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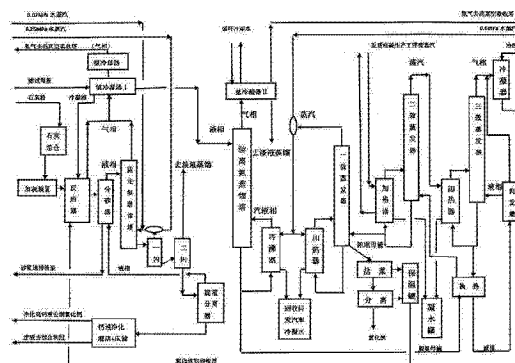
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(54) 发明名称

利用氨碱滤过母液制备氯化钙溶液的工艺方
法

(57) 摘要

本发明公开了一种利用氨碱滤过母液制备氯化钙溶液的工艺方法,涉及氯化钙的生产方法领域。本发明所述的利用氨碱滤过母液制备氯化钙溶液的工艺方法是将滤过母液经过母液蒸馏生成脱氨母液,脱氨母液三效蒸发、分离制得氯化铵饱和溶液,然后在反应器中氯化铵饱和溶液和石灰粉反应,生成氯化钙溶液,最后对氯化钙溶液进行净化,制得成品氯化钙溶液。在确保氨和二氧化碳回收循环利用的前提下,实现碱钙联产,使其氯化钙溶液达到 30% (重量比) 以上。



1. 利用氨碱滤过母液制备氯化钙溶液的工艺方法,其特征在于:所述的利用氨碱滤过母液制备氯化钙溶液的工艺方法为:

(1)滤过母液脱氨:来自重碱车间的滤过母液,经氨冷凝器 I 加热至 $75 \sim 80^{\circ}\text{C}$,氨冷凝器 I 闪发出少量的二氧化碳气体汇入蒸馏气体中;被加热的滤过母液经热母液泵进入游离氨蒸馏塔上部,与来自塔底再沸器的蒸汽逆流接触换热,蒸出全部游离氨和二氧化碳,液体自塔底流出为脱氨母液;

(2)脱氨母液蒸发分离:脱氨母液经换热器先进入闪发罐,后送入三效蒸发器,自三效蒸发器流出的浓缩母液进入稠厚器,然后将经稠厚器的盐浆送至分离机分离,得到固体氯化钠和滤盐液,滤盐液送至保温灌存放,滤盐液为氯化铵饱和溶液;

(3)氯化钙溶液的生成:氯化铵饱和溶液送入反应器,在反应器内汇同氨冷凝器 I 蒸氨冷凝液与石灰粉进行反应,分解后的反应液与旋液分离器部分循环回来的氯化钙溶液一起进入分砂器,分离出较大砂粒后再进入固定氨蒸馏塔,自上而下与蒸汽逆流接触换热,将全部氨蒸出,钙液自塔底排出,并进入第一闪发器,闪发后的废液进入第二闪发器,二次闪发后的钙液经钙液泵进入旋液分离器,控制一定的顶流量返回分砂器分砂,底流送往钙液净化装置;反应器中产生的气体和固定氨蒸馏塔产生的气体经氨冷凝器 I、氨冷却器换热后送至低真空吸收塔;分砂器分出的砂浆送至排渣泵;

(4)氯化钙溶液的净化:由旋液分离器来的钙液进入澄清桶,在澄清桶内经重力沉降,顶流澄清液自流入浓钙液桶,再由浓钙液泵送至氯化钙生产装置;底流增厚泥浆由加料加压泵送入板框压滤机压滤,滤饼经皮带运输机送至碱渣堆场,合格滤液自流入浓钙液桶。

2. 根据权利要求 1 所述的利用氨碱滤过母液制备氯化钙溶液的工艺方法,其特征在于:所述滤过母液脱氨过程中,游离氨蒸馏塔蒸出的游离氨和二氧化碳送至氨冷凝器 II 与循环冷却水进行热交换后去高真空吸收系统;游离氨蒸馏塔塔底再沸器热源为系统来的水蒸汽和第一效蒸发器排出的二次蒸汽经蒸汽喷射式热泵压缩后的蒸汽;所述系统来的水蒸汽的表压为 0.6MPa ;所述氨冷凝器 I 闪发出少量二氧化碳气体汇入蒸馏气体中的蒸馏气体是指氯化钙溶液的生成过程中反应器中产生的气体和固定氨蒸馏塔产生的气体经氨冷凝器 I、氨冷却器后的气体。

