮,托轮因荷重大而采用滚动轴承,后端支座装有防止炉体轴向串动的挡轮,靠近托轮与挡轮的炉体上装有齿轮圈,由此带动筒体回转。炉体内设有三层蒸气加热管,并以管架支承于炉上,管外边焊有螺旋导热片以增大传热表面。气室设在炉尾,接通高压蒸气后,冷凝水仍由原管回气室,并流入外圈的冷凝水室,以疏水器送往扩容器,闪蒸一部分蒸气后,凝水返回锅炉。

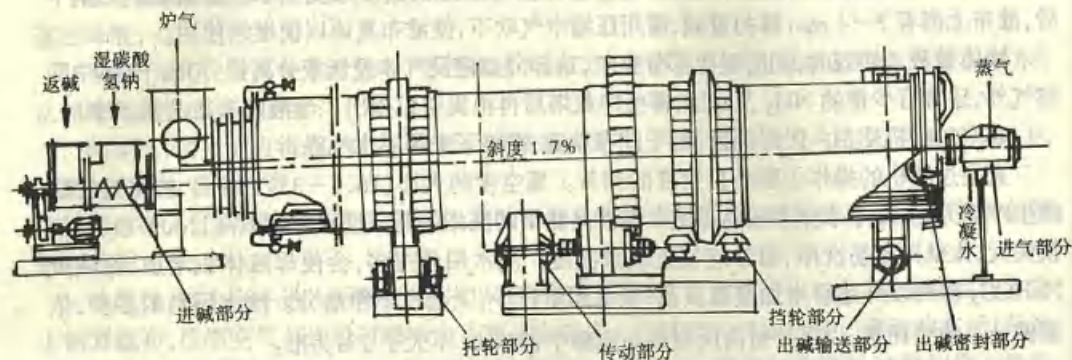


图 7-14 蒸汽煅烧炉

蒸汽煅烧炉的炉头有进碱螺旋输送机和炉气出口, 炉层有出碱螺旋输送机、蒸汽进口及冷凝水出口。

内热式蒸汽煅烧炉具有生产能力大、维修较少、劳动条件好、热效率高等优点。

(二) 重碱煅烧的流程及操作

1. 重碱煅烧流程

采用内热式蒸汽煅烧炉煅烧重碱的工艺流程如图 7-15 所示。重碱由皮带输送机运来, 经

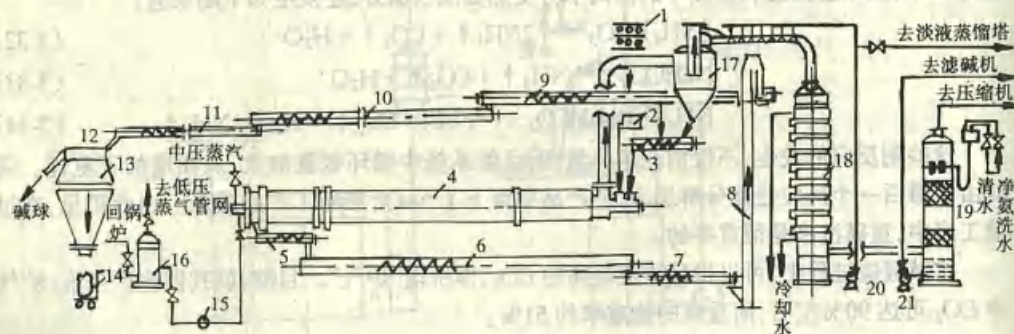
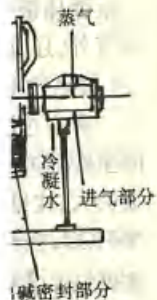


图 7-15 蒸汽煅烧炉工艺流程图

1—皮带输送机; 2—圆盘加料器; 3—返碱螺旋输送机; 4—煅烧炉; 5—出碱螺旋输送机; 6—地下螺旋输送机; 7—喂碱螺旋输送机; 8—斗式提升机; 9—分配螺旋输送机; 10—成品螺旋输送机; 11—筛上螺旋输送机; 12—圆筒筛; 13—碱仓; 14—磅秤; 15—疏水器; 16—扩容器; 17—分离器; 18—冷凝塔; 19—洗涤塔; 20—冷凝泵; 21—洗水泵



气进口及冷

送机运来,经



一地下螺旋
几; 11—筛上
8—冷凝塔;

重碱流子进入圆盘加料器控制加碱量,再经进碱螺旋输送机与返碱混合,并与炉气分离器来的粉尘混合进炉,经中压蒸气间接加热分解约停留 20 min,即由出碱螺旋输送机自炉内卸出,再经一系列输送设备,将一部分成品送回炉内体返碱,一部分送往圆筒筛入仓。

煅烧过程中产生的炉气,经除尘、冷却、洗涤,CO₂ 浓度可达 90% 左右,由 CO₂ 压缩机抽送碳化塔使用。

近年来天津碱厂在 0.6 Mt 纯碱扩建工程中,采用了三台 $\phi 3.6$ m,长 34 m,重 194 t 的煅烧炉,这是我国制碱工业目前最大的煅烧炉。

2. 蒸气回转煅烧炉的操作控制要点

(1) 出碱温度 为使重碱分解完全,一般控制在 150~190℃,如低于 150℃,则质量不合格。为了避免把包装袋烧坏,根据包装袋的材质要求,出炉热碱应进一步冷却到 50~100℃ 左右。

(2) 炉气温度 炉气温度应尽量保持在 108~115℃;为了使出气管及旋风除尘器不粘不堵,须用蒸气保温。

(3) 中压蒸气 一般由电厂供给。压力为 2.9~3.3 MPa,其过热温度视输送距离而定,一般过热 25~50℃,从而保证入炉时稍有预热,以免在总管中蒸气冷凝。

(4) 返碱量 生产中为避免因重碱含水分较高,导致炉内结疤,将一定量煅烧后的成品碳酸钠(称为返碱)与重碱混合,使其平均水分降至 6%~8% 为宜。

(5) 存灰量 煅烧炉中存灰量的多少,标志着重碱在煅烧炉内反应时间的长短。为了保证重碱的完全分解,就必须保证一定的存灰量,该量与煅烧炉大小有关,对目前采用 $\phi 2.5$ m 的煅烧炉来说,存灰量应保持在 20~25 t。

(三) 纯碱规格及重质纯碱的制造

煅烧后所得最终产品——纯碱,外观为白色粉末,其组成应符合表 7-5 中的规格要求。

表 7-5 纯碱产品规格

指 标 名 称		国家标准(GB210—80)		
		一级品	二级品	三级品
总碱量(以 Na ₂ CO ₃ 计)(%)	≥	99.0	98.5	98.0
氯化物(以 NaCl 计)(%)	≤	0.80	1.0	1.2
铁(以 Fe ₂ O ₃ 计)(%)	≤	0.008	0.01	0.02
水不溶物(%)	≤	0.10	0.15	0.20
烧失量(%)	≤	0.5	0.5	0.7

通常生产的纯碱堆积密度为 0.5~0.6 t/m³,称为轻质纯碱或轻灰。这种纯碱占体积大,不便于包装运输,且在使用过程中飞散损失较多。因此,目前生产中多加工到堆积密度为 0.8~1.1 t/m³ 左右,这种纯碱称为重质纯碱或重灰。

重灰制造的主要方法如下:

1. 水合法

水合法制重质纯碱的流程如图 7-16 所示。

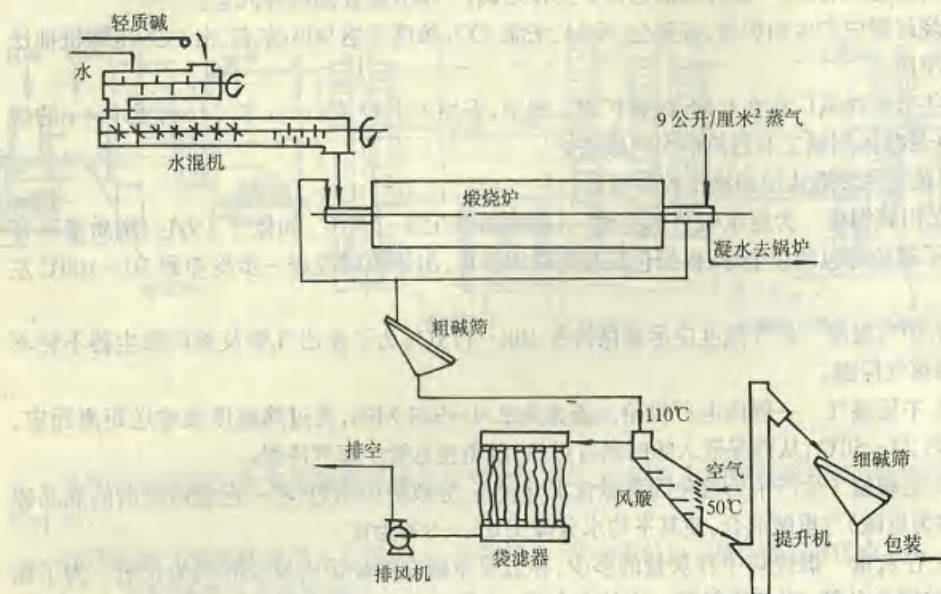
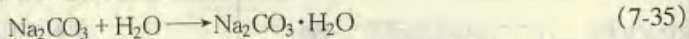


图 7-16 水合法制重质纯碱流程

由煅烧炉来的轻灰,温度在 $150 \sim 170^{\circ}\text{C}$,用螺旋输送机送入水混机内,同时在水混机内喷入热水让其均匀混合,并发生下列反应:



水混时间为 20min,混合物中含水量在 $17\% \sim 20\%$,温度为 $90 \sim 100^{\circ}\text{C}$,所得一水碳酸钠在重灰煅烧炉内与低压蒸气(约 1 MPa)进行间接热交换,一水碳酸钠受热失去结晶水,即得重灰。部分作返碱,部分成品经过筛、冷却、包装。

炉内生成炉气带有碱尘,经除尘、洗涤后排空。

2. 机械挤压法

机械挤压法是生产重灰的一种新方法。来自煅烧工序的轻灰由刮板运输机运到与轧机相连的料仓,经垂直及水平螺旋运输机(给料机)给轧机喂料,轻灰在 230 t 的机械压力下,将碱粉挤碎后,通过刮板运输机、斗式提升机,运到第一级振动筛过筛,大于 2 mm 送磨碎机粉碎,0.3~2 mm 的送成品工序、小于 0.2 mm 的返回到轻灰工段。从磨碎机出来的颗粒再经二级振动筛,大于 2 mm 的再去磨碎机,0.3~2 mm 的送到成品工序。小于 0.2 mm 的返回轻灰仓。

由一、二级分筛机来的重灰再经分筛机分级,0.3~2 mm 与 0.2~1 mm 分开包装。流程如图 7-17 所示。

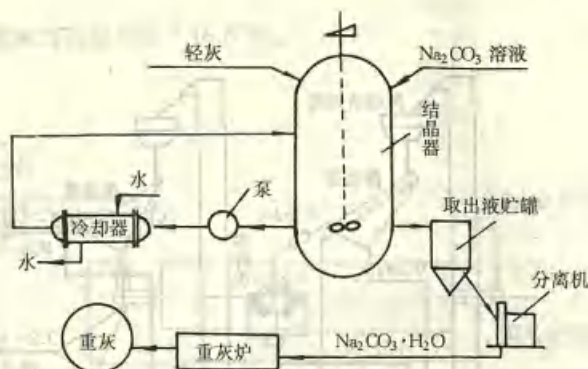


图 7-18 结晶法制重灰流程示意图

7.2.8 氨的回收

氨碱法生产中所用的氨是循环使用的,制备 1t 纯碱所需氨量约为 0.4~0.5 t,加入系统的氨,由于逸散、滴漏等原因而造成损耗。为了保持系统有一定量的循环氨量,每生产 1 t 纯碱,约需补充氨 1.5~3 kg。由此可知,减少氨的损失和尽力做好氨的回收是氨碱法生产中一个十分重要的问题。现代氨碱法生产中,一般均将含氨的各种料液收集起来进行氨的回收。

含氨料液主要指过滤母液和淡液。过滤母液含有可直接加热分解蒸出的“游离氨”(约 25 tt 以及需要加石灰乳(或其它碱类物质)使之反应才能蒸出的“结合氨”(约 75 tt)。由于料液中还含有 CO_2 ,为了避免石灰的不必要损失,故均采用两步进行。先将料液加热以逐出液中游离氨和 CO_2 ,然后再加石灰乳与结合氨作用,使其变为游离氨而蒸出。

生产中的炉气洗涤液、冷凝液及其它含氨杂水等统称为淡液,其中只含有游离氨,这些淡液中的氨的回收比较简单。为了减少蒸氨塔预热段的负荷,目前淡液多与过滤母液分开,使其在淡液蒸馏塔中加热蒸出,并予以回收。

母液和淡液的总容量约为 $6\sim7\text{ m}^3/\text{t}$ 纯碱,其中母液当中约为 $5.5\sim6.5\text{ m}^3/\text{t}$ 纯碱,而淡液约为 $0.5\sim1.0\text{ m}^3/\text{t}$ 纯碱。

(一) 蒸氨过程的流程与设备

蒸氨过程的流程见图 7-19,其主要设备有蒸氨塔,见图 7-20。它包括母液预热器、预热段和石灰蒸馏段。

母液预热器和气体冷凝器两部分的作用是回收热量和降低氨气中的水分。它们由 7~

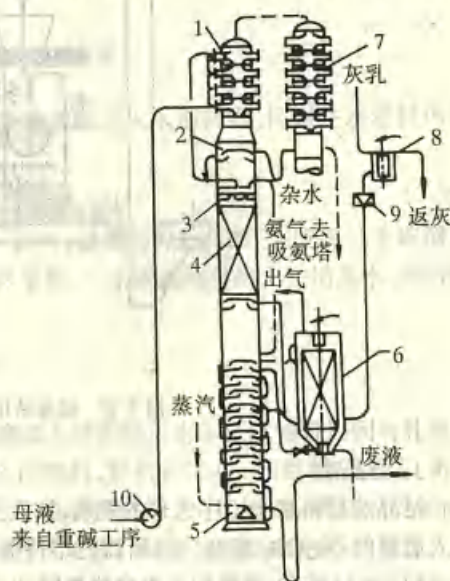


图 7-19 蒸氨流程简图

1—母液预热器;2—精馏段;3—分液槽;4—预热段;5—石灰乳蒸馏段;6—预灰桶;7—气体冷凝器;8—加石灰乳缸;9—石灰乳流堰;10—母液泵

10个卧式水箱组成,管外走热气,管内走母液或冷却水。冷母液在母液预热器中与蒸出的热气体间壁换热,使其温度由25~32℃升高到70℃左右,而后进入预热段。同时,热气体温度由88~90℃降到65~67℃后进入气体冷凝器,其中大部分水气经冷凝后进入吸氨塔。

预热段位于塔的中部,也可称为加热器。一般采用各种填料或设置“托液槽”,以使气、液良好接触,加大热量、反量传递表面。母液由上部经分液板加入,与下部来的热气体直接接触,蒸出所含的游离 NH_3 及 CO_2 ,最后剩下只含结合氨和盐的母液。

经预热段后,因母液中的结合氨在加热时不能分解,所以先将母液从塔中引入预灰桶与石灰乳混合。预灰桶上装有搅拌器,使用液与石灰乳混合均匀。此时,大部分结合氨即转变为游离氨,再进入塔的石灰乳蒸馏段进行蒸馏。石灰乳蒸馏段位于塔的下部,内设十多个单菌帽形泡罩板。预灰桶出来的含石灰乳的母液加入该段的上部,与塔底蒸汽逆流接触。通过这段蒸馏后,99%的氨已被蒸出,含微量氨的废液由塔底排出。

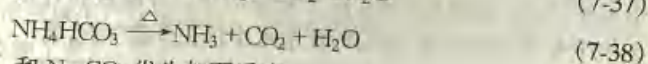
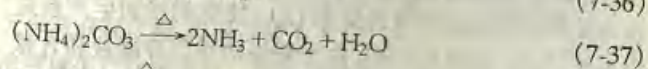
蒸馏塔所需热量是由塔底进入的低压蒸汽供给的,每生产1t纯碱的耗用蒸汽1.5~2.0 t。

近年来塔内采用聚丙烯玻璃纤维增强的鲍尔环 $\phi 75\text{mm} \times 75\text{mm} \times 12\text{mm}$,优点是质轻易装卸,破碎率低。

(二) 蒸氨过程中的化学反应

母液是含有多种化合物的溶液,蒸氨过程中所发生的主要化学反应如下。

1. 预热段中的反应



溶解于过滤母液中的 NaHCO_3 和 Na_2CO_3 发生如下反应:

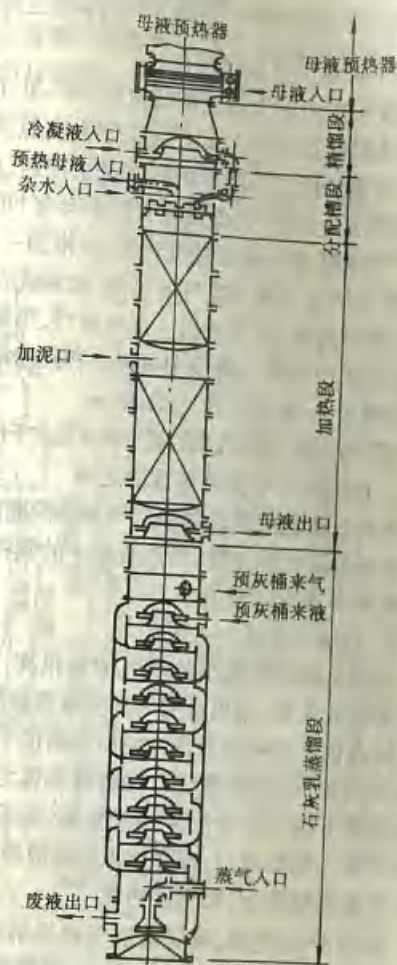
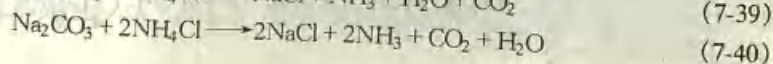
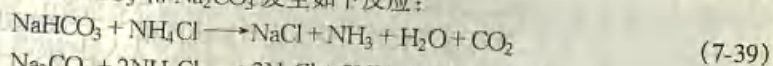
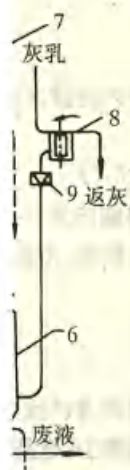


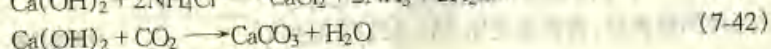
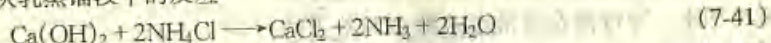
图 7-20 蒸氨塔

5 t, 加入系统
每生产 1 t 纯
碱法生产中一
氨的回收。
“离氨”(约 25



灰槽; 4—预热
7—气体冷凝
; 10—母液泵

2. 在调和槽及石灰乳蒸馏段中的反应



(三) 蒸氨工艺条件分析

温度和压力不太高的废蒸汽(0.16~0.17 MPa),由蒸氨塔底直接通入,其量应使预热段底部液体温度达 100℃,以尽量除净游离氨及 CO₂。一般来说,蒸气消耗量为(1.5~2)t 蒸气/纯碱。塔顶温度以冷凝器的冷水量来控制,应使送至吸氨系统的气温维持在 60~62℃ 左右,过高则带水分太多;过低则在管道中会有 NH₄HCO₃ 等盐类结晶析出而造成堵塞。

对于蒸氨来说减压是有利的,故塔顶一般略呈约 666 Pa 的真空,这样虽能防止氨的逸散损失,但又产生了漏入空气的可能,故系统应密闭以免冲淡氨气而不利吸收。塔下废液排出因系减压等焔过程,可释放出一部分蒸汽,用于预热水以制石灰乳;或者通入小蒸馏塔以蒸出各种含氨杂水中的氨。废液中氨损失和热量消耗与液量成正比,故应避免液体过于稀释,所以石灰乳应稠些,一般含活性 CaO 180tt。

为了蒸出氨,要求液相的氨平衡分压大于所相存在的氨分压,在这一方面应注意两个特殊地点。

1. 预热段与石灰乳蒸馏段之间

来自石灰乳蒸馏段的浓气与预热段底部的液体接触之处,在此液体中的氨全部是结合氨,其平衡氨分压应等于零,所以气相中的氨将有部分解于液相。这就是预热段出口溶液不能将游离氨全中逐出的理由。

2. 料液入口处

自预热段顶部逸出的氨气浓度很高,它较加入新料液的氨平衡分压高,结果会有一部分氨重新溶入料液,所以料液应加在该处气相氨分压比它所具有的平衡氨蒸气压力小的地方为宜,从而使推动力对蒸馏来说为一正值。由气体冷凝器流下的热凝液浓度一般较浓,如不另去淡液蒸馏塔而返回加入预热段顶,则必被入口料液冲淡,造成部分氨及 CO₂ 反复蒸发冷凝,浪费了热能。

每生产 1t 纯碱,蒸氨塔底部排出的废液量约为 7~10 m³。根据蒸馏塔底部的蒸气压力,废液温度为 90~120℃。其中除了 NaCl、CaCl₂ 之外,有微量的 NH₃;还有少量 Ca(OH)₂、CaCO₃ 和 CaSO₄,它们有一部分溶解,有一部分是悬浮固态物。此外,差不多都是石灰乳带进蒸氨塔的砂子。