3. 根据权利要求 1 所述的利用氨碱滤过母液制备氯化钙溶液的工艺方法,其特征在于:所述脱氨母液蒸发分离过程中,闪发罐产生的气体和第三效蒸发器产生的气体送至冷凝器,其中的水蒸汽直接冷凝,不凝气体由真空泵排空;第二效蒸发器加热室的热源为重质纯碱生产工序来的废蒸汽,蒸汽温度为 95°C ;第二效蒸发器产生的二次蒸汽进入第三效蒸发器加热室;系统来的水蒸汽和第一效蒸发器排出的二次蒸汽经蒸汽喷射式热泵压缩后进入第一效蒸发器的加热室;所述系统来的水蒸汽的表压为 0.6MPa 。

4. 根据权利要求 1 所述的利用氨碱滤过母液制备氯化钙溶液的工艺方法,其特征在于:所述脱氨母液蒸发分离过程中,第一效蒸发器加热室和游离氨蒸馏塔再沸器排出的冷凝水汇入闪发器,闪发蒸汽进入三效蒸发器,冷凝水部分送入设备保温,排出的冷凝水汇集一并送入预热器,对由第二效蒸发器出来的原料母液进行预热;由预热器出来的冷凝水和第二效蒸发器加热室排出的冷凝水汇入闪蒸罐收集,汇集后的冷凝水和第三效蒸发器加热室排出的冷凝水汇入闪蒸罐收集,最后由冷凝水泵将冷凝水送入制碱或制钙装置使用。

5. 根据权利要求 1 所述的利用氨碱滤过母液制备氯化钙溶液的工艺方法,其特征在

于:所述氯化钙溶液的生成过程中,二次闪发后的钙液温度为 85℃,氯化钙的重量百分比含量不小于 30%;以表压为 0.25MPa 新鲜蒸汽作为工作蒸汽,与第一闪发器的闪发蒸汽经蒸汽喷射式热泵压缩后汇同表压为 0.07Mpa 的蒸汽一并进入固定氨蒸馏塔底圈,经分汽帽自下而上,经塔板同反应液逆流接触,进行热质交换,被蒸出的氨气自塔顶出来汇同反应器出气一并进入冷凝器 I 与滤过母液进行热交换,冷凝后的气体经冷却器冷却后进入低真空吸收系统,其冷凝液送至反应器。

6. 根据权利要求 1 所述的利用氨碱滤过母液制备氯化钙溶液的工艺方法,其特征在于:所述氯化钙溶液的生成过程中,来自石灰工序磨制的石灰粉,由气力输送进入灰粉仓,灰粉经仓底给料器计量后,通过螺旋输送机进入反应器与氯化铵饱和溶液反应;所述石灰粉中活性氧化钙含量 $\geq 75\%$ 。

利用氨碱滤过母液制备氯化钙溶液的工艺方法

技术领域

[0001] 本发明涉及氯化钙的生产方法领域,具体是指氨碱法制碱中利用滤过母液制备氯化钙的方法,即利用氨碱滤过母液制备氯化钙溶液的工艺方法。

背景技术

[0002] 我国作为世界纯碱生产第一大国,实行了氨碱法、联碱法和天然碱法三种生产方法、多种工艺技术共同发展的策略,促进了从产量大国向技术强国的转变。联碱法纯碱生产在我国占有较大比重,其优点在于通过联产氯化铵解决了氨碱法的废液排放问题,但副产的氯化化肥受适用局限性的限制,其销售市场问题随产量的增加日益严峻,上个世纪 70 年代,日本开发了新旭法,通过分解副产的氯化铵,解决氯化铵的产量调节问题。由于联碱法的上述缺点,氨碱法仍然是国内外纯碱生产的主要方法,但是氨碱法所产生的废液问题不容忽视。采用氨碱法生产纯碱,每吨产品要排放 $9 \sim 10\text{m}^3$ 的蒸馏废液,其中含有 3% 左右的固体废渣,废液中含有 10% 左右的氯化钙,5% 左右的氯化钠,由于产量大,废液排放量大,难于实现彻底治理,因此,氨碱法纯碱生产技术的改造成为世界性的难题。

[0003] 传统的氨碱法制纯碱,制碱滤过母液利用工艺过程为:

1、精制盐水:由于所使用的氯化钠溶液中含有 Ca^{2+} 、 Mg^{2+} 等杂质,它们在氨化或碳酸化过程中会生成碳酸钙等其他不溶性复盐,堵塞设备和管道,影响传热和成品质量。故盐水在进入吸氨塔前必须除去这些杂质。其精制的方法是加入碱性物质如氢氧化钙和碳酸钠等,使 Ca^{2+} 、 Mg^{2+} 生成沉淀除去。

[0004] 2、精制盐水的氨化:由于氯化钠水溶液不能吸收二氧化碳,为了更好的完成反应、制取纯碱,必须先用氯化钠溶液吸收氨气,再吸收二氧化碳,这一过程在吸氨塔内完成。

[0005] 3、氨盐水的碳酸化:经 2 氨化的精制盐水进入碳酸化塔内,完成反应,形成固体碳酸氢钠和滤过母液。

[0006] 4、重碱的分离:将固体碳酸氢钠和滤过母液分离。

[0007] 5、重碱的煅烧:将分离出来的碳酸氢钠煅烧生成纯碱。

[0008] 6、滤过母液的利用工艺过程:滤过母液主要含有氯化铵,并含有未转化的氯化钠和碳酸氢铵。首先制碱母液进入加热器,使其为转化的碳酸氢铵分解为氨气、二氧化碳和水,以气相溢出;滤过母液从加热器出来后进入调和槽,加入石灰乳,使其氯化铵生成氨气、水和氯化钙;将调和槽出口的溶液送入灰蒸塔,在加热的情况下,将氨气蒸出,氨气回收利用,灰蒸塔底部排走的溶液含氯化钙和氯化钠,此外还含有石灰乳中带来的大量水不溶物,称为蒸馏塔废液,一般情况下直接排弃。

[0009] 传统的蒸馏塔废液都是丢弃,但是氨碱法生成纯碱,每吨产品要排放 10 立方米的废液废渣,废液废渣量大,不仅污染环境,并且由于废液中含有一定量的氯化钙、氯化钠等物质,而导致物质浪费。随着人们认识的进步和对环保的要求,需要对废液进行处理,方法之一是利用废液制备氯化钙。氯化钙生产的纯碱废液回收法通常直接采用蒸馏废液或经过滩晒增浓的蒸馏废液为原料,蒸发浓缩生产氯化钙产品。如中国专利申请(申请号为

200710139304.6)《由氨碱法废液直接生产氯化钙的方法》,即是利用晾晒的废液制备氯化钙;如中国专利申请(申请号为 200710139305.0)《由氨碱法废液直接生产无水球状氯化钙的方法》,即是利用蒸馏废液而制备氯化钙。技术人员对废液处理的第二种思路是废液回收到自身制碱系统加以利用,如中国专利申请(申请号为 00130228.0)《一种纯碱生产工艺》,是将蒸氨母液(蒸氨母液是指滤过母液进入蒸馏塔后所形成的母液)中的氯化钙与水蒸汽反应生成 HCL 和 CaO, HCL 作为联合产品分出,纯净的氧化钙返回蒸氨系统。

[0010] 技术人员对废液处理的第二种思路是把废液回收到自身制碱系统加以利用,虽然解决了废液的利用问题,但是却不能制备氯化钙,因此,现有工艺中氨碱废液回收法制备氯化钙是其制备氯化钙的主要工艺方法。但是该制备氯化钙的方法是将蒸馏废液净化后直接蒸发,由于其含氯化钙浓度低,蒸汽消耗量大,成本高;蒸馏废液经过滩晒可以将氯化钙浓度提高到 20%,但需要较大的滩晒场地和废液的往返输送,随着用地日益紧张,获得滩晒后高浓度钙液原料越来越困难。

发明内容

[0011] 本发明的目的是为了解决上述技术问题的不足,提供一种在不改变氨碱法纯碱生产主体工艺的条件下,通过改变母液蒸馏工艺,在确保氨和二氧化碳回收循环利用的前提下,实现碱钙联产,使其氯化钙溶液达到 30% (wt) 以上的利用氨碱滤过母液制备氯化钙溶液的方法。

[0012] 本发明为了实现上述目的,所采用的技术方案为:提供一种利用氨碱滤过母液制备氯化钙溶液的工艺方法,所述利用氨碱滤过母液制备氯化钙溶液的工艺方法为:

(1)滤过母液脱氨:来自重碱车间的滤过母液,经氨冷凝器 I 加热至 75 ~ 80℃,氨冷凝器 I 闪发出少量二氧化碳气体汇入蒸馏气体中;被加热的滤过母液经热母液泵进入游离氨蒸馏塔上部,与来自塔底再沸器的蒸汽逆流接触换热,蒸出全部游离氨和二氧化碳,液体自塔底流出为脱氨母液;

(2)脱氨母液蒸发分离:脱氨母液经换热器先进入闪发罐,后送入三效蒸发器,自三效蒸发器流出的浓缩母液进入稠厚器,然后将经稠厚器的盐浆送至分离机分离,得到固体氯化钠和滤盐液,滤盐液送至保温罐存放,滤盐液既为氯化铵饱和溶液;

(3)氯化钙溶液的生成:氯化铵饱和溶液送入反应器,在反应器内汇同氨冷凝器 I 蒸氨冷凝液与石灰粉进行反应,分解后的反应液与旋液分离器部分循环回来的氯化钙溶液一起进入分砂器,分离出较大砂粒后再进入固定氨蒸馏塔,自上而下与蒸汽逆流接触换热,将全部氨蒸出,钙液自塔底排出,并进入第一闪发器,闪发后的钙液进入第二闪发器,二次闪发后的钙液经钙液泵进入旋液分离器,控制一定的顶流量返回分砂器分砂,底流送往钙液净化装置;反应器中产生的气体和固定氨蒸馏塔产生的气体经氨冷凝器 I、氨冷却器换热送至低真空吸收塔;分砂器分出的砂浆送至排渣泵;

(4)氯化钙溶液的净化:由旋液分离器来的钙液进入澄清桶,在澄清桶内经重力沉降,顶流澄清液自流入浓钙液桶,再由浓钙液泵送至氯化钙生产装置;底流增厚泥浆由加料加压泵送入板框压滤机压滤,滤饼经皮带运输机送至碱渣堆场,合格滤液自流入浓钙液桶。

[0013] 所述滤过母液脱氨过程中,游离氨蒸馏塔蒸出的含氨和二氧化碳蒸汽送至氨冷凝器 II 与循环冷却水进行热交换后去高真空吸收系统;游离氨蒸馏塔塔底再沸器热源为系统

来的水蒸汽和第一效蒸发器排出的二次蒸汽经蒸汽喷射式热泵压缩后的蒸汽;所述系统来的水蒸汽的表压为 0.6MPa;所述氨冷凝器 I 闪发出少量二氧化碳气体汇入蒸馏气体中的蒸馏气体是指氯化钙溶液的生成过程中反应器中产生的气体和固定氨蒸馏塔产生的气体经氨冷凝器 I、氨冷却器后的气体。

[0014] 所述脱氨母液蒸发分离过程中,闪发罐产生的气体和第三效蒸发器产生的气体送至冷凝器,其中的水蒸汽直接冷凝,不凝气体由真空泵排空;第二效蒸发器加热室的热源为重质纯碱生产工序来的废蒸汽,蒸汽温度为 95℃;第二效蒸发器产生的二次蒸汽进入第三效蒸发器加热室;系统来的水蒸汽和第一效蒸发器处理的二次蒸汽经蒸汽喷射式热泵压缩后分别进入流离氨蒸馏塔的再沸器和第一效蒸发器的加热室;所述系统来的水蒸汽压力的表压为 0.6MPa。

[0015] 所述脱氨母液蒸发分离过程中,第一效蒸发器加热室和游离氨蒸馏塔再沸器排出的冷凝水汇入闪发器,闪发蒸汽进入三效蒸发器,冷凝水部分送入设备保温,排出的冷凝水汇集一并送入预热器,对由第二效蒸发器出来的原料母液进行预热;由预热器出来的冷凝水和第二效蒸发器加热室排出的冷凝水汇入闪蒸罐收集,汇集后的冷凝水和第三效蒸发器加热室排出的冷凝水汇入闪蒸罐收集,最后由冷凝水泵将冷凝水送入制碱或制钙装置使用。

[0016] 所述氯化钙溶液的生成过程中,二次闪发后的钙液温度为 85℃,氯化钙的重量百分比含量不低于 30%;以表压为 0.25MPa 新鲜蒸汽作为工作蒸汽,经蒸汽喷射器引射第一闪发器的废液闪发汽并汇同表压为 0.07Mpa 的蒸汽一并进入固定氨蒸馏塔底圈,经分汽帽自下而上,经塔板同反应液逆流接触,进行热质交换,被蒸出的氨气自塔顶出来汇同反应器出气一并进入冷凝器 I 与滤过母液进行热交换,冷凝后的气体经冷却器进入低真空吸收系统,其冷凝液送至反应器。