(四) 淡液蒸馏

淡液蒸馏过程也是直接用水蒸气“气提”的过程,靠直接热量和质量传递而蒸出氨和 CO₂,使它们回到生产系统中重复使用。实际生产中,由于煅烧的炉气冷凝液和含氨杂水中含有少量纯碱,所以即使杂水中存在少量“结合氨”,也会转变为游离氨。因此,淡液是一个不含 NaCl 和 NH₄ 的 NH₃-CO₂-H₂O 系统,其蒸馏过程的主要反应与加热段相同。其流程如图 7-21 所示。

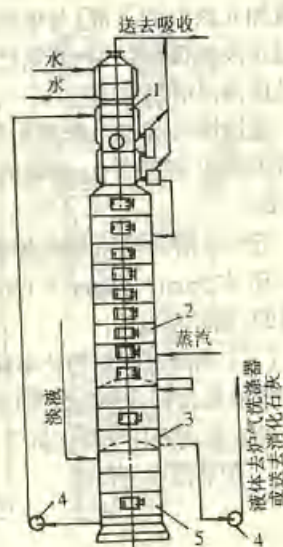


图 7-21 淡液蒸馏工序流程图

- 1—淡液蒸馏气体冷凝-冷却器;
- 2—淡液蒸馏塔;3—脱气液体贮槽;
- 4—泵;5—淡液贮槽

(7-42)

防止氨的逸散
下废液排出因
留塔以蒸出各
一稀释,所以石

全部是结合氨，
口溶液不能将

吸收

凝-冷却器;
脱气液体贮槽;

7.2.9 氨碱法生产总流程

氨碱法制碱总工艺流程见图 7-22,从中可以看出生产过程中各工序间的相互关系。

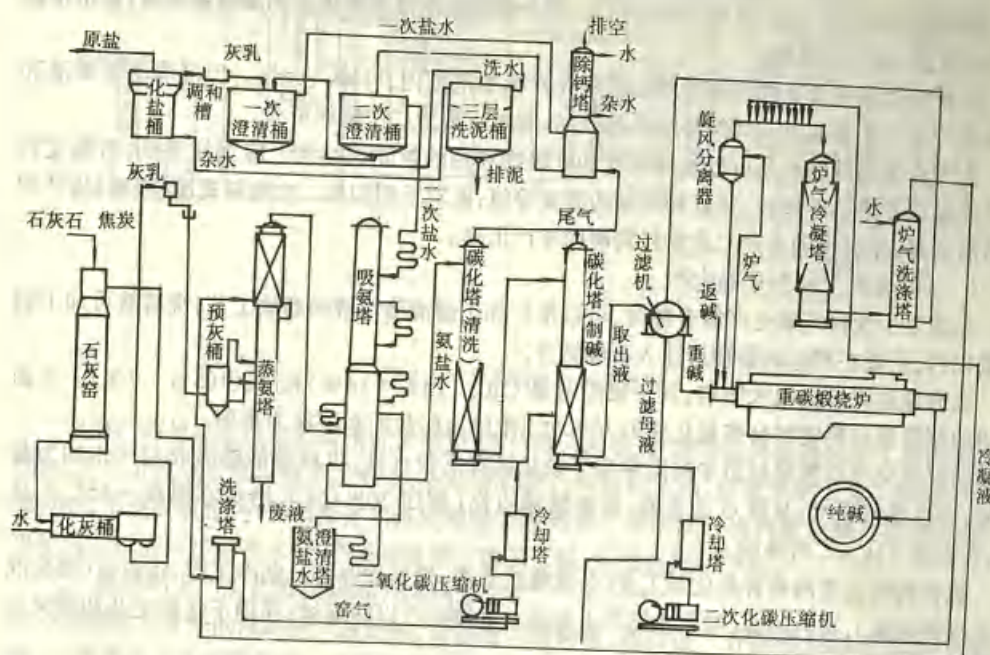


图 7-22 氨碱法制纯碱工艺总流程

7.2.10 氨碱法纯碱生产二次物料资源的加工

随着大工业的飞速发展,由于环境的污染,破坏了自然界原有的动态平衡,严重地威胁着人类的生存和发展,因此,在我国乃至全世界,都已经开始或进行着对改善环境质量的研究。在化工生产中,理想的是无废物工艺,即保证需要某一产品时能够充分地、最合理地利用天然资源,不使固体和液体废物排入露天水域或存放场,而且不将有害废气排入大气。但实施这样的流程,特别是对于大吨位的氨碱法纯碱生产非常困难。目前只能减轻对环境的污染,还不能完全消除污染,因此,只能建立少废物工艺。

在建立少废物工艺时,力求最充分地利用天然资源,保证对规定产品的需求,即要求组织二次物料资源的加工,不把有害物质排入大气和水系,并应最大限度地减少散入周围环境的热损失。

在尽可能减少废物的同时,应强化生产过程和提高生产效益。例如,提高生产过程的完备程度(借助于选择最佳条件,提高碳化中钠的利用率),就能提高生产效率和减少废物量。因此建立少废物工艺无论在技术上还是在经济上都是解决环境保护问题的合理途径,而且这也是主要的途径。

到目前为止,在建立少废物工艺过程方面已确定了以下的主要方向:

- ① 研究开发使液体废物和有害废气的排放符合本地区排放标准的工艺体系和水循环系统;
- ② 将二次物料资源加工为有用产品;
- ③ 回收利用二次能源,降低环境热损失;
- ④ 在企业内部建立原料和废料封闭式结构的地区工业综合体。

氨碱法纯碱生产工艺循环中排出物有:可分离成澄清液和固体渣的蒸馏悬浮液;盐水精制工序的废渣;及气态废物。

如果气体废物含有的有害物质在极限允许标准范围内,可排入大气。但澄清的蒸馏液和固体渣可加工成有益于人类经济活动的产品,所以应视为二次物料资源。

生产众多品种的产品可以实现原料和废物料利用的封闭式结构。应当注意到,对氯化钙的需要量近年来已经增长,并且和纯碱的需要等值;而对于用固体二次物料资源(废渣)生产的产品需要量,超过纯碱生产二次物料资源的年产出率。

(一) 氯化钙及再制盐的生产

在建立少废物纯碱生产综合体时,可以推广加工澄清蒸馏液的高效工艺,澄清液可加工制取氯化钙,或者在相应的处理后注入石油钻井。

蒸馏液是无机盐的水溶液,其主要组分是 CaCl_2 (10%~14%) 和 NaCl (5%~7%)。下面叙述的制取氯化钙同时分离氯化钠的方法均以浓缩这些盐的水溶液为基础。

所制氯化钙在国民经济中的应用基于氯化钙有强吸水性,也就是能够吸收空气中的大量水分,并且易溶于水;其冰点比水低,浓溶液沸点高(例如 30% CaCl_2 溶液在温度 -55℃ 下冻结,在温度 111.6℃ 时沸腾)。

氯化钙的主要消费者是化学工业(合成橡胶生产、浮选作业等)、制冷工程、建筑业(提高混凝土凝固速度)、有色冶金(制取含钙巴士合金)、处理矿石以防冻结;还用于纺织工业和国民经济其他部门。

伴生产品氯化钠的主要消费者是农业(制取配合饲料和混合饲料),有时 NaCl 返回生产过程用于制碱。

1. 氯化钙的主要性能

氯化钙溶于水并放热,在有实用价值的温度范围内的溶解度为:

t, (°C)	60	80	90	100	120	140	160	170
C, (重量%)	57.8	59.5	60.6	61.4	763.4	65.6	69.0	71.8

由蒸馏液制取工业熔融氯化钙时,在温度 179~188℃ 范围内可得到含 CaCl_2 70% 左右的溶液。这种溶液稍加冷却即结晶出二水氯化钙。下面是氯化钙水溶液沸点与浓度的关系:

CaCl_2 (重量%)	70	71	72	73
沸点, (°C)	165	168	171	173

2. 再制盐生产工艺流程见图 7-23 所示。

产过程的完备
废物量。因此
2,而且这也是

和水循环系统;

浮液;盐水精制

清的蒸馏液和

意到,对氯化钙
氯(废渣)生产的

澄清液可加工制

6~7%)。下面

空气中的大量
温度-55℃下冻

建筑业(提高混
织工业和国民经

NaCl 返回生产

0 170

.0 71.8

CaCl₂ 70%左右的
浓度的关系:

3

13

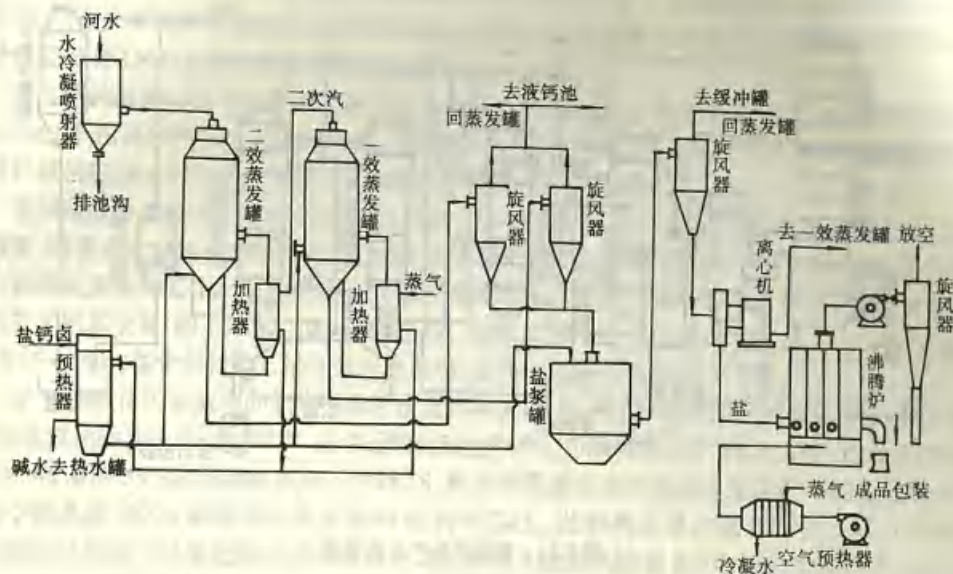


图 7-23 再制盐生产工艺流程

氨碱厂蒸氨塔的废液经澄清除去杂质,然后溶入粗盐,此液为盐钙卤进入本工序经预热器预热,然后进入双效蒸发罐蒸发浓缩,蒸发器底析出再制盐结晶,往旋风器分离。器底出晶浆罐,用盐水洗去氯化钙;器顶液体回蒸发罐或去液钙池。盐浆罐盐将再经旋风分离出盐结晶,再经离心机进一步除去水分,然后经沸腾干燥炉干燥,即得再制盐产品。

3. 氯化钙生产工艺流程如图 7-24 所示。

由制盐工序来的液钙进入液钙池,由泵送入液钙罐,然后进入升膜蒸发器底部,经升膜浓缩、由器顶进入分离器分离。分离器顶出水汽经水射冷凝器冷凝后入下水道,分离器底出液钙再去降膜蒸发器进一步加热浓缩,器底出浓缩氯化钙进入贮槽装桶,即得 70% 固钙。如带有二个结晶水,称为水钙。

来自堆场澄清池的液钙进入高卤罐,自压入预热器由升膜蒸发器的冷凝液加热,然后进入升膜蒸发器加热提浓后,进入分离器进行分离,液钙入液钙池。

如将含量 70% 的固体氯化钙破碎成小块,放在干燥坑上再次干燥,即得无水氯化钙。

以上介绍的是再制盐和氯化钙的生产,分别由两个流程来完成,其消耗定额为:

燃煤 300 kg/t 再制盐; 800 kg/t 70% 氯化钙; 1 200 kg/t 无水氯化钙

粗盐 800 kg/t 再制盐

这种方法生产再制盐时要消耗粗盐,生产氯化钙时采用升、降膜蒸发器,浓热的氯化钙溶液对其腐蚀较严重。下面介绍一种由蒸氨塔废液制取氯化钙同时分离 NaCl 的方法,可以克服这一缺点。

4. 制到氯化钙同时分离 NaCl 的工艺流程如图 7-25 所示。

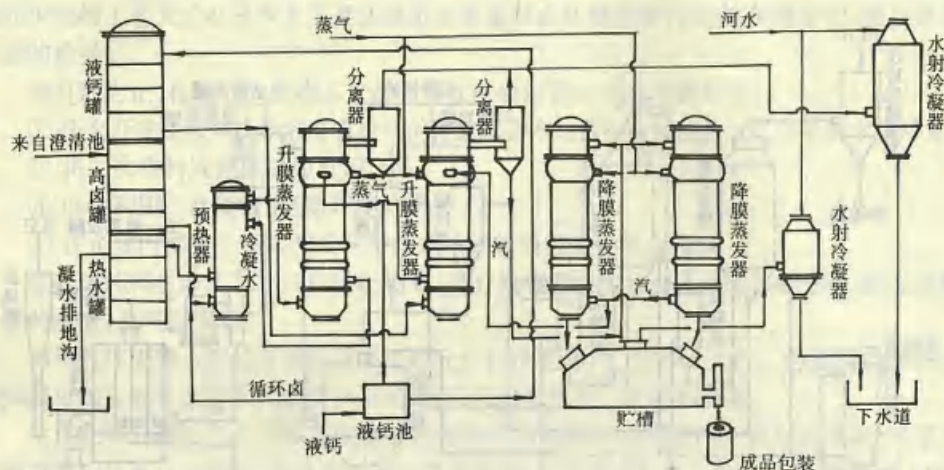


图 7-24 氯化钙生产工艺流程

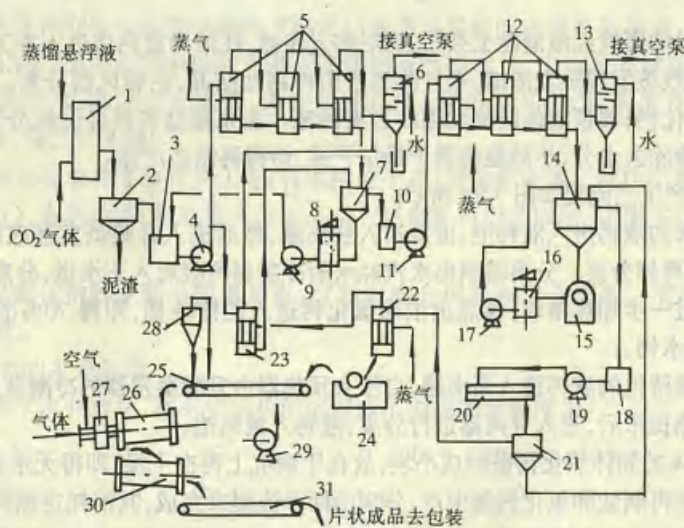


图 7-25 氯化钙生产流程图

1—碳化器;2、7、14、21—沉淀器;3、8、18—容器;4、9、11、17、19—泵;5、12—蒸发器;6、13—混合冷凝器;10—贮槽;15—离心机;16—分离液贮槽;20—真空结晶器;22—蒸发器;23—余热利用;24—成片机;25、31—输送带;26—硬化器;27—燃烧室;28—旋风分离器;29—风机;30—冷却转筒。

淀器
一步
种活
18%
有搅
在这
后一
结的
(以生
15,固
器 14,
在真空
40%集
器 14。
有
分离出
澄
72%Ca
钙熔体
输送带
燃烧天
排入大
含
鳞片用
此
碳
效容积
澄清
蒸发
晶种
熔融
质和载热
真空
干燥
和载热体



进入氯化钙车间的蒸馏悬浮液先在碳化器1中Cl用含有 CO_2 的气体预碳化,然后送入沉淀器2沉降出悬浮粒子(也可以在碳化前和碳化后设双重沉降)。沉渣(固相)由沉淀器送去进一步加工,生产石灰质土壤改良剂和饲料添加剂;而澄清溶液则流入容器3。同时向该容器加晶种活性硬石膏 CaSO_4 ,用以防止蒸发器组的传热表面结垢。

含有晶种的澄清蒸馏液用泵4由容器3送入三效并流蒸发器组5,在这里,液体蒸浓到含18% CaCl_2 。由蒸发器最后一效出来的悬浮液流入沉淀器7。作为晶种的浓稠悬浮液经过装有搅拌机的容器8用泵9送回容器3,继续用作晶种。

部分蒸浓并且脱去了晶种的蒸馏液用泵11由贮槽10送入第二台三效并流蒸发器12。在这里,蒸馏液浓缩到含有氯化钙38%,并且分离出主要部分的氯化钠。蒸发器5和12的最后一效都在真空下工作。来自最后一效的二次蒸汽进入混合冷凝器6和13。空气和没有凝结的蒸气用真空泵(图上未示)由冷凝器抽出。在蒸发器中生成的冷凝水之量为 $5.5 \text{ m}^3/\text{t碱}$ (以生产67%的氯化钙计算),送往盐水制备场,这样可以适当地减少水用量。

在38%氯化钙溶液中的氯化钠悬浮液流入沉淀器14,浓稠部分随后由沉淀器进入离心机15,固体氯化钠从这里送往用户,或者返回纯碱生产中。分离液经过贮槽16用泵17送回沉淀器14。澄清的38%氯化钙溶液放入容器18,然后用泵送往真空结晶装置循环泵的吸收管线。在真空结晶器20中,溶液进一步浓缩到含40% CaCl_2 ,此时剩余量的氯化钠析出进入固相。40%氯化钙溶液中的氯化钠悬浮液由真空结晶器送入盐泥沉淀器21;浓稠的盐浆再进入沉淀器14。

有的氯化钙制取流程用蒸发器组代替真空结晶器,即用蒸发器使 CaCl_2 浓缩到48%,然后分离出氯化钠。

澄清的40%氯化钙溶液送入在常压下工作的蒸发器22,溶液在此蒸浓至熔融状态,含72% CaCl_2 。蒸发器22的二次蒸汽用于加热与蒸发器5并联作业的余热利用换热器23。氯化钙熔体送入成片机24的槽中,成片机转筒内加冷却水降温。粗鳞片用刮刀由转筒刮下,并用输送带25送入硬化器26,鳞片的干燥用逆流通过的烟道气进行。烟道气来自燃烧室27,室内燃烧天然气和空气的混合物。硬化转筒后的烟道气通过旋风除尘器28,再用通风机29抽出排入大气。

含有主要物质约78%的 CaCl_2 热鳞片卸入冷却转筒,转筒壁用循环水冷却。冷却的成品鳞片用输送机引送去包装,然后运入成品仓库。

此流程的主要设备有:

碳化蒸馏悬浮液使用下部有鼓泡器的空心碳化器。碳化器直径3.0m,有效高度17m,有效容积 119 m^3 。

澄清蒸馏悬浮液使用标准的重力式沉淀器。

蒸发器为带有外置加热室和沸腾区的同一型号设备。每台设备的加热面为 384 m^2 。

晶种在中央传动的重力型单层增稠器中析出;增稠器直径25m,沉降面 500 m^2 。

熔融设备采用加热面 350 m^2 和平均传热系数 $430 \text{ W}/(\text{m}^2 \cdot \text{K})$ 的罗伯特蒸发器。工作介质和载热体之间的温差为 20°C ,设备直径2.4m、高10.1m。

真空结晶器外径2.4m、高18.15m、容积 32.7 m^3 。

干燥氯化钙鳞片用的转筒式逆流干燥器容积 60.8 m^3 ,直径2.2m、长16.0m。工作介质和载热体之间的平均温差为 200°C 。载热体是气态燃料的燃烧产物。

13—混合冷凝器;
24—成片机;
25—输送带;
26—硬化器;
27—燃烧室;
28—旋风除尘器;
29—通风机。

转筒式冷却器直径 2.5 m、长 25 m,用空气和水为工质冷却鳞片。

所用设备均为标准产品。

(二) 生产土壤改良剂和无机饲料添加剂

为了熟化酸性和碱性土壤并提高肥效,需要往土壤中施用石灰质土壤改良剂。

生产以石灰质物质为基础的无机饲料添加剂也是重要的课题。

据资料介绍,由纯碱生产的派生碳酸盐产品制取的土壤改良剂,在效果上不仅不亚于石灰粉、石膏、白垩和其它改良剂,而且往往更有效,这是因为蒸馏悬浮液固(渣)相中钙离子活性较高,物理状态更好,且含有硫酸镁。

施用土壤改良剂对于土壤的物理化学性质有良好的影响,改变土壤溶液的反应,降低水解酸度和将 pH 值由 5.5~5.6 提高到 6.2~6.4;降低土壤分散度和有机物流动性,尤其是在春季;改善可耕层的结构并使土壤的粘附性降低 $\frac{1}{2} \sim \frac{1}{3}$ 。

无机饲料添加剂还可以有效地代替农业禽畜饲料配给量中的白垩。

1. 土壤改良剂生产流程见图 7-26。

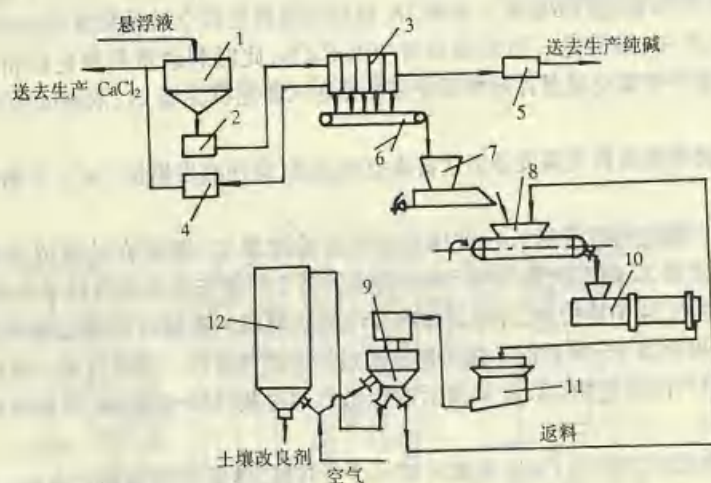


图 7-26 土壤改良剂生产流程图

- 1—沉淀器;2—中间容;3—室式压滤机;4—滤液贮槽;5—水洗贮槽;6—运输机;
7—振动计量给料器;8—混合器;9—风动装置;10—滚筒干燥机;11—锤式破碎机;
12—筒仓

蒸馏塔悬浮液进入沉淀器 1,澄清部分从这里送去生产氯化钙,浓稠部分送入中间容器 2,然后进入室式压滤机 3。滤液由贮槽 4 送去生产氯化钙。洗涤滤液以及洗涤滤布后的回收液收集在容器 5 中,送去消化石灰、制备石灰乳和供其它工艺需要。

滤出的滤渣用运输机 6 送入振动给料器 7,然后进入混合器 8。一部分成品作为返料(比例 1:1.5)也送入混合器。湿渣和返料混合以后送入滚筒干燥机 10,干燥到含水分 8%。干燥以后用锤式破碎机 11 粉碎物料并送入风动装置 9,然后进入筒仓 12,从这里发送给用户。

由流程主要设备有:

沉淀增稠器直径 40 m,标准沉降表面 1 250 m²。

过滤
混合
筒直径 2
成品
粉碎
2. 制
与土
由沉淀器
化钙。含
混合器的
之间的比
渣、白
械运输机
转筒干燥
所用设备
(三)
碳酸
于锅炉和
造化妆用
氨碱

盐水废
水
废水
CO₂

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 实用无机化工工艺学 *Practical Inorganic Chemical Technology* 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.