[0017] 所述氯化钙溶液的生成过程中,来自石灰工序磨制的石灰粉,由气力输送进入灰粉仓,灰粉经仓底给料器计量后,通过螺旋输送机进入反应器与氯化铵饱和溶液反应;所述石灰粉中活性氧化钙含量 $\geq 75\%$ 。

[0018] 本发明所述的利用氨碱滤过母液制备氯化钙溶液的工艺方法其有益效果在于:本发明所提供的利用氨碱滤过母液制备氯化钙溶液的工艺方法,是在不需要改变传统的氨碱法制纯碱工艺,只是改变滤过母液的后处理工序,生产氯化钙溶液。本发明所述的利用氨碱滤过母液制备氯化钙溶液的工艺方法,滤过母液脱氨是将滤过母液中未分解的碳酸氢铵、碳酸铵分解,氨气、二氧化碳以气体形式排出;脱氨母液蒸发分离是提高滤过母液的溶质浓度,不仅分离出高质量氯化钠,并且制备成氯化铵饱和溶液;氯化钙溶液的生成是将氯化铵饱和溶液和石灰粉反应生产氯化钙溶液,石灰粉的用量为工业常规的用量即可;氯化钙溶液的净化是将生成的氯化钙溶液澄清、压滤去除废渣。

[0019] 本发明所述的利用氨碱滤过母液制备氯化钙溶液的工艺方法,较传统氨碱废液回收法氯化钙生产,可节约大量废液摊晒用地,回收优质原盐 150kg/t 碱,母液蒸馏、蒸发新鲜蒸汽消耗约 1.6t/t 碱,与传统蒸馏技术持平;该法联产二水氯化钙蒸发浓缩及干燥用蒸汽消耗约为 1.8~2.0t/t 钙,氨碱法废液经摊晒后蒸发蒸汽消耗 3.0~3.8t/t 钙,氨碱法废液未经摊晒直接蒸发蒸汽消耗 5.2~6.0t/t 钙,相比较该法氯化钙产品蒸汽消耗降低分别为:未经过摊晒 3.4~4.0t/t 钙,经过摊晒 1.2~1.8t/t 钙。

[0020] 本发明所述的利用氨碱滤过母液制备氯化钙溶液的工艺方法,在确保氨和二氧化碳回收循环利用的前提下,实现碱钙联产,使其氯化钙溶液达到 30% (重量比) 以上。整个工艺过程充分利用系统产生的蒸汽和热量,如滤过母液的加热是利用反应器和固定氨蒸馏塔所产生的气体,游离氨间接蒸馏和一效蒸发利用了一效蒸发排出的蒸汽;并且本系统内还充分利用了制碱其他工序排出难于利用的废蒸汽,如第二效加热室就是利用重质纯碱生产过程中一水碱干燥排放的废蒸汽。

附图说明

[0021] 本发明所述的利用氨碱滤过母液制备氯化钙溶液的工艺方法简易流程图。

具体实施方式

[0022] 以下结合具体实施方式,对本发明所述的利用氨碱滤过母液制备氯化钙溶液的工艺方法进行详细解释。

[0023] 本发明所述的利用氨碱滤过母液制备氯化钙溶液的工艺方法是对传统的氨碱法制纯碱工艺中利用蒸馏废液制备氯化钙的改进。制碱过程与传统过程相同:

1、精制盐水:由于所使用的氯化钠溶液中含有 Ca^{2+} 、 Mg^{2+} 等杂质,它们在氨化或碳酸化过程中会生成碳酸钙等其他不溶性复盐,堵塞设备和管道,影响传热和成品质量。故盐水在进入吸氨塔前必须除去这些杂质。其精制的方法是加入碱性物质如碳酸钠和氢氧化钠等,使 Ca^{2+} 、 Mg^{2+} 生成沉淀除去。

[0024] 2、精制盐水的氨化:由于氯化钠水溶液不能直接吸收二氧化碳,为了更好的完成反应、制取纯碱,必须先用氯化钠溶液吸收氨气,再吸收二氧化碳,这一过程在吸氨塔内完成。