Signature:

WenLi Zhang

Name:

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Informative Abstract

This book is compiled based on principles of basic theory, prominent practicability and comprehensiveness, and easy operability. The content relates to basic chemical industry of sulfuric acid industry, chlor-alkali industry, soda ash industry, synthetic ammonia and nitric acid industry, chemical fertilizer industry, etc., and inorganic salt industry of fluoride salt, chromium salt, phosphate, aluminium salt, imine, sodium percarbonate, hydrogen peroxide, silicate of soda, etc. Product performances, production raw materials, processes, production devices, subsequent products, etc. are introduced in detail. This book is suitable for students majored in inorganic chemical engineering in vocational university as a teaching material and also researchers and factory technicians as a reference.

(Shan) Xindeng007

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Foreword

As another form of higher education, vocational university has been valued and vigorously promoted by the State Council and the Ministry of Education. It is an established higher education system equal to ordinary higher education and an important reform on the education system of our country that focuses on theory over practice and where teaching and production practice are disconnected. At present, the ministry of education focuses on supporting 4 national exemplary vocational universities and provides that the vocational universities should make corresponding reforms on teaching materials, teaching methods, experiments, and examination methods to enhance training of practical ability of students and make up for defects of ordinary higher education. Since original teaching materials of ordinary universities are far from being able to meet requirements of the teaching reform in vocational universities, the reform on teaching materials is a core of reforms on vocational higher education. Therefore, we decide to compile “Practical Inorganic Chemical Technology”. The teaching material has characteristics of sufficient theory, emphatic practicality, prominent technology, convenient operation, and enlarged coverage of content, etc. to highlight training of ability and technology. It shortens a gap between book knowledge and production practicality, deletes some unnecessary theoretical derivations, and increases newly developed products and technologies. Besides, it has relatively high reference value for students in vocational universities and adult education, researchers, and factory technicians.

The whole book is divided into nine chapters. Dexue Fu from Jiaozuo University, Henan participated in the compilation of chapters 1, 4, 5, and 9, Changchun Liu participated in the compilation of chapter 2, Jingcheng Tian participated in the compilation of chapters 5 and 6, Longdao Wang participated in the compilation of chapter 9, and Zhansheng Cheng participated in the compilation of chapter 6, Xiangyu Shi participated in the compilation of chapters 3 and 7, Chunli Xing participated in the compilation of chapters 6 and 7, Cunhong Li participated in the compilation of chapters 5 and 8, Tianlin Zhu participated in the compilation of chapters 3 and 8, Yong Liu participated in the compilation of chapters 3 and 4, Li Huo participated in the compilation of chapters 2 and 8, Yongxiang Su participated in the compilation of chapters 2 and 5, Yanqin Huang from Pingyuan University, Henan participated in the compilation of chapters 6 and 7, and Shaohong Xu participated in the compilation of chapters 2 and 8, and the whole book is examined and approved by Dexue Fu.

Due to the limited abilities of the editors, there are definitely still shortcomings and readers are welcome to make comments.

Compiling group of “Practical Inorganic Chemical Technology”

October 1997

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7.1.4 Overview on Chinese Soda Ash Industry

Before 1949, there were only two soda ash factories using an ammonia soda process in Tanggu District of Tianjin, and Dalian with a maximum output of 101 kt (in 1940). After the founding of the People's Republic of China, in order to meet demands of industrial development, soda ash production has been greatly developed. In addition to restoration and expansion of the two original soda ash factories, there are also dozens of small and medium-sized soda ash factories are designed and constructed in Zigong of Sichuan, Qingdao, Yingcheng of Hubei, Longshan of Hangzhou, etc. The output has grown from 88 kt in 1949 to 2.37 Mt in 1987 (not including Taiwan Province), ranking third in the world. The consumption of main raw materials is also reduced and processes and devices are greatly improved. Although our country's self-developed soda ash joint production is later in production than Japan, its technical level is not much different. At present, sea salt is mainly used as a raw material. Besides, there is still a certain amount of trona in the mainland. Over the years, certain achievements have been made in scientific researches on processing and utilization of a trona mine in Chaganlimennuoer, Inner Mongolia, a trona lake in Dabusu, Jilin, and a trona mine in Wucheng, Henan. In recent years, more than 20 underground rock salt resources have been discovered in coastal provinces. For example, the rock salt reserves are quite considerable in Huai'an, Jiangsu Province. If the brine is used to prepare soda ash, it will reduce production costs and improve production of soda ash.

Although remarkable achievements are made in our country in various aspects over the past 40 years, there is still a big gap between the national economy's demand for soda ash industry and the world's average level of soda ash of 7.5 kg per person. Since the average amount of soda ash produced in 1987 of our country is only 2.2 kg per person, the self-produced soda ash cannot meet the consumption requirement and a considerable amount of soda ash still needs to be imported from abroad. In order to rapidly change the situation of shortage of soda ash supply and partial dependence on import, a large soda ash factory with an annual production of 0.6 Mt has been newly built in Weifang in Shandong, Tangshan in Hebei, and Lianyungang in Jiangsu in our country. In addition, a main difference in soda ash industrial technology between our country and advanced countries is high energy consumption. The energy consumption of unit of products in the same process is about 25%-33% higher. The energy consumption index of 1 t of soda ash produced in the advanced countries is 13 GJ by an ammonia soda process and 9 GJ by a soda ash joint production process.

7.1.5 Main raw material for preparing soda ash-raw salt

Raw salt is a main raw material for preparing soda ash and mainly from sea salt, rock salt, and natural brine.

1. Sea salt Various salts are dissolved in seawater, mainly NaCl. The seawater is introduced into a salt pan and sun-dried to obtain sea salt whose composition varies due to different places and sun-drying conditions. The following is chemical components of sea salt in a certain place (wt%):

NaCl.....	89.93	MgBr ₂	0.01
CaSO ₄	0.48	KCl.....	0.22
MgSO ₄	0.57	Moisture	6.48
MgCl ₂	0.52	Others	0.27

2. Rock salt Natural sodium chloride in the form of deposits still existing in the strata is called rock salt. A method of injection and melting is commonly used for mining and the obtained brine has different components. Here is an example:

NaCl 297.84 kg/m³; CaSO₄ 4.77 kg/m³; MgCl₂ 1.68 kg/m³;
MgSO₄ 0.76 kg/m³; and Relative density 1.199 (23°C)

3. Natural brine The Natural brine generally contains more than 12% of NaCl and impurities such as KCl, NH₄Cl, CaSO₄, MgCl₂, etc.

At present, my country's sea salt production is the largest. Due to convenient transportation and proximity to soda ash factories, the cost is the lowest and the sea salt is an important source of raw salt.

7.2 Preparation of Soda Ash by ammonia soda Process

7.2.1 Overview on production by ammonia soda process

1. Production process Soda ash consists of 98%-99% by weight of Na₂CO₃. Soda ash is prepared from edible salt (active ingredient NaCl) and limestone as follows:



however, the soda ash cannot be directly prepared according to the route and can only be realized through an intermediate product of NH_4HCO_3 and NaHCO_3 . The more expensive ammonia, NH_3 , only acts as a medium here. It is not consumed in the production process and can be continuously recycled.

Since a NH_3 circulation system is involved in a main production process, the production process of the soda ash is more complicated in equipment and operation. To maintain a balance of original production links, it is necessary to operate carefully and have rich production experience. From an economical view, every effort must be made to keep the ammonia consumption as low as possible.

Figure 7-1 is a flow diagram of production of soda ash by an ammonia soda process.

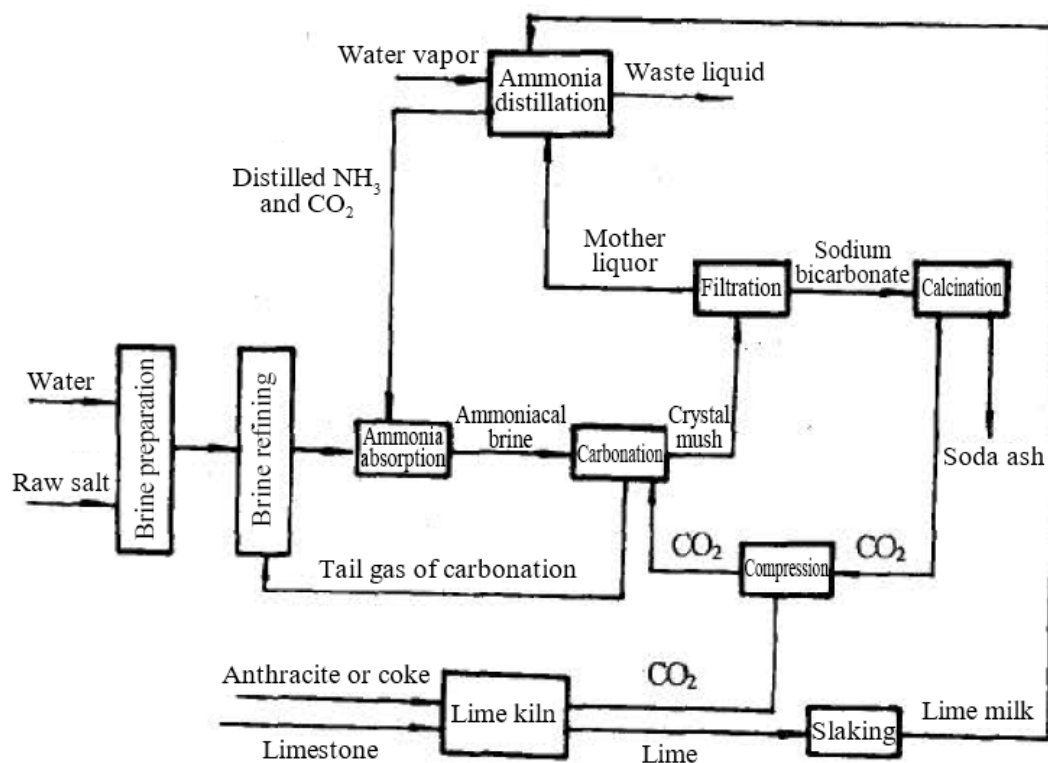
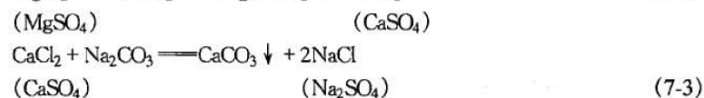
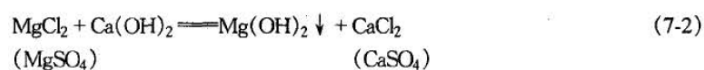


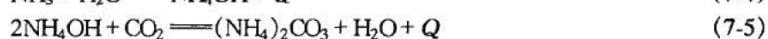
Figure 7-1 Flow diagram of ammonia soda process

2. Production of soda ash NaCl enters the production process in a form of an aqueous solution. Brine can be prepared from solid NaCl or natural brine can be used.

In order to avoid scaling of equipment and pipelines, Na_2CO_3 and $\text{Ca}(\text{OH})_2$ are often added to a brine refining device to precipitate calcium and magnesium.

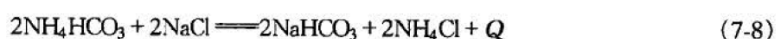
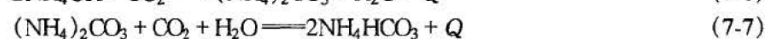
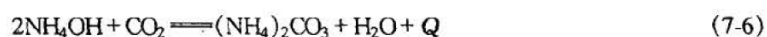


The brine enters an ammonia absorption tower to absorb the required amount of NH_3 and also absorbs a small amount of CO_2 at the same time.



The reaction heat of the two exothermic reactions is conducted in a staged manner for cooling.

Ammoniacal brine with a low carbonation degree is cooled and then subjected to a carbonation process, and enters a tower here, and CO_2 is introduced.



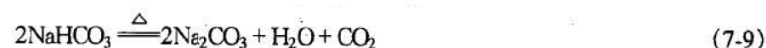
A part of CO₂ comes from a lime kiln; and a part comes from calcination of NaHCO₃. NaHCO₃ is seldom dissolved in mother liquor of soda ash preparation, such that it is precipitated in a form of crystals. In an actual production, the precipitation amount of NaHCO₃ is equivalent to 70%-75% of the amount of Na brought in by NaCl, and the remaining Na remains in the solution and cannot be used in a subsequent process.

The absorption of CO₂ and the production of NaHCO₃ are also exothermic processes, such that the carbonation tower should be fully cooled.

The NaHCO₃ crystals suspended in taking-out liquid of the carbonation tower are subjected to a solid-liquid separation by a rotary vacuum filter.

The air sucked in from the filter contacts with the mother liquor to bring out NH₃. The ammonia-containing air is washed with water in an ammonia purification tower and the ammonia is recovered into the system.

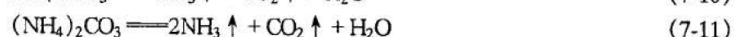
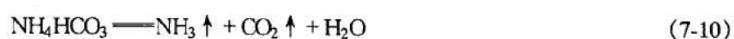
A filter cake containing NaHCO₃ is calcined to obtain final products Na₂CO₃ and CO₂:



At the same time, a small amount of NH₃ is driven out and the part of ammonia is brought to the calcination process by the remaining mother liquor adhering to the crystals of the filter cake.

3. Recovery of NH₃ A large amount of NH₃ remains in the mother liquor in a form of NH₄Cl, NH₄HCO₃ and (NH₄)₂CO₃. The NH₃ in the mother liquor must be distilled out and returned for absorption. The ammonia is driven out by steam in a gas-liquid counterflow device.

In a mother liquor preheating section of an ammonia distillation tower, gas passes through a heat exchange surface to preheat the mother liquor and some CO₂ escapes. In the preheating section, the gas directly contacts with the liquid. Finally, almost all CO₂ in the mother liquor is driven out and a small amount of NH₃ is converted from liquid to gas with CO₂. The reaction is as follows:



Then the mother liquor enters a preliher and Ca(OH)₂ is added to decompose NH₄Cl.



Finally, in a distillation section, steam is used to drive out NH₃ until only a trace amount of NH₃ remains in the solution. A solution at an end point from the distillation section enters a flasher and is discharged after cooled slightly.

The gas containing NH₃ and CO₂ of a very high concentration from the ammonia distillation tower passes through a condenser to an absorption process.

4. Carbon dioxide

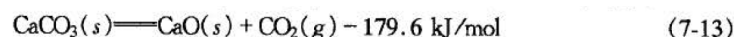
The gas from calcination, and absorption and washing contains approximately less than half the amount of CO₂ required to form NaHCO₃. The remaining CO₂ comes from a lime kiln. Calcium carbonate is decomposed into CO₂ and CaO in the lime kiln. Kiln gas is washed and dedusted with water in a washing tower, sulfur compounds are removed, and the gas is cooled and then sent to the carbonation tower by a gas compressor together with CO₂ gas in the production process.

7.2.2 Calcination of limestone and slaking

In the brine refining and ammonia recovery, a large amount of lime milk is required. The carbonation process requires a large amount of CO₂ gas, such that limestone is calcined to produce CO₂ and lime, and then the lime slakes to produce lime milk, which has become an indispensable preparation process in the production by the ammonia soda process.

1. Calcination of limestone

(1) Basic principle of calcination of limestone The main component of the limestone is CaCO₃ with the better content about 95%. In addition, there are still 2%-4% of MgCO₃ and a small amount of SiO₂, Fe₂O₃, Al₂O₃, etc. The main reaction in the calcination process is:



According to thermodynamic data, when a partial pressure of CO₂ reaches 0.1 MPa, the theoretical decomposition temperature of the limestone is 1,180 K.

The actual operating temperature is higher than the above theoretical decomposition temperature, and therefore, the decomposition rate of the limestone is slow at 1,180 K. The decomposition rate of ore is represented by a speed (R) that a reaction surface (an interface between produced CaO and internal CaCO_3) advances to the interior. The speed is not related with the size of the ore and has a relationship with a temperature t ($^{\circ}\text{C}$) as:

$$\lg R = 0.003145t - 3.3085 \text{ cm/h} \quad (7-14)$$

It can be seen from formula (7-14) that calcination time can be shortened by high temperature.

At a certain temperature, the calcination time required for ores of different sizes is shown in Figure 7-2. However, raising the temperature is also limited by a series of factors. If the temperature is too high, a molten or semi-molten state may occur, wall hanging or nodulation may occur, and the ore will become solid “over burnt lime” not easy for slaking. Practice has proved that the temperature of burning limestone is generally controlled within a range of 940-1,200 $^{\circ}\text{C}$.

The calcination of the limestone is an endothermic reaction. Heat is usually supplied by burning coke or anthracite (also gas or oil). Fuel is required to be completely burned in the kiln to provide the most heat. However, sometimes due to insufficient oxygen or local hypoxia caused by nodules in the kiln, the fuel cannot be completely burned and a small amount of CO is produced. Therefore, it is necessary to strictly control the amount of air in the operation to control the content of CO in the kiln gas to be less than 0.6% and the content of O_2 to be less than 0.3%.

There are two sources of CO_2 in the kiln gas: one from decomposition of CaCO_3 ; and the other from a product of fuel combustion. The former is pure CO_2 gas; and the latter is mixed gas of CO_2 and N_2 . Theoretically, when pure carbon is burned, the CO_2 in the gas can reach 21%, but the concentration of the CO_2 can be reduced due to excess oxygen or production of CO . It can be seen that burning limestone uses less fuel, which not only saves fuel, but also improves the concentration of CO_2 in the kiln gas. But enough heat must be provided for the decomposition reaction. Now the number of kg of fuel in 100 kg of limestone is called “coking rate” and expressed by symbol F , then

$$\text{Concentration of } \text{CO}_2 \text{ in kiln gas} = \left[\frac{\text{CaCO}_3 \%}{100} + \frac{\text{MgCO}_3 \%}{84.3} + \frac{\text{C} \%}{12} \times F \right] \times 100 \quad (7-15)$$

$$\left[\frac{\text{CaCO}_3 \%}{100} + \frac{\text{MgCO}_3 \%}{84.3} + \frac{\text{C} \%}{12} \times F \times \frac{1}{0.21} \right]$$

In the formula, $\text{CaCO}_3\%$ and $\text{MgCO}_3\%$ -percentages of CaCO_3 and MgCO_3 in limestone respectively;

$\text{C}\%$ -percentage of fixed carbon in fuel; and

0.21-mole fraction of oxygen in the air.

Theoretically, the concentration of CO_2 in the kiln gas is 44.2%, but generally around 40%. Therefore, the produced kiln gas must be exported in time, otherwise the reaction will be affected. During the production, the kiln gas is purified, cooled and continuously pumped out by a compressor to continuously decompose the limestone.

2. Lime kiln and its operation At present, limestone is mostly calcined by a mixing vertical shaft kiln. The kiln has advantages of large production capacity, fully mechanized loading and unloading, high concentration of kiln gas, high heat utilization rate, and good quality of lime.

The structural schematic diagram of the lime kiln is shown in Figure 7-3.

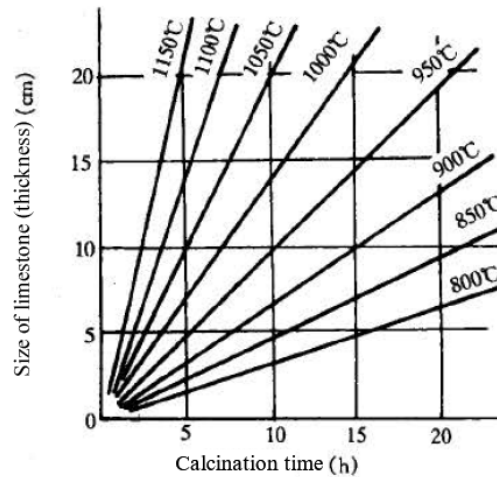


Figure 7-2 Relationship between limestone size and calcination temperature and calcination time

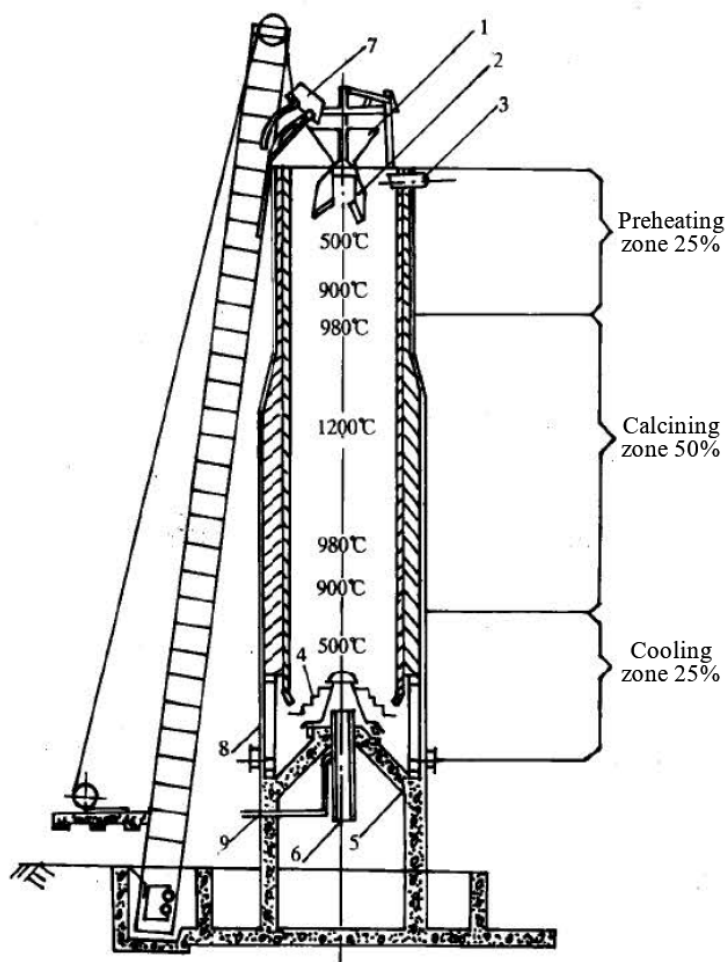


Figure 7-3 Schematic diagram of lime kiln

1-funnel; 2-limestone distributor; 3-air outlet; 4-lime output rotary table; 5-periphery air duct; 6-center air duct; 7-limestone lifting tank; 8-lime outlet; and 9-adaptor tube of draftmeter

The kiln body is made of ordinary bricks or steel plates, with refractory bricks inside. A thermal insulation material is filled between the two layers to reduce heat loss. The kiln is divided into three zones from the top to the bottom: a preheating zone, a calcining zone, and a cooling zone. The preheating zone is located at an upper part of the kiln, accounting for about a quarter of the total height. The preheating zone functions to use hot kiln gas rising from the calcining zone to preheat and dry limestone and fuel to recover waste heat of the kiln gas and improve thermal efficiency. The calcining zone is located in a middle part of the kiln. The preheated mixed materials are calcined here to decompose the limestone. To avoid nodulation by over-burning, the temperature in the calcining zone should not exceed 1,350°C. The cooling zone is located in a lower part of the kiln, accounting for about a quarter of the effective height of the kiln. The cooling zone mainly functions to preheat the air entering the kiln to cool the hot lime, such that the heat is recovered and the kiln grate is maintained.

The proportion of ingredients, the size of blocks, the air pressure and air volume, and the speed of feeding and discharging are main conditions for maintaining the normal operations of the lime kiln.

The equilibrium state in the kiln is easily disturbed by operational errors or breaks, and thus measures must be taken to return to normal as soon as possible. Under the premise that the proportion of the amount of the limestone and coke is appropriate, the following measures should be taken:

Whether the position of the calcining zone is too low can be known from too high lime temperature. The position of the calcining zone can be increased by increasing the air blowing amount.

Whether the position of the calcining zone is too high can be known from too high air-out temperature. The measures are more complicated. Lime discharge must be enhanced while the air volume is reduced as much as possible until the calcining zone is mechanically restored to its normal position. Then the kiln is filled up by a quick feeding and the normal air flow is restored.

When the calcining zone is extended (both upper and lower temperatures are high), the lower limit of the calcining zone is first moved upward by air intake, then the lime discharge must be enhanced, and the kiln is filled by feeding, such that the calcining zone shrinks to the middle. Under the normal condition in the reaction zone where a coke-stone ratio has been adjusted, only the air volume is adjusted to maintain the normal state of the kiln. Under the normal condition, the gas in the kiln is controlled to be neutral or slightly reducing gas.

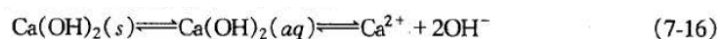
It is most important is to carefully adjust the air volume. In order to avoid the inlet of the air, the whole kiln needs to maintain a positive pressure which is formed by a blower sending the air into the kiln from a lower part.

Since dust is easily produced from the lime, dust prevention of all lime treatment devices should be paid attention to and the devices should be frequently maintained.

If dust raising is unavoidable, the dust-containing air can be drawn out and washed with water, and the washing water can be used for lime slaking.

2. Lime slaking

Ca(OH)_2 , instead of CaO , is used for brine refining and ammonia distillation. CaO can be converted into Ca(OH)_2 by slaking using an appropriate amount of water. But the solubility of the Ca(OH)_2 is very low and decreases with the increase of temperature. Besides, powdered slaked lime is very inconvenient to use, such that its suspension, also called lime milk, is used in the production. The following balance exists:



The lime milk is relatively thick and thus more favorable for production. But its viscosity increases with the thickness. If the lime milk is too thick, it will settle and block the pipelines and equipment. The generally used lime milk contains about 160-220 tt^① of active CaO and has the relative density about 1.27.

The dispersion degree of suspended particles in the lime milk is very important. When the particles are small, they are easy to be made into a uniform milky substance not easy to sink, which is convenient for transportation and use. The factors affecting the size of the suspended particles are purity of lime, water quantity, water temperature, and stirring strength. Too many impurities in lime or over-burning will reduce the quality of the lime milk. The high temperature of water for slaking can accelerate the slaking and form a powder with a finer suspension particle size. Generally, warm water at 65-80°C is suitable for the production.

Flow diagram of lime slaking system is shown in Figure 7-4.

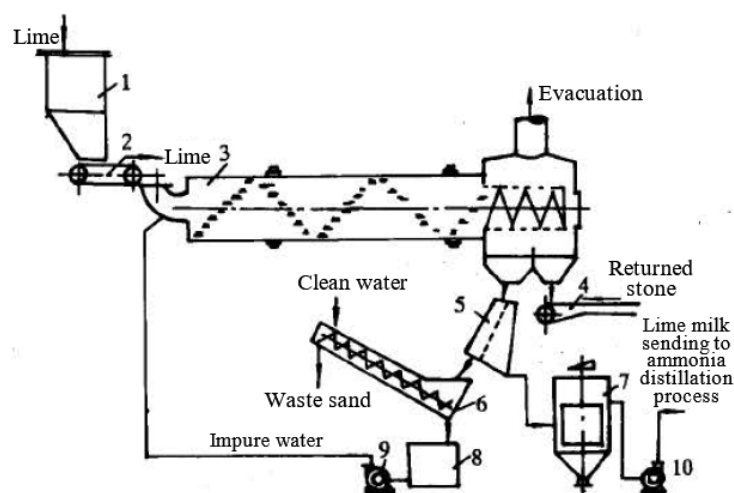


Figure 7-4 Schematic diagram of lime slaking process and lime slaking machine

1-lime bin; 2-chain plate machine; 3-lime slaking machine; 4-returned stone belt; 5-vibrating sieve; 6-spiral sand washing machine; 7-lime milk bucket; 8-impure water bucket; 9-impure water pump; and 10-lime milk pump

The lime slaking machine (slaking machine) is a horizontal rotary cylinder slightly inclined to one end of an outlet (about

① A unit of concentration is commonly used in soda ash factories and called "titer". Symbols can be tt or ti. $1 \text{ tt} = \frac{1}{20} \text{ mol/L}$. This is the meaning of "tt" in the following chapters.

0.5 degrees). Lime and water are added from one end to be mixed and reacted with each other. The cylinder is equipped with a number of spirally arranged shoveling plates which push the solid mixture towards the other end when rotate. There are two layers of sieves with different apertures at a tail. The produced lime milk flows out from sieve holes and enters a lime milk bucket through a vibrating sieve. The remaining under-burnt or over-burnt lime flows out from the sieve. The large blocks of under-burnt lime can be returned to the kiln to be reused and are called returned stone. The small blocks from the vibrating sieve are called waste sand, and are discharged and discarded.

7.2.3 Brine refining

1. Objective of brine refining

Converted Na in soda ash production is provided by edible salt. A nearly saturated NaCl aqueous solution is introduced into a system as crude brine. The natural brine is often found in nature and pumped from a deep part of a well. The crude brine can also be prepared by dissolving solid salt with water. For example, the saturated crude brine can be prepared using sea salt. The approximate composition (kg/m^3) of the crude brine is as follows:

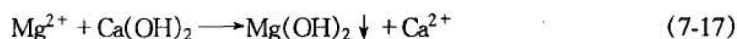
NaCl 300.4; CuSO_4 4.81; CaCl_2 0.8; and MgCl 0.35

Although the amount of calcium salts and magnesium salts contained in the crude brine is not large, they can be reacted with NH_3 and CO_2 to form a precipitate of double salts in each subsequent process, which causes scaling or even blocking of equipment and pipelines, and will increase loss of raw salt and ammonia. These impurities will also be mixed into sodium bicarbonate, which will eventually affect the quality of the soda ash. Therefore, a pre-refining measure is used in the production to remove these impurities. Generally, it is required that the accuracy of removing calcium and magnesium is above 99%.

2. Method for brine refining

(1) Lime and soda ash method

Magnesium is precipitated with $\text{Ca}(\text{OH})_2$ (lime milk) and calcium with NaCO_3 :



to obtain a first brine and a first sludge.



to obtain a second brine and a second sludge.

$\text{Mg}(\text{OH})_2$ and CaCO_3 are precipitated out as a precipitate, but CaCl_2 , NaCl and Na_2SO_4 are still dissolved in the brine. The Na^+ brought in with CaCO_3 also exists in a form for producing soda ash. But in a sodium bicarbonate making tower, only a part of this Na^+ is converted into NaCO_3 due to limitation of a conversion rate. The diameter of the CaCO_3 crystals is 1-10 μm , while the diameter of the produced $\text{Mg}(\text{OH})_2$ crystals is only a few μm . A single $\text{Mg}(\text{OH})_2$ crystal cannot settle at all, while the sedimentation velocity of the CaCO_3 crystals in the brine at 15°C is 0.1 m/h or below. The CuCO_3 crystals are added into the $\text{Mg}(\text{OH})_2$ crystals which can grow into aggregates with a very fast sedimentation velocity, and therefore a clear precipitated sludge interface can be obtained in a clarifying device. In the production process, it is the reason that the second sludge is returned to a primary refining device to accelerate the coagulation and sinking of the precipitate.

(2) Lime-tower gas method (lime-ammonium carbonate method)

The “first brine” is treated with tail gas containing NH_3 and CO_2 at a top of the carbonation tower to precipitate CaCO_3 with very little solubility.



Mg^{2+} is removed using the same above method.

In addition, polyacrylamide (PAM) can also be used. Due to its large molecule and polar group, the polyacrylamide is easy to adsorb precipitated particles and can “bridge” particles to form flocs with a spatial network structure, which is quite effective to shorten the settling time and improve the production capacity of the equipment. The total chloride ion concentration (represented by the symbol T_{Cl}) in the second brine prepared by the production factory generally reaches about 105 tt.

The brine refining process of the lime-tower gas method is shown in Figure 7-5.

② Interaction of solubility of raw salt and ammonia

The solubility of NaCl in water does not change much with the temperature, but the ammonia absorption in the saturated brine will slightly reduce the solubility of NaCl. The solubility of the ammonia in water is very large, but it is also reduced in the brine, that is, the equilibrium partial pressure of ammonia above the ammoniacal brine is larger than that above pure ammonia water. The effect of the temperature on the solubility of ammonia is the same as that of general gases, that is, high temperature leads to low solubility. In the process of ammonia absorption by brine, since CO₂ exists in a gas phase, the CO₂ can be dissolved in a liquid phase to produce (NH₄)₂CO₃, such that the solubility of the ammonia can be improved.

In the production of soda ash, ammonia absorption by second brine only requires free ammonia to reach 99-102 tt. This concentration is still far from the saturated concentration of ammonia at a room temperature. In theory, it seems to be better to absorb more ammonia. Although this is beneficial to the carbonation reaction, the solubility of NaCl in the liquid phase will decrease with the increase of the concentration of ammonia, which will cause adverse consequences on the availability and yield of sodium in the production of soda ash. Therefore, the relative concentrations of ammonia and salt in the ammoniacal brine must be both taken into account. According to the theoretical reaction, the value of F_{NH_3}/T_{Cl^-} should be 1. However, in consideration of the escape loss of ammonia, etc., the value is generally taken as 1.08-1.12 and according to experience, generally $F_{NH_3} = 99-102$ tt and $T_{Cl^-} = 89-94$ tt.

③ Thermal effect of ammonia absorption process

In the process of ammonia absorption, a lot of heat is released, including the heat of dissolution of NH₃ and CO₂, the heat of reaction of mutual neutralization, and the heat of condensation of water vapor contained in the gas from ammonia distillation. Under normal production conditions, about 2.16×10^6 kJ of heat is released per 1 t of soda ash produced. If this heat is not drawn out of the system, it will be enough to raise the temperature of the solution up to about 120°C, completely disabling the ammonia absorption tower. Therefore, cooling is the key to the ammonia absorption process.

④ Volume change in ammonia absorption process

After absorbing the ammonia, the brine has decreased relative density and increased volume. Besides, since the water vapor brought by the gas is condensed to dilute the saturated brine, the volume is more increased. In general, after the ammonia absorption, the volume increases by about 13.5%.

⑤ Essence of ammonia absorption process

Since the ratio of NH₃ and CO₂ molecules in the gas from ammonia distillation is about 4:1 to 5:1, the ammonia absorption by brine is essentially the process of absorbing NH₃ and CO₂ gases by the liquid phase at the same time. The absorption includes physical absorption and chemical absorption, wherein the chemical absorption is the combination of a part of NH₃ and CO₂ in the liquid phase. Besides, the rate of the chemical absorption is directly proportional to the concentration of free ammonia. The data is searched according to the production in recent years. It is found that the concentrations of CO₂ and NH₃ in the liquid phase at different heights along the tower are about a constant, such that the absorption of the CO₂ and NH₃ by the brine is

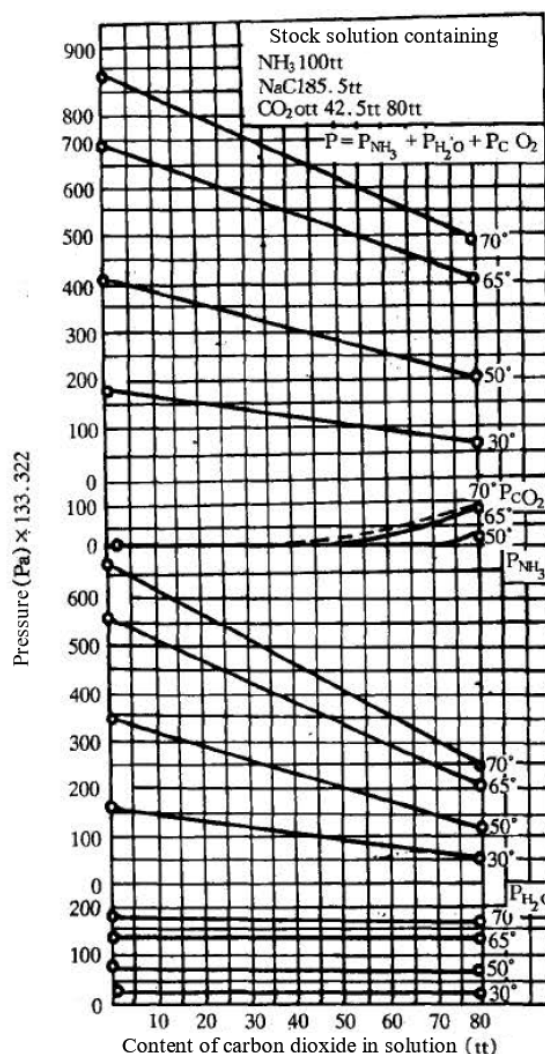


Figure 7-6 Partial pressures of NH₃, CO₂ and H₂O above ammoniacal brine

Notes: 1 tt = $\frac{1}{20}$ mol/L

proportional.

(2) Main device and process of ammonia absorption by brine

The main device of ammonia absorption is the ammonia absorption tower shown in Figure 7-7.

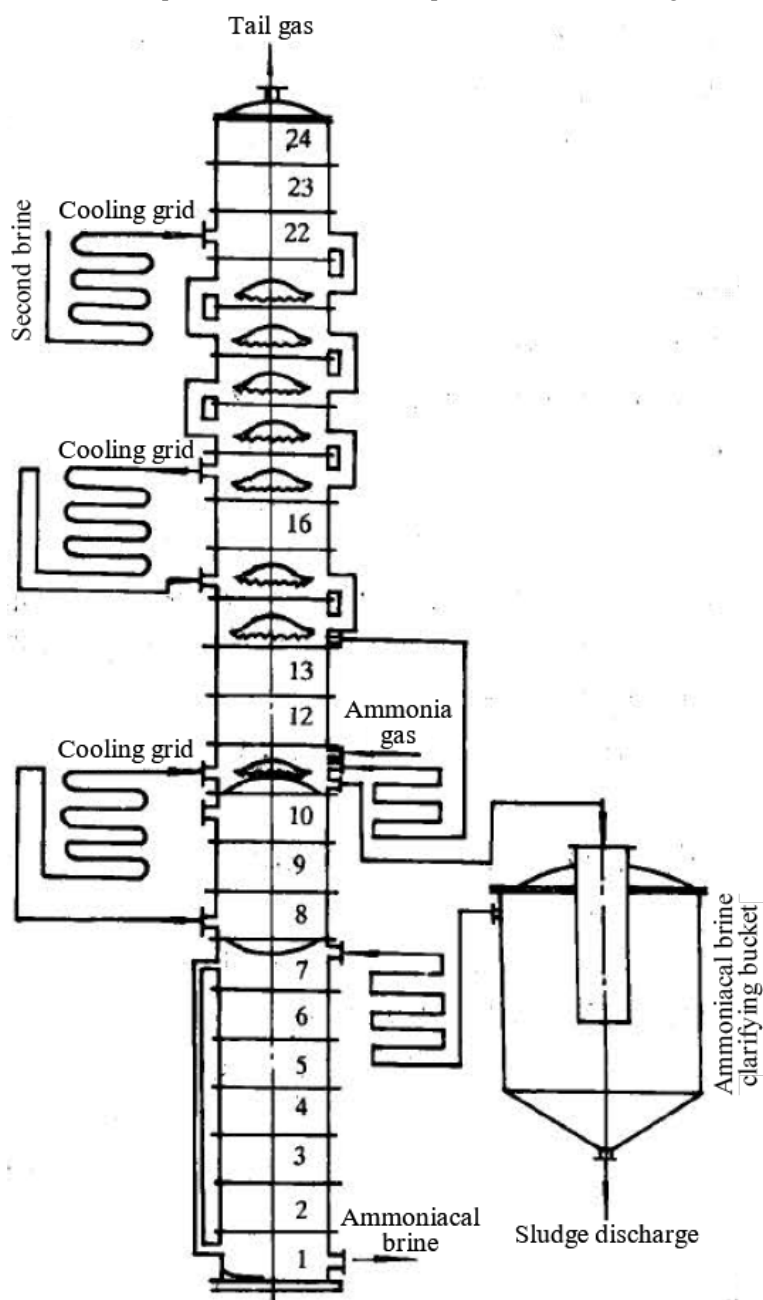


Figure 7-7 Structure of ammonia absorption tower and process

The ammonia absorption tower is a multi-section cast iron single bubble-cap tower. The process is also centered on the ammonia absorption tower. Refined brine is pumped into the top of the tower and gradually flows down from the top of the tower by its own weight. A single cap is installed in each circle to facilitate absorption. Since this absorption process is exothermic, in order to ensure good absorption, the brine is drawn out twice at upper and middle parts of the tower to a cooling grid (or a plate heat exchanger) for cooling, and then return to the next circle to continue to absorb ammonia. After the second cooling, the brine enters the ammonia gas inlet circle where the ammonia concentration is the highest and the heat release is the strongest. In order to ensure a good ammonia absorption effect and a certain concentration requirement, the brine is circulated for cooling and absorption, and a part of ammoniacal brine can be drawn out at any time. After sludge discharge by a clarifying bucket, the ammoniacal brine is cooled and sent into an ammoniacal brine tank (located at the lower 7th circle of the bottom of the tower). In countercurrent contact of gas and liquid, the ammonia content of the brine increases from the top to the bottom and the concentration of ammonia gas decreases from the bottom to the top. The trace ammonia contained in the tail gas from the tower is sent to an ammonia purification tower to be absorbed by water, and the obtained dilute ammonia water can be sent

to be dissolved into a salt.

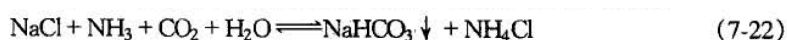
In order to save power, when the brine is drawn out to be cooled, it is necessary to ensure that the liquid has enough static head, such that it can overcome the resistance of the pipeline and return to the tower. To this end, it is necessary to carefully determine positions of inlets and outlets in the tower body, and add an empty circle if necessary.

Since the absorbed ammonia comes from the ammonia distillation tower, in order to reduce the leakage of the ammonia absorption system due to the unfirmness of the unit, speed up the distillation of CO_2 and NH_3 in the ammonia distillation tower, improve the production capacity of the ammonia distillation tower, and save the amount of water vapor, the ammonia absorption operation is performed under partial vacuum.

Although more than 99% of calcium and magnesium impurities have been removed from the refined brine, it is inevitable that a small amount of impurities will enter the ammonia absorption tower to form carbonate and a double salt precipitate. In order to ensure the quality of the ammoniacal brine, the clarifying bucket is provided for clarification again. The precipitation contained in the ammoniacal brine sent to carbonation should not exceed 0.1 g/L.