[0025] 3、氨盐水的碳酸化:经 2 氨化的精制盐水进入碳酸化塔内,完成反应,形成固体碳酸氢钠和滤过母液。

[0026] 4、重碱的分离:将固体碳酸氢钠和滤过母液分离。

[0027] 5、重碱的煅烧:将分离出来的碳酸氢钠煅烧生成纯碱。

[0028] 6、滤过母液的利用工艺过程:本发明所述的利用氨碱滤过母液制备氯化钙溶液的工艺方法既滤过母液的利用工艺,不同于传统工艺。

[0029] 所述利用氨碱滤过母液制备氯化钙溶液的工艺方法为:

(1) 滤过母液脱氨:来自重碱车间的滤过母液,经氨冷凝器 I 加热至 $75 \sim 80^{\circ}\text{C}$,氨冷凝器 I 闪发出少量的二氧化碳气体汇入蒸馏气体中;被加热的滤过母液经热母液泵进入游离氨蒸馏塔上部,与来自塔底再沸器的蒸汽逆流接触换热,蒸出全部游离氨和二氧化碳,液体自塔底流出为脱氨母液。

[0030] (2) 脱氨母液蒸发分离:脱氨母液经换热器先进入闪发罐,后送入三效蒸发器,自三效蒸发器流出的浓缩母液进入稠厚器,然后将经稠厚器的盐浆送至分离机分离,得到固体氯化钠和滤盐液,滤盐液送至保温灌存放,滤盐液为氯化铵饱和溶液。

[0031] (3) 氯化钙溶液的生成:氯化铵饱和溶液送入反应器,在反应器内汇同氨冷凝器 I 蒸氨冷凝液与石灰粉进行反应,分解后的反应液与旋液分离器部分循环回路的氯化钙溶液一起进入分砂器,分离出较大砂粒后再进入固定氨蒸馏塔,自上而下与蒸汽逆流接触换热,

将全部氨蒸出,钙液自塔底排出,并进入第一闪发器,闪发后的废液进入第二闪发器,二次闪发后的钙液经钙液泵进入旋液分离器,控制一定的顶流量返回分砂器分砂,底流送往钙液净化装置;反应器中产生的气体和固定氨蒸馏塔产生的气体经氨冷凝器 I、氨冷却器换热后送至低真空吸收塔;分砂器分出的砂浆送至排渣泵。

[0032] 控制一定的顶流量返回分砂器分砂是指回流的量为总重量的 20 ~ 30%。

[0033] (4)氯化钙溶液的净化:由旋液分离器来的钙液进入澄清桶,在澄清桶内经重力沉降,顶流澄清液自流入浓钙液桶,再由浓钙液泵送至氯化钙生产装置;底流增厚泥浆由加料加压泵送入板框压滤机压滤,滤饼经皮带运输机送至碱渣堆场,合格滤液自流入浓钙液桶。

[0034] 滤过母液脱氨过程中,游离氨蒸馏塔蒸出的游离氨和二氧化碳送至氨冷凝器 II 经循环冷却水冷却后去高真空吸收系统;游离氨蒸馏塔塔底再沸器热源为系统来的水蒸汽和第一效蒸发器排出的二次蒸汽经蒸汽喷射式热泵压缩后的蒸汽;所述系统来的水蒸汽压力的表压为 0.6MPa。

[0035] 所述氨冷凝器 I 闪发出少量二氧化碳气体汇入蒸馏气体中的蒸馏气体是指氯化钙溶液的生成过程中反应器中产生的气体和固定氨蒸馏塔产生的气体经氨冷凝器 I、氨冷却器的气体。

[0036] 滤过母液在氨冷凝器 I 中与氯化钙溶液的生成过程中反应器中产生的气体和固定氨蒸馏塔产生的气体进行换热,换热过程中滤过母液闪蒸出的少量二氧化碳与经氨冷却器换热后的气体会合,送至低真空吸收塔。

[0037] 脱氨母液蒸发分离过程中,闪发罐产生的气体和第三效蒸发器产生的气体送至冷凝器,其中的水蒸汽直接冷凝,不凝气体由真空泵排空;第二效蒸发器加热室的热源为重质纯碱生产过程中一水碱干燥排放的废蒸汽,蒸汽温度为 95℃;第二效蒸发器产生的二次蒸汽进入第三效蒸发器加热室;系统来的水蒸汽和第一效蒸发器排出的二次蒸汽经蒸汽喷射式热泵压缩后分别进入流离氨蒸馏塔的再沸器和第一效蒸发器的加热室;所述系统来的水蒸汽压力的表压为 0.6MPa。