7.2.5 Carbonation of ammoniacal brine

Carbonation of ammoniacal brine is an important process in the production of soda ash by an ammonia soda process and simultaneously has unit processes such as absorption, crystallization, and heat transfer. These unit processes are interrelated and restrict each other. The basic reaction of the carbonation can be summarized by the following equations:



The purpose of the carbonation is to obtain NaHCO_3 crystals with high yield and good quality so as to be filtered and calcined to obtain a final product. The high yield of the crystals indicates that the utilization rate of NaCl and NH_3 is high, and therefore the product cost is reduced. The crystals have good quality, that is, the particles are large and uniform, and easy to separate from mother liquor, thus the amount of washing water can be correspondingly reduced, so as to obtain a final product of soda ash with relatively high purity and reduce the load of ammonia distillation.

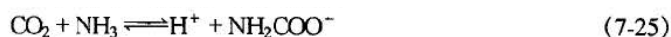
1. Reaction mechanism of CO_2 absorption by ammoniacal brine

Many researchers believe that the reaction mechanism can be divided into three steps: (1) production of ammonium carbamate; (2) hydrolysis of ammonium carbamate; and (3) precipitation of sodium bicarbonate crystals.

(1) Production of ammonium carbamate Experimental studies have confirmed that when CO_2 is introduced into concentrated ammoniacal brine, ammonium carbamate always appears initially.



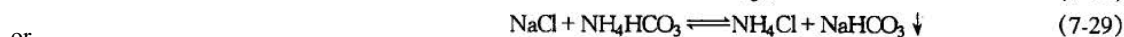
The possibility of this trimolecular reaction is very small, such that the reaction should be regarded as the following two reactions



(2) Hydrolysis of ammonium carbamate The produced ammonium carbamate above is further hydrolyzed and the reaction is:



(3) Precipitation of NaHCO_3 crystals by double decomposition. The step is the final purpose of the carbonation. When the carbonation degree reaches a certain value and the concentration of HCO_3^- in the solution is quite high, the product of the concentrations of HCO_3^- and Na^+ exceeds the solubility product of NaHCO_3 at this temperature, a precipitate is produced, and the double decomposition is completed:



The ammonia concentration in carbonated liquid is always relatively high and many times larger than the concentration of OH^- , such that most of the absorbed CO_2 is consumed in the reaction to produce ammonium carbamate, which has been confirmed by experiments.

The reaction of precipitating NaHCO_3 will affect the balance of a series of complex ionic reactions. The most important is to shift the hydrolysis reaction of ammonium carbamate to right, thereby accumulating dissolved ammonia in the solution, which has a significant impact on the absorption process.

2. Process conditions

(1) Carbonation degree and its effect on utilization rate of sodium

$$\text{Carbonation degree } R = \frac{\text{Mole number of total } \text{CO}_2}{\text{Mole number of total } \text{NH}_3} \times 100\% \quad (7-30)$$

Since it is NH_4HCO_3 rather than NH_3 that directly affects the equilibrium yield of NH_4HCO_3 , the carbonation degree indicates the degree of total ammonia converted into NH_4HCO_3 . Therefore, in the case of appropriate composition of ammoniacal brine, the larger R , the more complete conversion of the total ammonia into NH_4HCO_3 , and the higher utilization rate U_{Na} of NaCl . Therefore, in industrial production, the carbonation degree of the solution should be increased as much as possible to improve the utilization rate of sodium. However, due to various limitations of conditions, the carbonation degree in the production can generally only reach 180%-190%.

(2) Composition of ammoniacal brine

In order to obtain the highest utilization rate of sodium, the ratio of ammonia to salt in the ammoniacal brine must be ensured. However, in the actual production process, in addition to the insufficient carbonation degree R , the influence of ammonia brought out by the tail gas and NH_4HCO_3 eutectoid in sodium bicarbonate must also be considered.

① Ammonia brought out by tail gas and insufficient carbonation degree The most appropriate composition of ammoniacal brine is obtained based on the premise that the carbonation degree $R = 200\%$ of crystal mush taken out from the carbonation tower and the tail gas at the top of the tower does not bring out ammonia. However, in the actual production, the carbonation degree is usually less than 200% and the percentage of ammonia brought out by the tail gas accounts for about 6%-12% of the total ammonia. Therefore, the ratio of NH_3/NaCl in the ammoniacal brine must be increased to make up for the lack of ammonia.

② Influence of NH_4HCO_3 eutectoid in sodium bicarbonate on ratio of ammonia to salt The ratio of ammonia to salt in the ammoniacal brine should be higher than the theoretically calculated ratio of ammonia to salt, which is not only because the tail gas at the top of the tower brings out ammonia, but also because a part of NH_4HCO_3 is brought out in a form of eutectic in the NaHCO_3 precipitate.

③ Optimum ammonia absorption amount As can be seen from the above discussion, properly increasing the ratio of ammonia to salt can improve the utilization rate of sodium, but in the process of ammonia absorption, every 1 mol of ammonia absorbed will bring in about 0.4 mol of water vapor. Therefore, the more ammonia is absorbed, the lower the concentration of NaCl in the ammoniacal brine, and the more deviated from the most appropriate composition of the ammoniacal brine.

The most appropriate ratio of ammonia to salt in the ammoniacal brine can be calculated using a solubility diagram of $\text{NH}_3\text{-NaCl-H}_2\text{O}$ and is generally 1.12-1.14.

(3) Influencing factors of carbonation absorption rate

In the carbonation process, increasing the pressure, lowering the temperature, and keeping a stage of low carbonation degree are all beneficial to increase the absorption rate.

(4) Crystallization process of sodium bicarbonate and influencing factors

Since the production conditions are different, the sodium bicarbonate crystal produced in the carbonation tower also has different quality. The crystal quality includes factors such as particle size and shape. The non-whisker-like crystals having large, uniform and complete grains, and similar three-dimensional lengths are considered to have good quality. When the crystal quality is good, filtration and washing are facilitated, the sodium bicarbonate contains less water, the yield is high, the content of salt is less after calcination, and the quality of soda ash can be improved. Therefore, crystallization is important to the product quality in the whole production of soda ash.

The solubility of NaHCO_3 in water decreases with the decrease of the temperature, but the NaHCO_3 can easily form a supersaturated solution. Since the precipitation of NaHCO_3 crystals in the supersaturated solution is similar to the general crystallization process, that is, the greater the degree of supersaturation, the faster the crystallization speed. However, the crystals have a small particle size and poor quality, which is unfavorable for filtration and calcination.

According to the crystallization kinetics, under the same supersaturation condition, a growth rate of crystal grains is greater than a generation rate of crystal nuclei at a high temperature. Therefore, maintaining a higher temperature (about 60°C) in the

initial stage of the crystallization will not produce too many small crystals. Experiments have shown that if 50% of NaHCO_3 is crystallized at a suitable temperature, in a second half stage of the crystallization, due to the existing good foundation, the overall quality is guaranteed. The higher temperature in the middle of the tower is maintained by the heat of reaction. The cooling process of the temperature in the middle decreased to about 25°C of the temperature of discharge from the tower should be performed gradually. Because although there is a good foundation at this time, too fast cooling will still cause excessive supersaturation, which may produce new small crystals.

The good operation of the carbonation tower should be to precipitate large and complete sodium bicarbonate crystals to meet the requirement of the next step of separation from mother liquor. Otherwise, the product quality will be affected and the load of the ammonia distillation process is also increased.

The quality of the crystals can be expressed by settling time and settling rate. The settling time is determined by taking 100 ml of the crystal mush under the tower with a measuring cylinder and measuring the time required from standing to separation of liquid and solid phases. Generally, 150-200 s is required to be qualified. The settling rate is the percentage of the volume of the solid phase layer to the total volume after layering and generally required to be 40%-50%.

A large amount of heat is released during the carbonation process, which will increase the temperature of the liquid entering the tower. But when the temperature is high, the solubility of the sodium bicarbonate is large. Therefore, the temperature should be gradually lowered after the crystallization, and thus the reaction tends to be completed and crystals are precipitated as many as possible. When the precipitation continues, the crystals can grow up and the quality is ensured. At this time, special attention should be paid to controlling the cooling rate. A relatively high temperature (usually the temperature at the middle part) should be maintained for a period of time in order to produce sufficient crystal nuclei. If the cooling time is too short, the crystal nuclei are not yet formed, thereby increasing supersaturation and finally resulting in a large number of small crystals which are not grown up even when taken out and form "small crystal mush" (also called "floating soda"). However, if the cooling time is too long, the utilization rate of equipment will be reduced. The lower part of the tower should not be cooled too fast to avoid the production of small crystals. Generally, the residence time of the liquid in the tower is about 1.5-2 h and the discharge temperature is about 25°C .

In order to keep the supersaturation at a constant value and not increased too quickly, the speed of cooling should be slow at the beginning. However, the cooling can be slightly faster before the final discharge from the tower, since the carbonation degree is already high, the reaction speed is slowed down, and the large supersaturation is not easy to form. Appropriate acceleration of the cooling will not produce small crystals, but can improve the yield. To ensure crystal quality, the temperature distribution of each layer in the tower is required as shown in Figure 7-8. It can be seen from the figure that the maximum reaction temperature is about 65°C at about 2/3 of the tower height and then the temperature is gradually cooled to reach the discharge temperature of $22\text{-}28^\circ\text{C}$ or slightly higher.

3. Carbonation process and carbonation tower

(1) A typical process for carbonation is shown in Figure 7-9.

The ammoniacal brine is injected into a washing tower (also known as a pre-carbonation tower and a neutralization tower), the kiln gas is blown into the tower to dissolve the scale in the tower, initially increases the carbonation degree, and then is sent to the sodium bicarbonate making tower, and the kiln gas and furnace gas obtained by calcining sodium bicarbonate are boosted by a (reciprocating or centrifugal) compressor and then sent to the tower. The crystal mush discharged from the tower is self-pressed to a sodium bicarbonate solution tank by the liquid level and sent to the filtration process. After a period of production by the sodium bicarbonate making tower, the scale in the tower is relatively thick and the heat transfer is poor, which is unfavorable for crystallization. At this time, the washing tower has been cleaned and can be used interchangeably, which is called "interchange of towers". The tail gas of the two towers contains a small amount of ammonia and carbon dioxide. After gas-liquid separation, the tail gas is sent to a brine workshop for refining the brine. In the actual production process, several towers consist of a group with one tower for washing and the other towers for producing soda ash.

2. Structure and performance of carbonation tower

The carbonation tower is one of the main devices for producing soda ash by an ammonia soda process. It is assembled

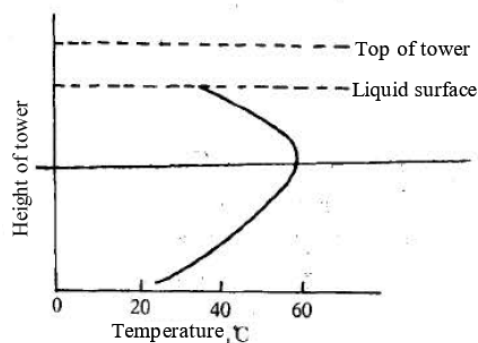


Figure 7-8 Temperature distribution of carbonation tower at different heights

from many cast iron tower circles and its structure can be roughly divided into upper and lower parts: The upper part is a CO₂ absorption tower section. A hat-shaped plate and a slightly downwardly inclined liquid leakage plate are arranged between each circle. Teeth are arranged for dispersing air bubbles on the edges of the plates and the hats to increase the contact area of gas and liquid to promote absorption. About ten cooling water tanks are arranged in the lower part of the tower to cool the carbonated liquid to precipitate crystals. No cap is arranged in the middle of the water tanks. The bottom of the carbonation tower is provided with a crystal mush outlet and an inlet of concentrated CO₂ gas (lower-section gas) and the middle part of the cooling section is provided with an inlet of dilute CO₂ gas (middle-section gas) (this is the two-section gas intake). The top of the tower is provided with a liquid inlet and a tail gas outlet, and the tower is about 22-25 m high to maintain a certain liquid column and residence time. Since too high static pressure will cause a waste of compressor power, it is also unnecessary if the liquid column is too high. The carbonation degree of the crystal mush discharged from the tower will not increase much.

FIG 7-9 Schematic flow diagram of carbonation

The diameter of the carbonation tower is generally 1.98-3.2 m. There is a trend of large-scale development at present.

Each soda ash factory in our country still mainly uses traditional equipment whose main performances are shown in Table 7-4.

Tower diameter (mm)	1,200	1,600	1,980	2,500	3,200
Tower height (mm)	22,542	18,200	25,069	25,117	26,650
Cap Upper section	16	16	21	21	29
Number Lower section	0	0	11	10	
Height of tower circle (mm)	600	450	375, 506	420	540, 800
Opening percentage of separation plate (%)	11.3	9.55	9.0	8.4	9.8
Opening percentage of upper cover (%)	33.7	23.4	33.5	31.5	-
Number of water tanks	10	10	11	9	12
Cooling area (m ²)	128	200	Inside 459 Outside 533	Inside 737 Outside 912	1,921
Operating pressure (Mpa)	1.3	0.7	0.4	0.4	0.3
Production capacity (t/d)	21	35.6	74	122	220-240
Air speed of empty tower (m/s)	0.0355	0.038	-	-	-
Production intensity (t/m ³ .d)	0.843	0.554	0.716	0.98-1.15	1.22-1.33

Since the water tank hat-type carbonation tower has disadvantages of scaling of cooling surface, short production cycle, complex structure, large construction investment, etc., the natural circulation external cooling-type carbonation tower developed in our country has been tested on an industrial scale in 1985. The tower is shown in Figure 7-11.

The diameter of the upper section is 2.5 m, the diameter of the lower section is 2.8 m, and the height is 26.5 m. Two external coolers have a diameter of 1.3 m and a height of 7.4 m. The upper part of the tower is a sieve plate and a bubble cap, the middle and lower parts are provided with multiple central circulation pipes, a suspension in the tower is discharged through the circulation outlet j, and after cooling, the liquid returns to the tower through the circulation inlet m and is taken out from the sodium bicarbonate outlet a.

3. Operation of carbonation tower

In order to ensure that a sodium bicarbonate crystal mush is continuously sent to the filtration process, several carbonation towers are connected into a group to operate. Usually four towers are used as a group, wherein three towers are used for producing sodium bicarbonate; and one tower is a pre-carbonation tower.

In the past, one-section gas intake was used in the carbonation tower. The intake gas is a mixture of kiln gas and furnace gas (CO_2 gas from combustion) and the concentration is very difficult to exceed 60%. Two-section gas intake is used later, that is, the furnace gas with a high concentration is fed from the bottom of the tower, and the kiln gas (with a concentration about 36%-40%) is fed into the middle part of the cooling section, which is more in line with a countercurrent principle. Therefore, absorption is strengthened, carbonation degree is improved, and the utilization rate of sodium is improved. The washing tower is mainly used for washing the scales and required to promote the dissolution and increase the temperature appropriately. Therefore, the kiln gas is introduced from the bottom of the tower and the cooling water and the middle-section gas inlet are closed. In the operation of the carbonation tower, it is generally necessary to master the amount and concentration of the lower-section gas. Practice has pointed out that a part of the kiln gas is sent to the lower section, such that the concentration of the lower-section gas is reduced from 90% to 82%-84%, the carbonation cycle is increased, and a conversion rate can be high and stable. This is mainly due to the fact that the increase of the volume of the lower-section gas improves efficiency. However, if the volume of the lower-section gas is too large, the reaction zone will move down, which will increase the scaling of cooling water pipes and shorten the carbonation cycle in turn. Experience has proved that if the volume of the lower-section gas is appropriately increased and the concentration of CO_2 is maintained at about 84%, the yield will not decrease, but the conversion rate will increase.

The appropriate control conditions of the carbonation tower are as follows:

(1) The height of the liquid level of the carbonation tower should be controlled within 0.8-1.5 m from the top of the tower. If the liquid level is too high, a phenomenon of liquid in the tail gas will be frequent and an air outlet header pipe is blocked. If the liquid level is too low, the output gas will contain a large amount of ammonia and CO_2 , which will increase the loss and reduce the production capacity of the tower.

(2) It is better to strictly control the temperature in the middle part of the tower to be higher, and a warm area distributed in a height direction should be wider to ensure the crystal quality. This is because maintaining a high temperature in the middle part not only has a high conversion rate, but also can enable NaHCO_3 crystal grains to be large and uniform. The area with the

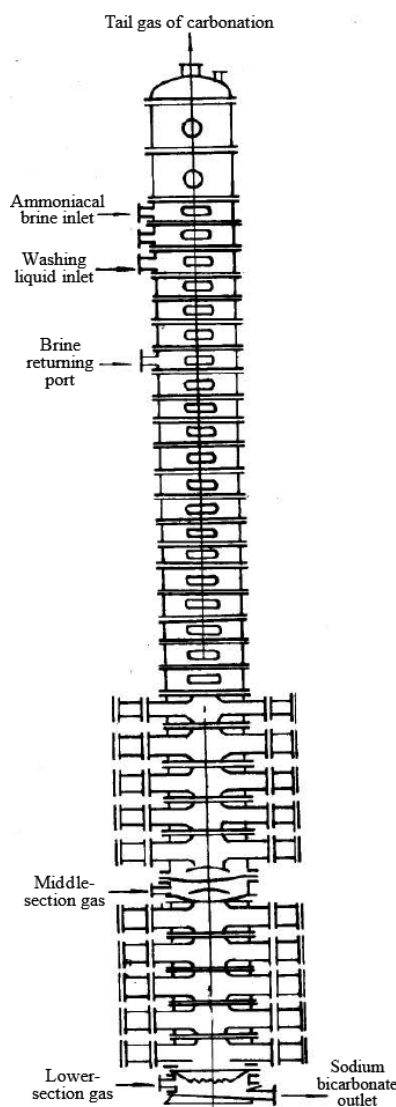


Figure 7-10 Carbonation tower

highest temperature in the middle part is about 3/5 of the tower height.

(3) The gas intake amount of the carbonation tower corresponds to the sodium bicarbonate discharge speed. Otherwise, if the sodium bicarbonate discharge speed is too fast and the gas intake amount is insufficient, the reaction zone will move down, resulting in production of small crystals and decrease of yield. On the contrary, the reaction zone will move up and the loss of NH_3 and CO_2 at the top of the tower will be too large.

(4) The sodium bicarbonate discharge temperature should be kept appropriate. If the sodium bicarbonate discharge temperature is low, more NaHCO_3 will be precipitated, the conversion rate is high, and the yield is increased. However, if the temperature is too low, too much cooling water will be consumed, the tower is blocked and the operation cycle is shortened. The sodium bicarbonate discharge temperature is mainly achieved by adjusting the volume of cooling water. But it must be noted that the adjustment should not be too fast, so as to avoid sudden cooling to produce small crystals and block the tower.

(5) The tower should be replaced according to the specified time and return to normal within 2 h. In the operation of the carbonation tower, severe fluctuations in temperatures, flow rate, etc. should be avoided as much as possible. During normal operation, the composition of gas and liquid phases, temperatures, etc. are different on cross sections of different tower heights, but are required to be stable on the cross section.

7.2.6 Filtration of sodium bicarbonate

In the production of soda ash, the filtration process is used to separate NaHCO_3 crystals in a suspension from the carbonation tower. The obtained crystals are sent to a calcination section, and mother liquor together with washing water (called filtrate) is sent to the ammonia distillation section to recover ammonia.

The main task of the filtration section of soda ash is to enable the NaHCO_3 sent into the calcination section to form a continuous material flow. The process indicators are: water content in the wet NaHCO_3 is 13%-18%, NaCl content is less than 0.4%, and total ammonia content is less than .8%. Therefore, a filter cake must be washed during the filtration to wash away the residual mother liquor in the sodium bicarbonate to minimize the NaCl contained in the soda ash. Soft water should be used as the washing water so as to prevent Ca^{2+} and Mg^{2+} contained in the water from forming a precipitate to block a filter cloth.

(I) Filter

The main equipment in the filtration section is a continuous rotary drum vacuum filter.

Vacuum filtration is as follows: a filter drum of the filter is pumped into negative pressure by a vacuum machine, a pressure difference is formed on both sides of the filter cloth, such that the mother liquor is pumped away through the filter cloth, and the sodium bicarbonate is trapped on the surface of the filter cloth, then removed by a scraper, and sent to the calcination process to be calcined into soda ash. The continuous rotary drum vacuum filter has advantages of continuous operation, large production capacity, and high degree of automation, and thus is suitable for large-scale production. However, the filtered sodium bicarbonate has relatively high water content, the lowest water content is about 15%, and sometimes the water content is as high as 20% or more.

The vacuum filter is as shown in Figure 7-12.

According to the process, the rotary drum of the filter can be conditionally divided into the following zones:

filtration zone: under vacuum, the mother liquor is sucked into the rotary drum, but the NaHCO_3 crystals remain on the

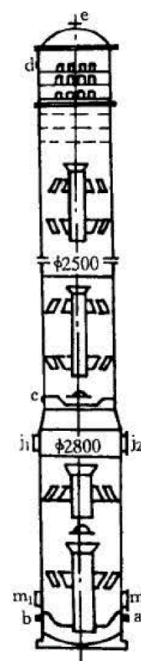


Figure 7-11 Natural circulation external cooling-type carbonation tower

a-sodium bicarbonate outlet; b-lower-section gas inlet; c-middle-section gas inlet; d-inlet of ammonia mother liquor II; e-tail gas outlet; j_{1,2}-external circulation outlet; and m_{1,2}-external circulation inlet

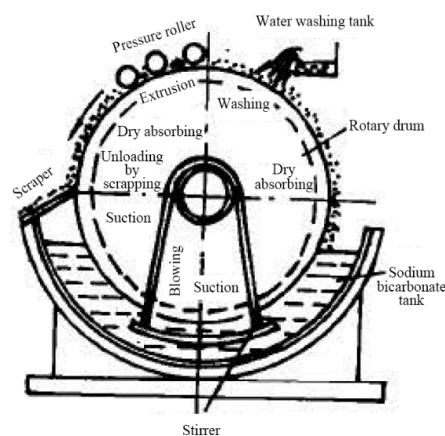


Figure 7-12 Schematic diagram of function of rotary drum of vacuum filter during process of one rotation

surface of the filter cloth to form a filter cake;

pre-drying zone: at this time, the surface of the rotary drum is above the suspension, and the mother liquor is sucked from the filter cake into the rotary drum;

filter cake washing zone: washing water is supplied to the surface of the rotary drum, passes through the filter cake, enters into the rotary drum, and drives out the mother liquor from the intercrystalline space of the filter cake at the same time;

primary drying zone: air is supplied into the zone, passes through a NaHCO_3 filter cake layer, discharges the washing water from the intercrystalline space of the filter cake, and thus reduces the water content of the filter cake;

closed zone: the NaHCO_3 filter cake is scraped off from the surface of the rotary drum using a scraper and the air is prevented from being sucked into the rotary drum at a gap between the scraper and a mother liquor suction zone;

mother liquor suction zone: the so-called “wet” purging of the filter cloth is performed before blowing compressed air, which is a necessary operation to prolong the service life of the filter cloth;

Air blowing zone: the compressed air is fed into a small chamber to restore the filter cloth in an opposite direction to movement of a gas-liquid mixture (entering the rotary drum in vacuum), first passes through the filter cloth, and drives out the mother liquor that has entered the mother liquor suction zone from the small chamber; after passing through the filter cloth, the mother liquor drives out the NaHCO_3 crystals from the pores of the filter cloth and also dissolves the crystals, thereby speeding up the regeneration process of the filter cloth; and Then the filter cloth is purged with the compressed air; and

transition zone: the zone is used to prevent the compressed air fed into the purge from entering the vacuum chamber.

When the rotary drum rotates one circle to complete the entire process cycle, each chamber of the rotary drum passes through each zone.

The production capacity of the vacuum filter used in domestic soda ash factories is mostly 300-350 t soda ash/d and the daily production capacity of the large-scale vacuum filter is 500-600 t.

(II) Process and control requirements of vacuum filtration

A brief process of vacuum filtration is shown in Figure 7-13:

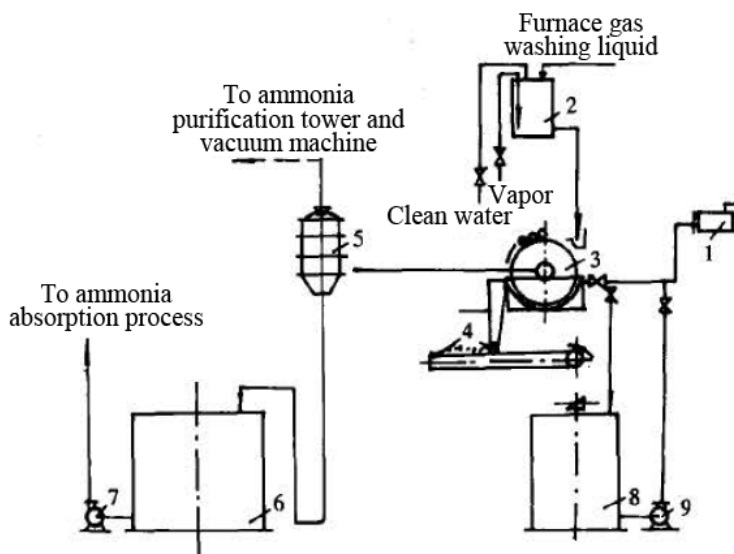


Figure 7-13 Flow diagram of filtration of sodium bicarbonate

1-sodium bicarbonate solution discharge tank; 2-washing water tank; 3-filter; 4-belt conveyor; 5-separator; 6-mother liquor I bucket; 7-mother liquor I pump; 8-sodium bicarbonate solution bucket; and 9-sodium bicarbonate solution pump

The sodium bicarbonate crystal mush from the bottom of the carbonation tower flows into a sodium bicarbonate tank of the vacuum filter through the sodium bicarbonate solution tank. There is a stirrer in the tank to prevent the sodium bicarbonate from depositing in the sodium bicarbonate tank. During normal operation, about two-fifths of the lower part of the filter drum is immersed in the sodium bicarbonate tank. Due to the action of the vacuum system, the liquid is drawn into the rotary drum through the pores of the filter cloth, but the sodium bicarbonate crystals are trapped on the filter cloth. With the rotation of the rotary drum, the sodium bicarbonate on the filter cloth is washed and sucked dry, then transferred to the scraper to be scraped off, and sent to the calcination process by the sodium bicarbonate belt conveyor. After the sodium bicarbonate is scraped off by the scraper, 3-4 mm thick sodium bicarbonate still remains on the filter cloth and needs to be blown off with compressed air to

restore the filter cloth for continued use.

When the liquid is sucked into the rotary drum, it absorbs a part of the air at the same time, and this part of the filtrate and the gas are separated by the gas-liquid separator. In addition to air, the gas also contains a small amount of NH_3 and CO_2 which need to be discharged from the vacuum machine after passing through the ammonia purification tower. The mother liquor is sent to the ammonia distillation process.

After the vacuum filter is used for a period of time, it needs to be stopped and washed with warm water due to the blockage of the filter cloth.

The operation of the vacuum filter is mainly by adjusting the vacuum degree. The vacuum degree (26.7-33.3 kPa) determines the production capacity of the filter, the water content in the sodium bicarbonate, and the quality of the final product. The second is the washing of the filter cake. If the temperature of the washing water is too high, the NaHCO_3 dissolution loss is large; and if the temperature of the washing water is too low, the filter cake is not easy to clean. Therefore, the temperature of the washing water usually should be close to the temperature of the crystal mush. Excessive amount of the washing water will increase the volume of the mother liquor, which increases the load of ammonia distillation in addition to increasing the loss of NaHCO_3 ; and If the amount of the washing water is too small, the salt cannot be washed completely. The amount of the washing water is determined by the quality of the sodium bicarbonate crystals to maintain the maximum amount of NaCl in the obtained final product of soda ash to be less than or equal to 1%.

If the filter uses a metal filter screen instead of coarse cotton cloth or man-made fibers, the operation cycle is longer and the utilization rate of the equipment can be improved.

7.2.7 Calcination of sodium bicarbonate

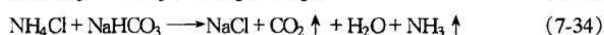
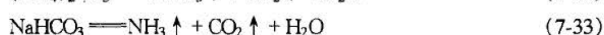
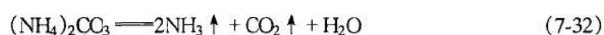
The sodium bicarbonate is calcined and decomposed to obtain a soda ash product. The requirement for calcination in production is that the final product contains less salt and does not contain undecomposed NaHCO_3 ; the produced furnace gas contains a high concentration of CO_2 and the loss is less; and less fuel is consumed.

(I) Principle and equipment of sodium bicarbonate calcination

Sodium bicarbonate is an unstable compound, and can be decomposed at a room temperature and rapidly decomposed by increasing the temperature.



Through thermodynamic calculation, it can be known that when the temperature is 100-101°C, the decomposition pressure has reached 0.1 MPa, that is, NaHCO_3 can be completely decomposed. But in practice, the reaction is very slow at this temperature. The higher temperature leads to the faster reaction. Under the condition of 190°C, NaHCO_3 can be completely decomposed within half an hour. Therefore, in fact, the soda ash discharging temperature of the calcination is mostly controlled at 165-190°C. In the calcination process, in addition to the above reaction and free water in the sodium bicarbonate being heated to water vapor, the following side reactions also occur:



These side reactions not only consume heat, but also increase the amount of circulating ammonia in the system, thereby increasing the ammonia consumption. At the same time, since the last reaction is a double decomposition reaction, NaCl is left in the product, which affects the quality of the product. It can be seen that in the filtration process, sodium bicarbonate washing is very important.

During the calcination process of the sodium bicarbonate, a very high concentration of CO_2 , the so-called “furnace gas”, can be obtained. At present, as for the production in our country, the CO_2 in the furnace gas can reach about 90%, while a calcination rate of sodium bicarbonate is about 51%.

The device for calcining sodium bicarbonate is called calcining furnace. At present, an internal heating-type steam calcining furnace is mainly used in the production. The steam calcining furnace is shown in Figure. 7-14. The furnace body is horizontally cylindrical. The furnace has the specification of $\phi 2.5$ m and the length of 27 m, and is provided with two rolling rings arranged 16 m apart. The weight of the furnace body and the material is transmitted to a supporting roller through the rolling rings. The supporting roller is in a form of a rolling bearing due to the heavy load. A rear end support is provided with a catch wheel to prevent the furnace body from axially moving, and a gear ring is arranged on the furnace body close to the supporting roller and the catch wheel to drive the cylinder body to rotate. The furnace body is internally provided with three layers of steam heating

pipes which are supported on the furnace by a pipe frame, and spiral heat-conducting fins are welded on the outsides of the pipes to increase the heat transfer surface. A gas chamber is located at the tail of the furnace. After a high-pressure steam is introduced, condensed water is still returned to the gas chamber from an original pipe, flows into a condensed water chamber of an outer ring, is sent to a flash vessel by a steam trap, a part of the steam is flashed out, and the condensed water returns to a boiler.

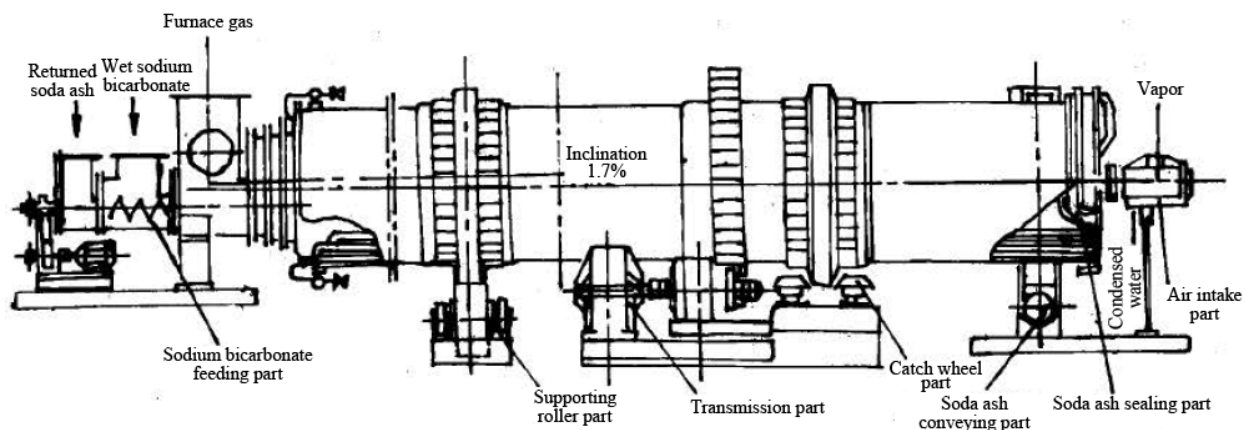


Figure 7-14 Steam calcining furnace

The head of the steam calcining furnace is provided with a sodium bicarbonate feeding screw conveyor and a furnace gas outlet, and the furnace layer is provided a soda ash discharging screw conveyor, a steam inlet, and a condensed water outlet.

The internal heating-type steam calcining furnace has advantages of large production capacity, less maintenance, good working conditions, high thermal efficiency, etc.

(II) Process and operation of sodium bicarbonate calcination

1. Process of sodium bicarbonate calcination

The process of sodium bicarbonate calcination using the internal heating-type steam calcining furnace is shown in Figure 7-15. The sodium bicarbonate is conveyed by a belt conveyor, enters a disk feeder to control the addition amount of the sodium bicarbonate, then is mixed with returned soda ash through the sodium bicarbonate feeding screw conveyor, and is mixed with dust from a furnace gas separator into the furnace. The mixture is indirectly heated and decomposed by a medium-pressure steam for about 20 min, a final product is discharged from the furnace by the soda ash outlet screw conveyor, conveyed by a series of conveying equipment, and then a part of the final product is sent back to the furnace body for returning soda ash and a part is sent to a cylinder sieve and a bin.

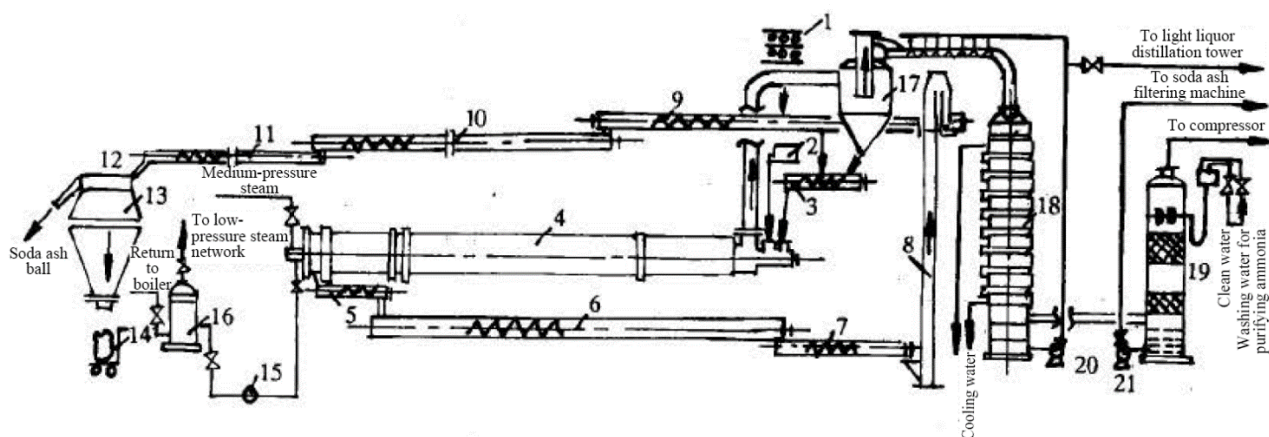


Figure 7-15 Process flow chart of steam calcining furnace

1-belt conveyor; 2-disk feeder; 3-returned soda ash screw conveyor; 4-calcining furnace; 5-soda ash discharging screw conveyor; 6-underground screw conveyor; 7-soda ash feeding screw conveyor; 8-bucket elevator; 9-distributing screw conveyor; 10-final product screw conveyor; 11-screw conveyor above sieve; 12-cylinder sieve; 13-soda ash bin; 14-weighing scale; 15-steam trap; 16-flash vessel; 17-separator; 18-condensing tower; 19-washing tower; 20-condensing pump; and 21-washing water pump;

The furnace gas generated in the calcination process is subjected to dust removal, cooling, and washing, the concentration of CO₂ is about 90%, and the furnace gas is pumped to the carbonation tower for use by a CO₂ compressor.

In recent years, Tianjin Soda Ash Plant has adopted three calcining furnaces with a diameter of 3.6 m, a length of 34 m, and a weight of 194 t in a 0.6 Mt soda ash extension project. The calcining furnaces are the biggest in the soda industry of our country at present.

2. Operation control points of steam rotary calcining furnace

(1) Soda ash discharge temperature The temperature is generally controlled at 150-190°C to completely decompose sodium bicarbonate. If it is lower than 150°C, the quality is unqualified. In order to avoid burning a packaging bag, according to material requirements of the packaging bag, the hot soda ash discharged from the furnace should be further cooled to about 50-100°C.

(2) Furnace gas temperature The furnace gas temperature should be kept at 108-115°C as far as possible. In order to make an air outlet pipe and a cyclone dust collector not sticky and not blocked, it is necessary to use steam to keep warm.

(3) Medium-pressure steam It is generally supplied by a power plant. The steam has a pressure of 2.9-3.3 MPa and a superheat temperature depending on a conveying distance, generally superheat for 25-50°C, so as to ensure that the steam is slightly overheat when entering the furnace and avoid condensation of steam in a header pipe.

(4) Soda ash returning amount In order to avoid scaling in the furnace due to relatively high water content of sodium bicarbonate in the production, a certain amount of calcined final product sodium carbonate (called returned soda ash) is mixed with the sodium bicarbonate to appropriately reduce the average moisture to 6%-8%.

(5) Amount of stored ash The amount of stored ash in the calcining furnace indicates length of reaction time of sodium bicarbonate in the calcining furnace. In order to ensure the complete decomposition of the sodium bicarbonate, it is necessary to ensure a certain amount of stored ash. The amount is related to the size of the calcining furnace. Currently, for a calcining furnace with a diameter of 2.5 m, the amount of stored ash should be kept at 20-25 t.

(III) Specifications of soda ash and manufacture of dense soda ash

The final product, soda ash, is obtained after the calcination, and is a white powder. Its composition should meet the specifications in Table 7-5.

Table 7-5 Specifications of soda ash product

Name of index	National standard (GB210-80)		
	First-grade product	Second-grade product	Third-grade product
Total amount of soda ash (calculated as Na ₂ CO ₃) (%) ≥	99.0	98.5	98.0
Chloride (calculated as NaCl) (%) ≤	0.80	1.0	1.2
Iron (calculated as Fe ₂ O ₃) (%) ≤	0.008	0.01	0.02
Water insoluble matter (%) ≤	0.10	0.15	0.20
Loss on calcination (%) ≤	0.5	0.5	0.7

The generally produced soda ash has a bulk density of 0.5-0.6 t/m³, which is called light soda ash or light ash. This soda ash occupies a large volume, is inconvenient for packaging and transportation, and is lost much due to scattering during use. Therefore, the soda ash is generally produced to a bulk density about 0.8-1.1 t/m³, which is called dense soda ash or dense ash.

The dense ash is mainly prepared by the following method:

1. Hydration method

The process of preparing dense soda ash by a hydration method is shown in Figure 7-16.

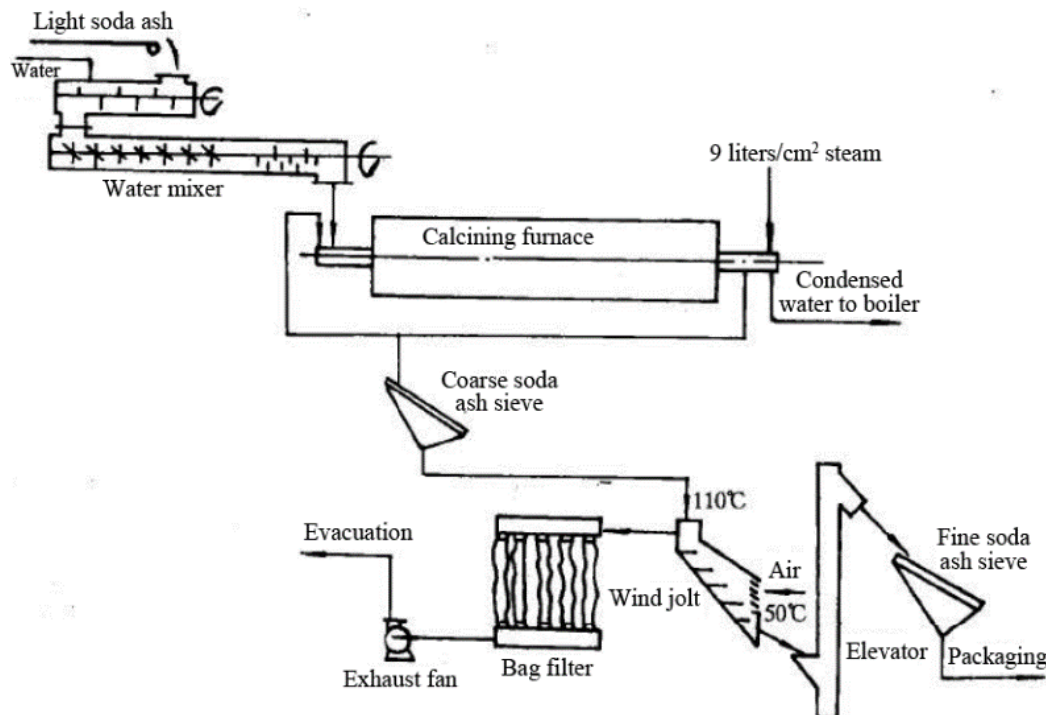
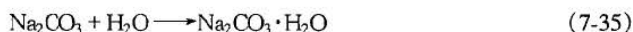


Figure 7-16 Process of preparing dense soda ash by hydration method

The light ash from the calcining furnace at a temperature of 150-170°C is sent into a water mixer by a screw conveyor, and at the same time, hot water is sprayed into the water mixer to be evenly mixed with the light ash. The following reactions occurs:



The water mixing is conducted at a temperature of 90-100°C for 20 min, wherein the water content in the mixture is 17%-20%. The obtained sodium carbonate monohydrate is indirectly heat exchanged with low-pressure steam (about 1 MPa) in a dense ash calcining furnace. The sodium carbonate monohydrate loses crystal water when heated to obtain the dense ash. A part of the dense ash is returned and a part of final product is sieved, cooled, and packaged.

Since the furnace gas produced in the furnace contains soda ash dust, dust removal and washing should be conducted before evacuation.

2. Mechanical extrusion method

The mechanical extrusion method is a new method for producing dense soda ash. The light ash from the calcination process is conveyed to a stock bin connected to a rolling mill by a scraper conveyor and fed to the rolling mill by a vertical and horizontal screw conveyor (a feeder). The light ash is crushed under a mechanical pressure of 230 t and the obtained particles are conveyed into a first vibrating sieve through a scraper conveyor and a bucket elevator for sieving. The particles larger than 2 mm are sent to a grinder to be ground, the particles of 0.3-2 mm are sent to a final product process, and the particles smaller than 0.2 mm are returned to the light ash section. The particles from the grinder pass through a secondary vibrating sieve, the particles larger than 2 mm are sent to the grinder again, and the particles of 0.3-2 mm are sent to the final product process. The particles smaller than 0.2 mm are returned to a light ash bin.