[0038] 脱氨母液蒸发分离过程中,第一效蒸发器加热室和游离氨蒸馏塔再沸器排出的冷凝水汇入闪发器,闪发蒸汽进入三效蒸发器,冷凝水部分送入设备保温,排出的冷凝水汇集一并送入预热器,对由第二效蒸发器出来的原料母液进行预热;由预热器出来的冷凝水和第二效蒸发器加热室排出的冷凝水汇入闪蒸罐收集,汇集后的冷凝水和第三效蒸发器加热室排出的冷凝水汇入闪蒸罐收集,最后由冷凝水泵将冷凝水送入制碱或制钙装置使用。

[0039] 氯化钙溶液的生成过程中,二次闪发后的钙液温度为 85℃,氯化钙的重量含量不低于 30%;以表压为 0.25MPa 新鲜蒸汽作为工作蒸汽,经蒸汽喷射器引射第一闪发器的废液闪发汽并汇同表压为 0.07Mpa 的蒸汽一并进入固定氨蒸馏塔底圈,经分汽帽自下而上,经塔板同调和液逆流接触,进行热质交换,被蒸出的氨气自塔顶出来汇同反应器出气一并进入冷凝器 I 与滤过母液进行热交换,冷却后的气体进入低真空吸收系统,其冷凝液送至反应器。

[0040] 氯化钙溶液的生成过程中,来自石灰工序磨制的石灰粉,由气力输送进入灰粉仓,灰粉经仓底给料器计量后,通过螺旋输送机进入反应器与氯化铵饱和溶液反应;石灰粉中活性氧化钙含量 $\geq 75\%$ 。