The dense ash from the first and secondary sieving machines is then graded by a sieving machine, and the particles of 0.3-2 mm and 0.2-1 mm are packaged separately. The process is shown in Figure 7-17.

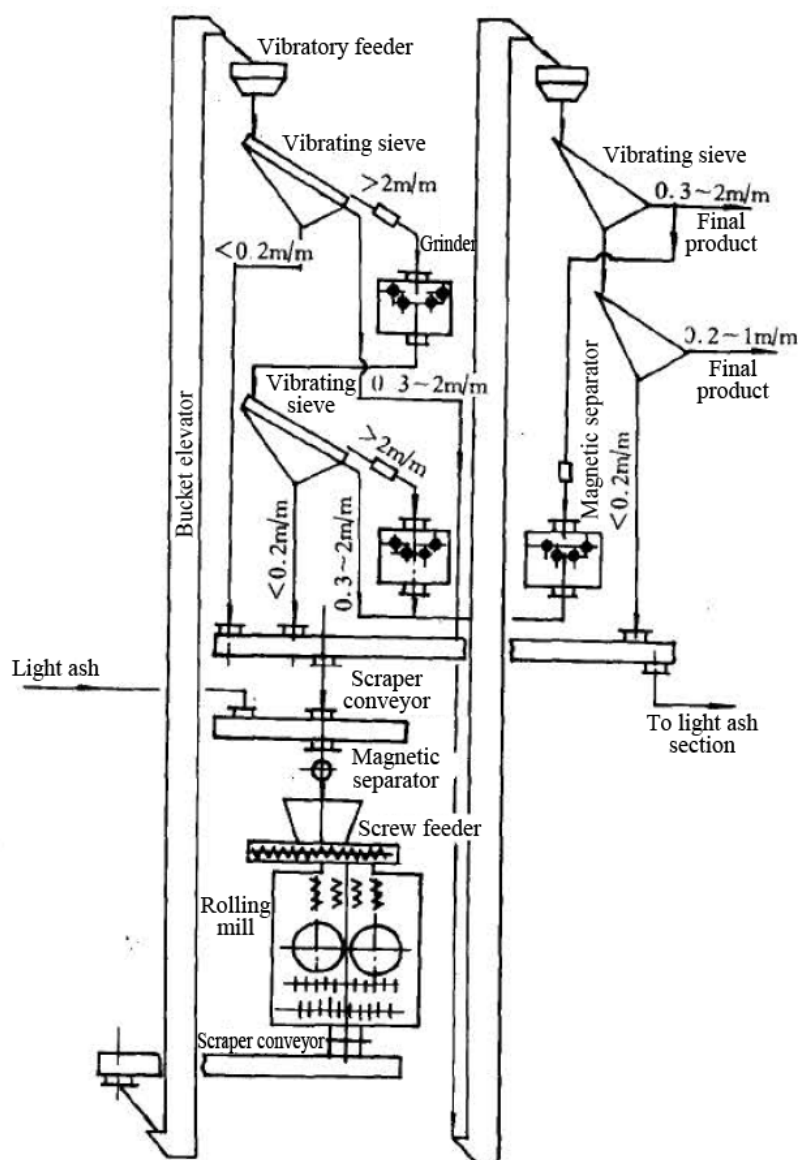


Figure 7-17 Process of preparing dense soda ash by mechanical extrusion method

3. Crystallization method

The crystallization method is as follows: the light ash sent from the calcination process is added into a crystallizer pre-stored with a NaCO_3 solution and an appropriate amount of a NaCO_3 solution is added while the light ash is added. The temperature within the crystallizer is kept at about 105°C . In this way, the light ash will be converted into $\text{NaCO}_3 \cdot \text{H}_2\text{O}$ crystals in the crystallizer. The reaction is the same as that of the hydration method.

In order to remove the heat of reaction and maintain the temperature of the crystallizer stable, a part of the solution must be withdrawn for circulating cooling. In the $\text{NaCO}_3 \cdot \text{H}_2\text{O}$ slurry in the crystallizer, the content of suspended solids is preferably below 50%. The obtained NaCO_3 slurry is filtered or centrifuged to obtain $\text{NaCO}_3 \cdot \text{H}_2\text{O}$ crystals which are then calcined in a dense ash calcination furnace to obtain dense ash. The process flow diagram is shown in Figure 7-18.

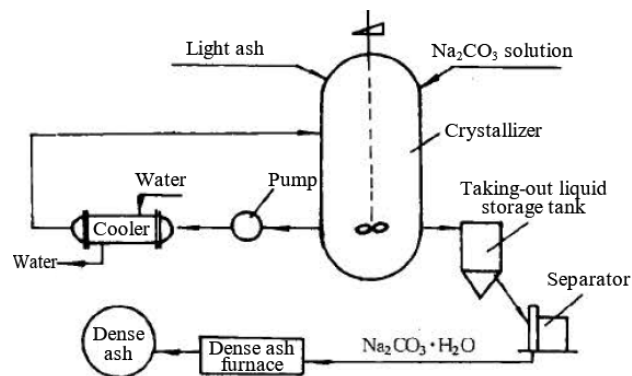


Figure 7-18 process flow diagram of preparing dense soda ash by crystallization method

7.2.8 Ammonia recovery

The ammonia used in the production by an ammonia soda process is recycled. The amount of ammonia required to prepare 1 t of soda ash is about 0.4-0.5 t. The ammonia added to the system will be lost due to escape, leakage by dripping, etc. In order to maintain a certain amount of circulating ammonia in the system, about 1.5-3 kg of ammonia needs to be supplemented for producing every 1 t of soda ash. It can be seen that reducing the loss of ammonia and recovering the ammonia as much as possible are very important in the production by an ammonia soda process. In the modern production by an ammonia soda process, various feed liquids containing ammonia are generally collected for ammonia recovery.

The ammonia-containing feed liquids mainly refer to filtered mother liquor and light liquor. The filtrated mother liquor contains “free ammonia” (about 25 tt) that can be decomposed and distilled by direct heating and “bound ammonia” (about 75 tt) that needs to be distilled after reacting with lime milk (or other alkali substances). Since the feed liquid also contains CO_2 , in order to avoid unnecessary loss of lime, two steps are performed. First, the feed liquid is heated to draw out free ammonia and CO_2 in the liquid, and then lime milk is added to be reacted with the bound ammonia to convert it into free ammonia to be distilled out.

The furnace gas washing liquid, condensate, and other ammonia-containing impure water in the production are collectively referred to as the light liquor. The light liquor only contains free ammonia and thus the ammonia in the light liquor is relatively easy to recover. In order to reduce the load of a preheating section of an ammonia distillation tower, currently, the light liquor is mostly separated from the filtered mother liquor and heated and distilled in a light liquor distillation tower, and the ammonia is recovered.

The total volume of the mother liquor and the light liquor is about 6-7 m^3/t soda ash, wherein the mother liquor is about 5.5-6.5 m^3/t soda ash and the fresh liquid is about 0.5-1.0 m^3/t soda ash.

(I) Process and equipment of ammonia distillation

The process of ammonia distillation is shown in Figure 7-19 and the main equipment is an ammonia distillation tower shown in Figure 7-20. The ammonia distillation tower comprises a mother liquor preheater, a preheating section and a lime distillation section.

The mother liquor preheater and the gas condenser are to recover heat and reduce water in ammonia gas. The mother liquor preheater and the gas condenser consist of 7-10 horizontal water tanks, hot gas is outside the pipe, and mother liquor or cooling water is inside the pipe. The cold mother liquor exchanges heat with the distilled hot gas in the mother liquor preheater, such that the mother liquor is heated from 25-32°C to about 70°C and then enters the preheating section. At the same time, the hot gas is cooled from 88-90°C to 65-67°C and then enters the gas condenser, wherein most of steam enters

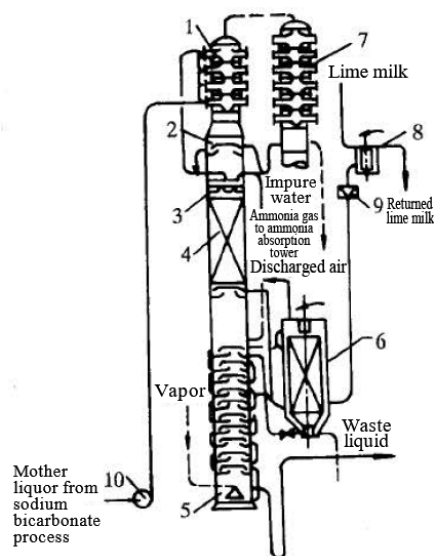


Figure 7-19 Process diagram of ammonia distillation

1-mother liquor preheater; 2-distillation section; 3-liquid separation tank; 4-preheating section; 5-lime milk distillation section; 6-prelimer; 7-gas condenser; 8-lime milk adding cylinder; 9-lime milk flow weir; and 10-mother liquor pump

an ammonia absorption tower after the condensation.

The preheating section is located in the middle of the tower and also known as a heater. Generally, various fillers or “liquid supporting tank” are used to achieve a better gas-liquid contact and increase the heat transfer surface. The mother liquor is added from an upper part through a liquid separation plate and directly contacts with the hot gas from a lower part, the contained free NH_3 and CO_2 are distilled out, and finally the mother liquor only containing bound ammonia and salt is left.

After the preheating section, since the bound ammonia in the mother liquor cannot be decomposed during the heating, the mother liquor is firstly introduced into the preliher from the tower to be mixed with lime milk. The preliher is provided with a stirrer to evenly mixing the mother liquor and the lime milk. At this time, most bound ammonia is converted into free ammonia, and then the mother liquor enters the lime milk distillation section of the tower for distillation. The lime milk distillation section is located at a lower part of the tower and internally provided with more than ten single cap-shaped bubble cap plates. The mother liquor containing lime milk from the preliher is added to the upper part of the section and in a countercurrent contact with the steam from the bottom of the tower. After the distillation section, 99% of the ammonia has been distilled out and waste liquid containing trace amount of ammonia is discharged from the bottom of the tower.

The heat required by the distillation tower is supplied by a low-pressure steam from the bottom of the tower and the steam consumption for producing 1 t of soda ash is 1.5-2.0 t.

In recent years, a Pall ring of $\phi 75 \text{ mm} \times 75 \text{ mm} \times 12 \text{ mm}$ reinforced by polypropylene glass fiber is used in the tower and has advantages of light weight, easy loading and unloading, and low breaking rate.

(II) Chemical reactions in process of ammonia distillation

The mother liquor is a solution containing various compounds. The main chemical reactions during the ammonia distillation process are as follows.

1. Reactions in preheating section

NaHCO_3 and Na_2CO_3 dissolved in the filtrated mother liquor are subjected to the following reactions:

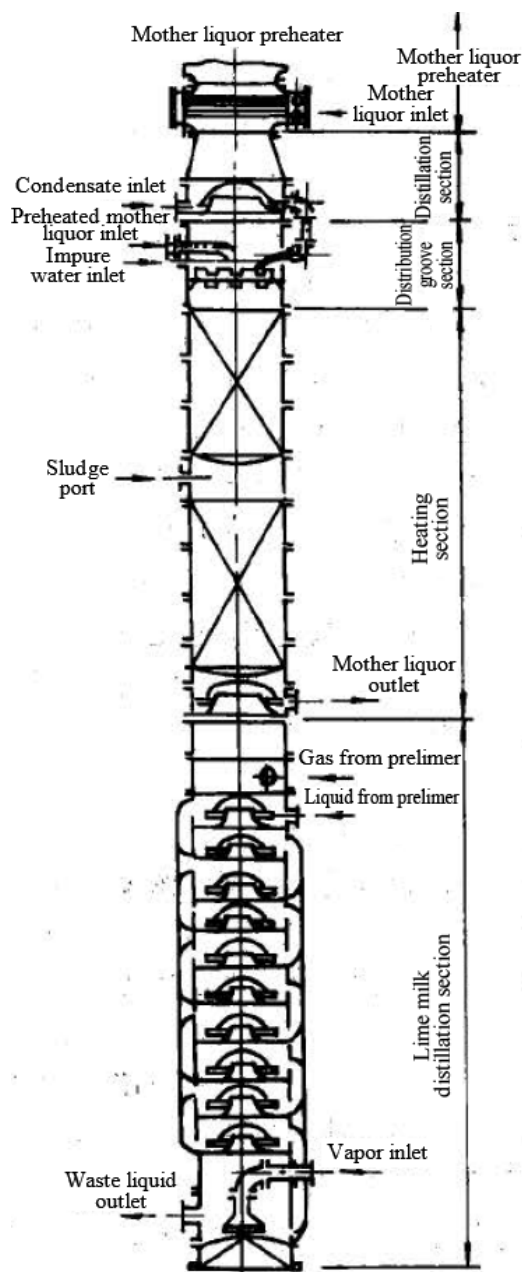
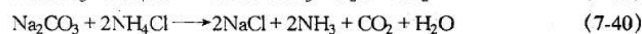
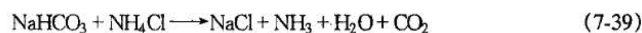
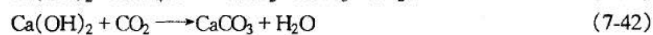


Figure 7-20 Ammonia distillation tower

2. Reactions in blending tank and lime milk distillation section



(III) Analysis of conditions of ammonia distillation process

Waste steam (0.16-0.17 MPa) with not too high temperatures and pressures is directly introduced from the bottom of the ammonia distillation tower. The amount of the water steam should enable the liquid temperature at the bottom of the preheating section to reach 100°C, so as to remove free ammonia and CO₂ as much as possible. Generally speaking, the steam consumption is (1.5-2) t steam soda ash. The temperature at the top of the tower is controlled by the amount of cold water in the condenser, and the temperature of the gas sent to the ammonia absorption system should be maintained at about 60-62°C. If the temperature is too high, the gas will bring too much water. If the temperature is too low, salts such as NH₄HCO₃ will crystallize out in the pipeline to cause blockage.

Decompression is beneficial for the ammonia distillation, such that the top of the tower is generally a slight vacuum of about 666 Pa. Although it can prevent escape loss of ammonia, it also produces the possibility of inlet of the air, such that the system should be closed to avoid diluting the ammonia gas to cause unfavorable absorption. The discharge of waste liquid under the tower is a decompression and isenthalpic process, such that a part of steam can be released to be used for preheating water to prepare lime milk; or the steam is introduced into a small distillation tower to distill out ammonia in various ammonia-containing impure waters. The ammonia loss and heat consumption in the waste liquid are proportional to the liquid volume, such that the liquid should not be too diluted, and the lime milk should be thicker and generally contains 180 tt of active CaO.

In order to distill out ammonia, the equilibrium partial pressure of ammonia in the liquid phase is required to be greater than the partial pressure of ammonia in the gas phase. Two special positions should be noted in this regard.

1. Position between preheating section and lime milk distillation section

The position is where the concentrated gas from the lime milk distillation section contacts with the liquid at the bottom of the preheating section. The ammonia in the liquid is all bound ammonia, its equilibrium partial pressure of ammonia should be equal to zero, and thus the ammonia in the gas phase will be partially dissolved in the liquid phase. This is the reason why the free ammonia in the solution at the outlet of the preheating section cannot be completely driven out.

2. Position at inlet of feed liquid

The ammonia gas escaping from the top part of the preheating section has a very high concentration and has a higher equilibrium partial pressure of ammonia than a newly added feed liquid. As a result, a part of ammonia will be re-dissolved into the feed liquid. Therefore, the feed liquid should be desirably added at a position where the partial pressure of ammonia in the gas phase is lower than its equilibrium ammonia vapor pressure, such that a driving force is positive for the distillation. The concentration of the hot condensate flowing down from the gas condenser is generally thicker. If it is returned to the top of the preheating section without passing through the light liquor distillation tower, the condensate will be diluted by an inlet feed liquid, and thus a part of ammonia and CO₂ is evaporated and condensed repeatedly to waste heat energy.

The amount of waste liquid discharged from the bottom of the ammonia distillation tower is about 7-10 m³ for producing every 1 t of soda ash. According to the vapor pressure at the bottom of the distillation tower, the temperature of the waste liquid is 90-120°C. In addition to NaCl and CaCl₂, the waste liquid also contains a trace amount of NH₃. There are also a small amount of Ca(OH)₂, CaCO₃ and CaSO₄, some of which are dissolved and some are suspended solids. In addition, the rest is almost the sand brought into the ammonia distillation tower by the lime milk.

(IV) Light liquor distillation

The light liquor distillation process is also a process of "stripping" directly with water vapor, ammonia and CO₂ are distilled out by direct heat and mass transfer, and they can be returned to the production system for reuse. In actual production, since the calcined furnace gas condensate and ammonia-containing impure water

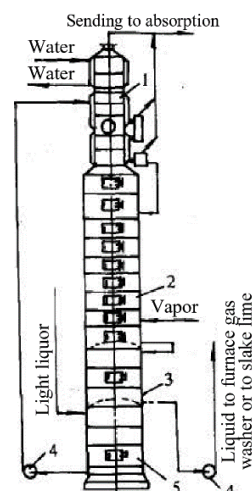


Figure 7-21 Process flow chart of light liquor distillation

1-light liquor distilled gas condensing-cooling machine;
2-light liquor distillation tower; 3-degassed liquid storage tank;
4-pump; and 5-light liquor storage tank

contain a small amount of soda ash, even if there is a small amount of “bound ammonia” in the impure water, it will be converted into free ammonia. Therefore, the light liquor is an $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ system without NaCl and NH_4 . The main reaction of the distillation process is the same as that of the heating section. The process is shown in Figure 7-21.

The light liquor produced by the production of soda ash is collected in a storage tank 5 and then sent to a cooling section of a light liquor distilled gas condensing-cooling machine 1. The light liquor passing through the light liquor distilled gas condensing-cooling machine at $73\text{-}77^\circ\text{C}$ enters a light liquor distillation tower by a distribution tower plate. In the light liquor ammonia distillation tower, NH_3 and CO_2 are desorbed by a mixed gas of liquid convection vapor and gas. The mixed gas of liquid convection vapor and gas passes through the light liquor ammonia distillation tower, passes through the light liquor distilled gas condensing-cooling machine, and is sent to absorb ammonia at $58\text{-}60^\circ\text{C}$. The liquid passing through the light liquor ammonia distillation tower is collected in a degassed liquid storage tank and sent to a kiln gas washer or a vacuum filter using a pump 4.

7.2.9 Overall process of production by ammonia soda process

The overall process of production by an ammonia soda process is shown in Figure 7-22. The relationships between various processes in the production process can be seen.

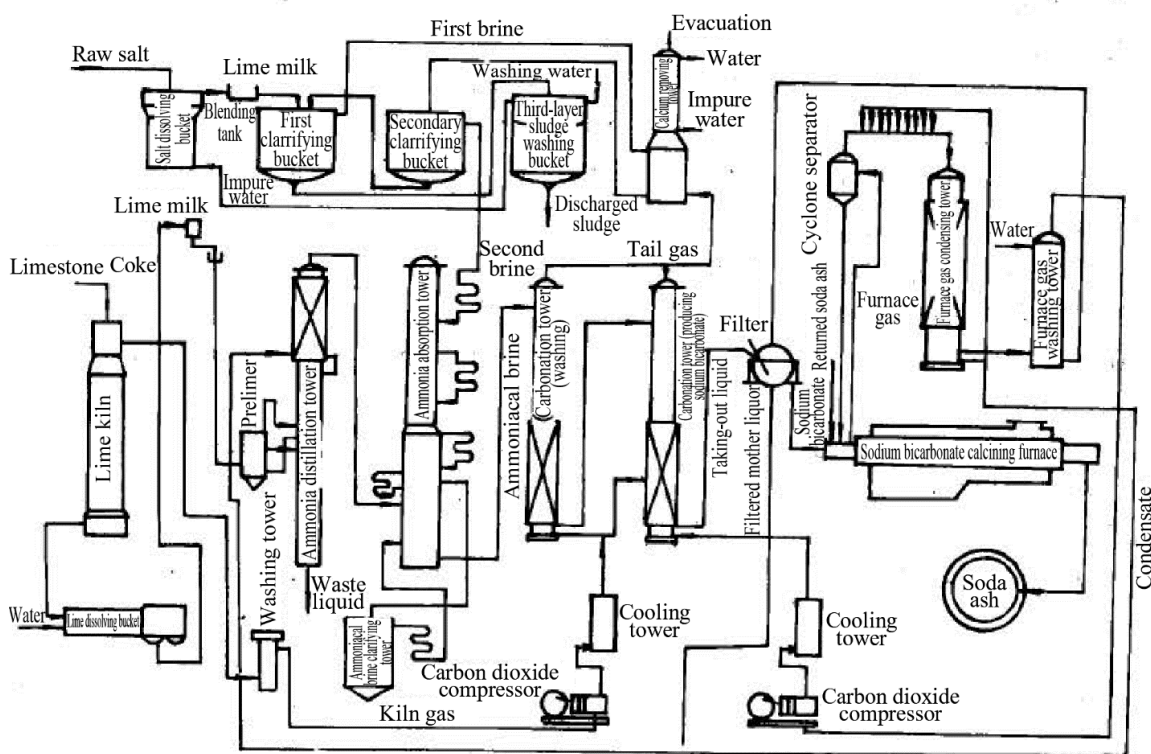


Figure 7-22 Overall process of preparation of soda ash by ammonia soda process

7.2.10 Processing of secondary material resources in preparation of soda ash by ammonia soda process

With the rapid development of the industry, environmental pollution destroys the original dynamic balance of the nature and seriously threatens the survival and development of human beings. Therefore, the research on improving the environmental quality is started or carried out in our country and even all over the world. In chemical production, it is desirable to have a waste-free process, that is, to ensure that the natural resources are fully and optimally utilized when a certain product is required, solid and liquid wastes are not discharged into open water areas or storing areas, and harmful waste gases are not discharged into the atmosphere. However, it is very difficult to carry out such a process, particularly for the large-tonnage production of soda ash by an ammonia soda process. At present, the environmental pollution can only be alleviated and cannot be completely eliminated, such that only a less-waste process can be established.

When the less-waste process is established, the natural resources are fully utilized to ensure the demand for specified products, that is, the secondary material resources are processed, harmful wastes are not discharged into the atmosphere and water system, and heat loss to the surrounding environment should be minimized.

When the waste is reduced as much as possible, the production process should be intensified and the production benefit improved. For example, increasing the completeness of the production process (by selecting optimal conditions to increase the utilization rate of sodium in the carbonation) can increase production efficiency and reduce the amount of wastes. Therefore, establishing a waste-free process is a reasonable approach, both technically and economically, to solve the problem of environmental protection, and is also a main approach.

So far, the following main directions have been identified in establishing the less-waste process:

- (1) studying and developing a process system and a water circulation system to ensure that discharge of a liquid waste and harmful waste gas meets discharge standards of the local region;
- (2) processing secondary material resources into useful products;
- (3) recycling secondary energy and reducing environmental heat loss; and
- (4) establishing a regional industrial complex with closed structures for raw materials and wastes within the enterprise.

The discharges in the production process cycle of soda ash by an ammonia soda process are: distilled suspensions capable of being separated into clarified liquid and solid residues; waste residues during brine refining process; and gaseous wastes

If the harmful substances contained in the gaseous wastes are within an allowable standard range, they can be discharged into the atmosphere. But the clarified distillate and solid residues can be processed into products beneficial to human economic activities and should be regarded as secondary material resources.

The production of a wide variety of products can realize a closed structure for utilizing the raw materials and waste materials. It should be noted that the demand for calcium chloride has grown in recent years and is equivalent to the demand for soda ash. The demand for products produced with solid secondary material resources (waste residues) exceeds the annual output rate of the secondary material resources produced by soda ash.

(I) Production of calcium chloride and refined salt

When the less-waste soda ash production complex is established, an efficient process for processing the clarified distillate can be promoted. The clarified liquid can be processed to produce calcium chloride or injected into oil wells after corresponding treatment.

The distillate is an aqueous solution of inorganic salts and its main components are CaCl_2 (10%-14%) and NaCl (5%-7%). The methods for preparing calcium chloride while separating sodium chloride described below are all based on concentrating the aqueous solutions of these salts.

The use of the prepared calcium chloride in the national economy is based on its high water absorption, that is, it can absorb a large amount of water in the air and is easily soluble in water. The calcium chloride has a freezing point lower than water and a boiling point at a concentrated solution higher than water (for example, a 30% CaCl_2 solution freezes at -55°C and boils at 111.6°C).

The calcium chloride is mainly consumed in chemical industry (synthetic rubber production, flotation, etc.), refrigeration engineering, construction industry (improving a solidification rate of concrete), non-ferrous metallurgy (preparing calcium-containing Babbitt metal), and ore processing (to prevent freezing). The calcium chloride can be also used in the textile industry and other sectors of the national economy.

The by-product sodium chloride is mainly consumed in agriculture (preparing a compound feed and a mixed feed) and sometimes NaCl is returned to the production process for preparing soda ash.

1. Main properties of calcium chloride

The calcium chloride dissolves in water, which is an exothermic process. In a temperature range of practical value, its solubility is:

t, ($^\circ\text{C}$)	60	80	90	100	120	140	160	170
C, (weight%)	57.8	59.5	60.6	61.4	763.4	65.6	69.0	71.8

When industrial molten calcium chloride is prepared from the distillate, a solution containing about 70% CaCl_2 can be obtained within a temperature range of $179\text{--}188^\circ\text{C}$. This solution is slightly cooled to crystallize calcium chloride dihydrate. The following is the relationship between the boiling point and concentration of the calcium chloride aqueous solution:

c_{CaCl_2} (weight%)	70	71	72	73
Boiling point, ($^\circ\text{C}$)	165	168	171	173

2. Production process of refined salt is shown in Figure 7-23.

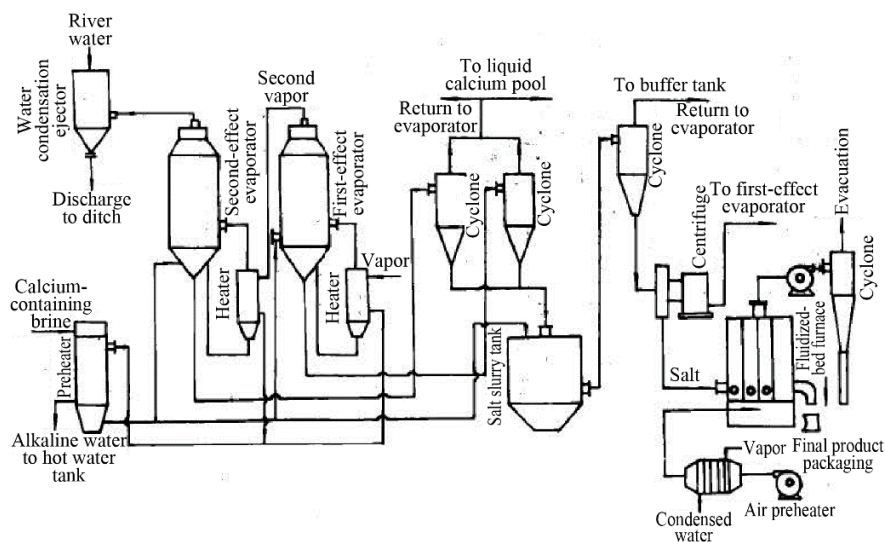


Figure 7-23 Production process of refined salt

The waste liquid of the ammonia distillation tower in the ammonia soda factory is clarified to remove impurities, then crude salt is dissolved to form the liquid, calcium-containing brine, the liquid enters this process and is preheated by a preheater, then the preheated liquid enters double-effect evaporators for evaporation and concentration, and refined salt crystals are precipitated at the bottoms of the evaporators and sent to cyclones for separation. The crystals from the bottoms of the cyclones are sent to a slurry tank and the calcium chloride is washed away with brine; and The liquid at the tops of the cyclones is returned to the evaporators or a liquid calcium pool. The salt in the salt slurry tank will be separated into salt crystals by a cyclone, water is further removed by a centrifuge, and then the salt is dried in a fluidized-bed drying furnace to obtain a refined salt product.

3. Production process of calcium chloride is shown in Figure 7-24.

The liquid calcium from the salt production process enters the liquid calcium pool, is pumped into a liquid calcium tank, then enters bottom parts of rising film evaporators to be concentrated, and enters separators from top parts of the rising film evaporators for separation. Water vapor from the top parts of the separators is condensed by a jet condenser and then enters a sewer. The liquid calcium from the bottom parts of the separators is sent to falling film evaporators for further heating and concentration, and the concentrated calcium chloride from the bottoms of the falling film evaporators enters a storage tank and packaged into a barrel to obtain 70% solid calcium chloride. If one calcium chloride binds to two crystal water, the calcium chloride is called water calcium chloride.

The liquid calcium from a clarification tank of an accumulation yard enters a high brine tank, self-presses into the preheater and heated by a condensate of the rising film evaporators, then enters the rising film evaporators to be heated and concentrated, and then enters the separators for separation, and the liquid calcium enters the liquid calcium pool.

For example, the 70% solid calcium chloride is broken into small blocks and dried again on a drying pit to obtain anhydrous calcium chloride.

The production of refined salt and calcium chloride is introduced above, and is completed by two processes separately. The consumption quota is:

fire coal 300 kg/t_{refined salt}; 800 kg/t_{70%calcium chloride}; 1200 kg/t_{anhydrous calcium chloride}; and
crude salt 800 kg/t_{refined salt}

The crude salt is consumed when the refined salt is produced by this method. The rising and falling film evaporators are used during production of the calcium chloride, thus the evaporators are relatively seriously corroded by the concentrated hot calcium chloride solution. A method for preparing calcium chloride from the waste liquid of the ammonia distillation tower and simultaneously separating NaCl is introduced below. The method can overcome the shortcoming.

4. Process of preparing calcium chloride and simultaneously separating NaCl is shown in Figure 7-25.

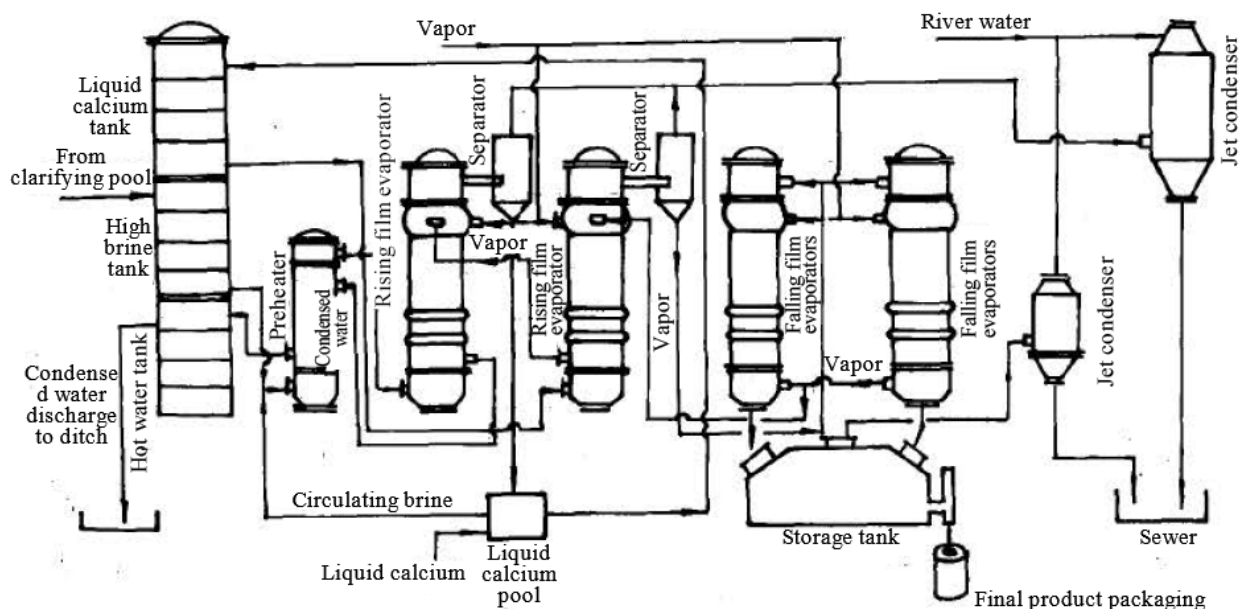


Figure 7-24 Production process of calcium chloride

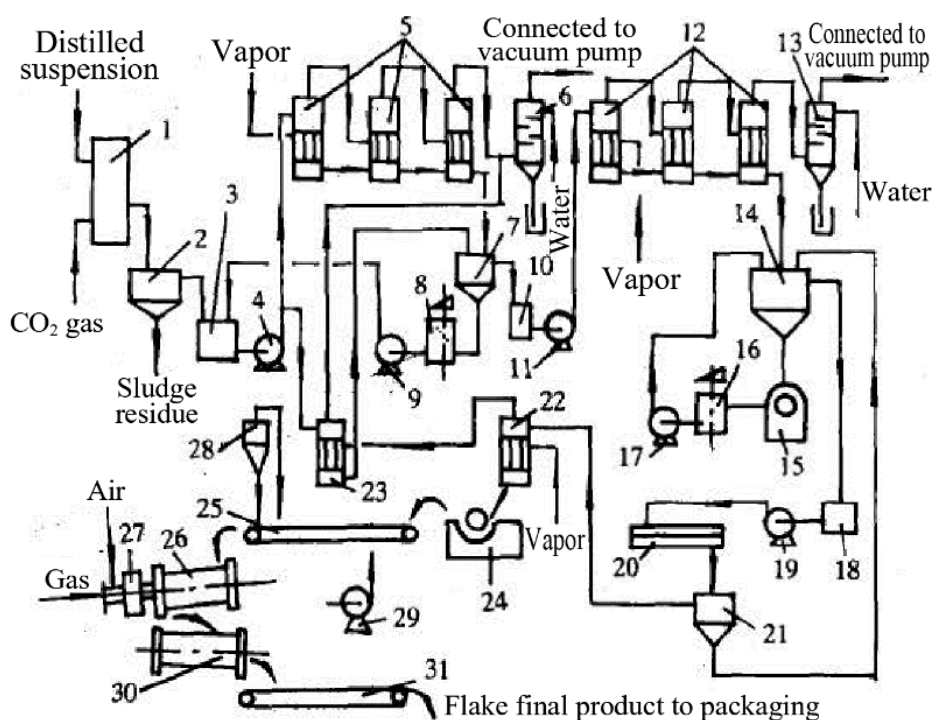


Figure 7-25 Production flow diagram of calcium chloride

1-carbonizer; 2, 7, 14, 21-precipitator; 3, 8, 18-container; 4, 9, 11, 17, 19-pump; 5, 12-evaporator; 6, 13-mixing condenser; 10-storage tank; 15-centrifuge; 16-separated liquid storage tank; 20-vacuum crystallizer; 22-evaporator; 23-waste heat utilization device; 24-flake forming machine; 25, 31-conveyor belt; 26-hardening device; 27-combustion chamber; 28-cyclone separator; 29-fan; and 30-cooling rotary cylinder

A distilled suspension entering a calcium chloride workshop is first pre-carbonized with gas containing CO_2 in a carbonizer 1, and then sent to a precipitator 2 to settle suspended particles (double sedimentation can also be provided before and after carbonation). The sediment (solid phase) is sent to the precipitator for further processing to produce a calcareous soil conditioner and a feed additive. The clarified solution flows into a container 3. A seed crystal active anhydrite CaSO_4 is added into the container at the same time to prevent scaling of heat transfer surfaces of an evaporator group.

The clarified distillate containing the seed crystal is sent from the container 3 to a triple-effect co-current evaporator group 5 by a pump 4, where the liquid is concentrated by evaporation to contain 18% CaCl_2 . The suspension from the last-effect evaporator flows into a precipitator 7. The thick suspension used as a seed crystal passes through a container 8 equipped with a stirrer and is sent back to the container 3 by a pump 9 to be continuously used as a seed crystal.

The partially concentrated and deseeded distillate is sent from a storage tank 10 to a second triple-effect co-current evaporator 12 by a pump 11. Here, the distillate is concentrated to contain 38% calcium chloride and a main part of sodium chloride is separated. The last effects of the evaporators 5 and 12 are both performed under vacuum. Secondary steam from the last effects enter mixing condensers 6 and 13. Air and non-condensed vapor are drawn from the condensers with vacuum pumps (not shown in the figure). The amount of condensed water generated in the evaporators is $5.5 \text{ m}^3/\text{t}_{\text{soda ash}}$ (calculated based on the production of 67% calcium chloride), and the condensed water is sent to a brine preparation field, and thus the water consumption can be appropriately reduced.

The sodium chloride suspension in the 38% calcium chloride solution flows into a precipitator 14, a thick part then enters a centrifuge 15 from the precipitator, and solid sodium chloride is sent to the user or returned to soda ash production. The separated liquid passes through a storage tank 16 and is sent back to the precipitator 14 by a pump 17. The clarified 38% calcium chloride solution is put into a container 18 and then pumped to an absorption pipeline of a circulating pump of a vacuum crystallizer. In the vacuum crystallizer 20, the solution is further concentrated to contain 40% CaCl_2 and at this time, the remaining amount of sodium chloride is precipitated into a solid phase. The sodium chloride suspension in the 40% calcium chloride solution is sent to a salt mud precipitator 21 by the vacuum crystallizer. The thick salt slurry then enters the precipitator 14 again.

In some production processes of calcium chloride, the vacuum crystallizer is replaced by an evaporator group, that is, the evaporators are used to concentrate CaCl_2 to 48%, and then the sodium chloride is separated.

The clarified 40% calcium chloride solution is sent to an evaporator 22 at a normal pressure, where the solution is concentrated to a molten state and contains 72% CaCl_2 . The secondary steam of the evaporator 22 is used to heat a waste heat utilization heat exchanger 23 operating in parallel with the evaporators 5. The calcium chloride melt is fed into a groove of a flake forming machine 24 and cooling water is added to a rotary cylinder of the flake forming machine for cooling. The coarse flakes are scraped off from the rotary cylinder with a scraper and fed into a hardening machine 26 with a conveyor belt 25, and the flakes are dried by counter currently passing flue gas. The flue gas comes from a combustion chamber 27 which burns a mixture of natural gas and air. The flue gas passing through the hardening rotary cylinder enters a cyclone dust separator 28 and then is extracted by a fan 29 and discharged into the atmosphere.

The hot flakes containing the main substance of about 78% CaCl_2 are discharged into a cooling rotary cylinder and the rotary cylinder wall is cooled with circulating water. The cooled final product flakes are conveyed by a conveyor for packaging and then transported into a final product warehouse.

The main devices of this process are:

The distilled suspension is carbonized using a hollow carbonizer with a lower bubbler. The carbonizer has a diameter of 3.0 m, an effective height of 17 m, and an effective volume of 119 m^3 .

The distilled suspension is clarified using a standard gravity-type precipitator.

Evaporators are of the same model with an external heating chamber and a boiling zone. Each device has a heating surface of 384 m^2 .

The seed crystal is precipitated in a centrally driven gravity-type single-layer thickener. The thickener has a diameter of 25 m and a settling surface of 500 m^2 .

A melting device is a Robert evaporator with a heating surface of 350 m^2 and an average heat transfer coefficient of $430 \text{ W}/(\text{m}^2 \cdot \text{K})$. A temperature difference between a working medium and a heat carrier is 20°C . The device has a diameter of 2.4 m and a height of 10.1 m.

A vacuum crystallizer has an outer diameter of 2.4 m, a height of 18.15 m, and a volume of 32.7 m^3 .

A rotary cylinder-type countercurrent dryer for drying calcium chloride flakes has a volume of 60.8 m³, a diameter of 2.2 m and a length of 16.0 m. An average temperature difference between a working medium and a heat carrier is 200°C. The heat carrier is a combustion product of gaseous fuel.

A rotary cylinder-type cooler has a diameter of 2.5 m and a length of 25 m. Air and water are used as a working medium to cool the flakes.

All the devices are standard products.

(II) Production of soil conditioners and inorganic feed additives

In order to maturing acidic and alkaline soils and improve fertilizer efficiency, calcareous soil conditioners need to be applied to the soil.

It is also important to produce inorganic feed additives based on calcareous substances.

According to data, a soil conditioner made from carbonate products derived from production of soda ash is effective as lime powder, gypsum, chalk and other conditioners, even more effective since a calcium ion in a solid (slag) phase of the distilled suspension has a relatively high activity, and the conditioner has a better physical state and contains magnesium sulfate.

The application of the soil conditioner has a good effect on the physical and chemical properties of the soil, changes reaction of a soil solution, reduces a hydrolysis acidity, and increases a pH value from 5.5-5.6 to 6.2-6.4. The soil conditioner reduces soil dispersion and mobility of organic matters, especially in spring. The soil conditioner improves a structure of an arable layer and reduces the adhesion of the soil by $\frac{1}{2} - \frac{1}{3}$.

The inorganic feed additives can also effectively replace chalk in an agricultural feed for poultry and livestock.

1. A production process of the soil conditioner is shown in Figure 7-26.

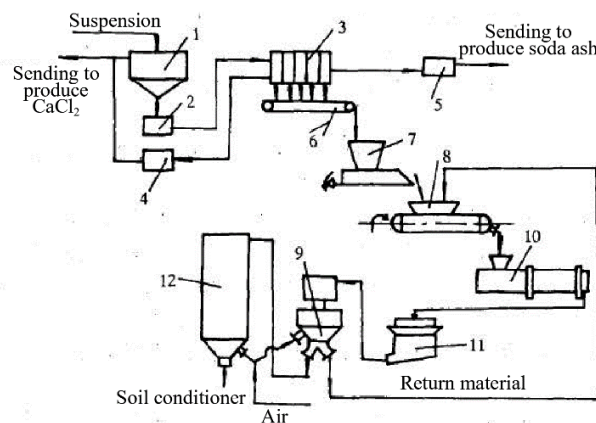


Figure 7-26 Production flow diagram of soil conditioner

1-precipitator; 2-intermediate container; 3-chamber filter press; 4-filtrate storage tank; 5-washing water storage tank; 6-conveyor; 7-vibratory metering feeder; 8-mixer; 9-pneumatic device; 10-rotary drum dryer; 11-hammer crusher; and 12-silo

A suspension from a distillation tower enters a precipitator 1, the clarified part is sent from here to produce calcium chloride, and the thick part is sent into an intermediate container 2 and then enters a chamber filter press 3. The filtrate is sent from a storage tank 4 to produce calcium chloride. Recovered liquid for washing the filtrate and the filter cloth is collected in a container 5 and sent to slake lime, prepare lime milk and perform other processes.

The filtered residue is fed into a vibratory feeder 7 by a conveyor 6 and then enters a mixer 8. A part of the final product is also sent to the mixer as a return material (at a ratio of the final product to the residue of 1 : 1.5). The wet residue and the return material are mixed and then sent to a rotary drum dryer 10 to be dried to a moisture content of 8%. After the drying, the material is crushed by a hammer crusher 11 and sent to a pneumatic device 9, and then enters a silo 12 and is sent to the user from here.

The main device of this process is:

A precipitation thickener has a diameter of 40 m and a standard settling surface of 1,250 m².