[0041] 以上所述,仅为本发明较佳的具体实施方式,但本发明的保护范围并不局限于此,

任何熟悉本技术领域的技术人员在本发明披露的技术范围内,根据本发明的技术方案及其发明构思加以等同替换或改变,都应涵盖在本发明的保护范围之内。

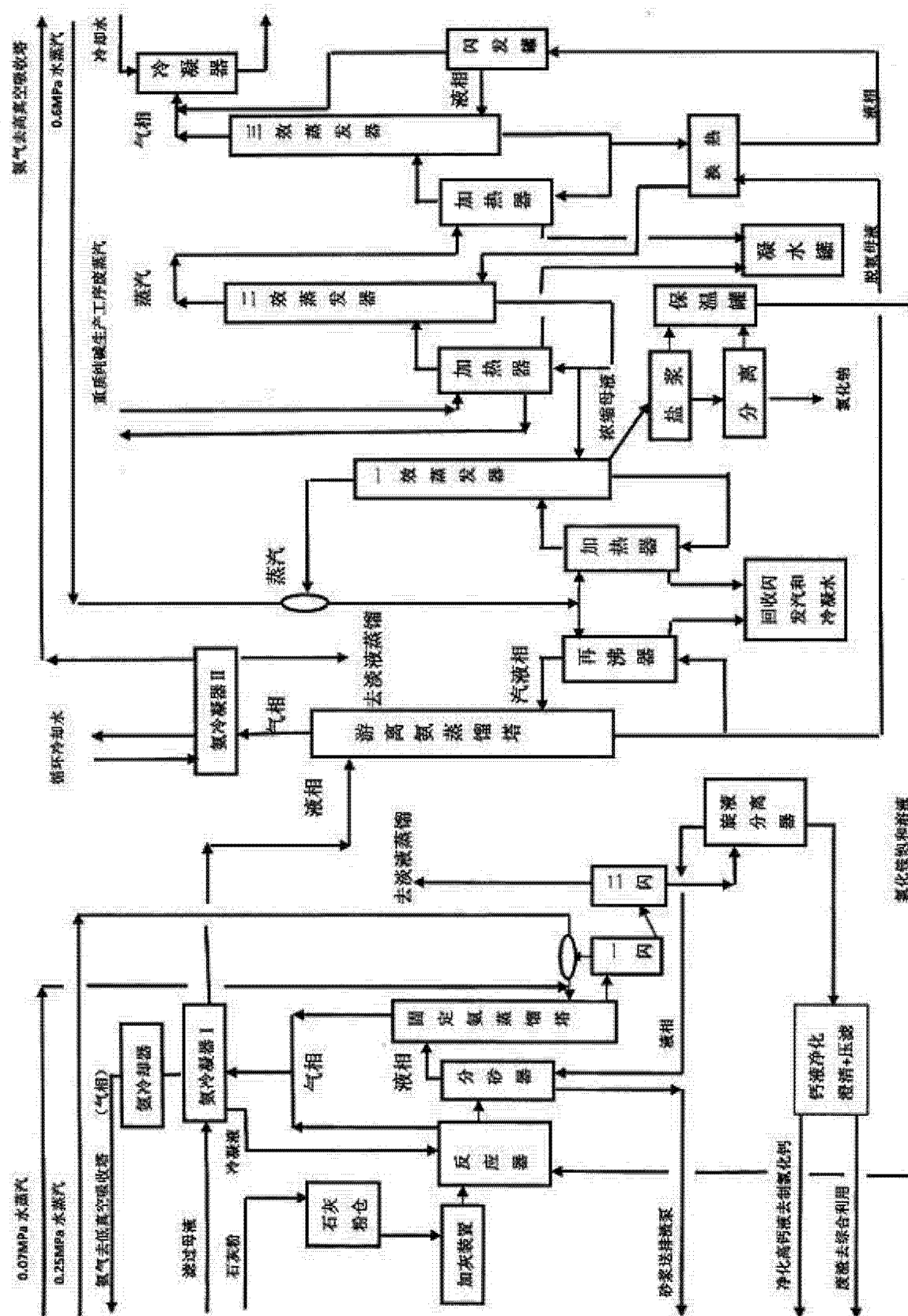


图 1

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 CN102145912A 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 30 day of Nov 2022.

Signature:

Name:

WenLi Zhang
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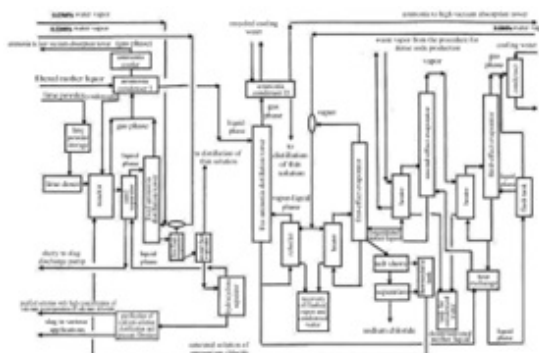
Claim(s): 2 page(s) Description: 6 page(s)
Accompanying drawing(s): 1 page(s)

(54) Title of invention

Processing method for preparing calcium chloride solution using filtered mother liquor in ammonia-soda process

(57) Abstract

A processing method for preparing calcium chloride solution using filtered mother liquor in ammonia-soda process is disclosed in the present invention, which relates to the technical field of the production method for calcium chloride. The processing method for preparing calcium chloride solution using filtered mother liquor in ammonia-soda process according to the present invention consists in the steps of the production of a deammoniated mother liquor by distillation of a filtered mother liquor, triple effect evaporation of the deammoniated mother liquor, obtaining a saturated ammonium chloride solution by separation, then the production of a calcium chloride solution through the reaction of the saturated ammonium chloride solution with lime powder in a reactor, and finally the purification of the calcium chloride solution, so as to obtain the finished product of calcium chloride solution. The joint production of the soda ash and calcium compound with a concentration of the calcium chloride solution of 30% or more by weight is realized, while guaranteeing the recovery and recycling of ammonia and carbon dioxide.



1. A processing method for preparing calcium chloride solution using filtered mother liquor in ammonia-soda process, wherein the processing method for preparing calcium chloride solution using filtered mother liquor in ammonia-soda process consists in the following steps:

(1) deammoniation of the filtered mother liquor: the filtered mother liquor from a plant for sodium bicarbonate is heated by an ammonia condenser I to 75 - 80°C, and the small amount of carbon dioxide gas, which is generated by flashing in the ammonia condenser I, is guided into a distillation gas; the heated filtered mother liquor is fed to an upper part of a free ammonia distillation tower through a pump for hot mother liquor and is brought into contact countercurrently with vapor from a reboiler at the bottom of the tower for heat exchange, evaporating all the free ammonia and carbon dioxide and the liquid discharged from the bottom of the tower being the deammoniated mother liquor;

(2) evaporation and separation of the deammoniated mother liquor: the deammoniated mother liquor is fed to a flash tank through a heat exchanger and then is sent into a triple effect evaporator, the concentrated mother liquor from the triple effect evaporator is fed to a thickener, and the thickened salt slurry is sent into a separator for separation, thus obtaining solid sodium chloride and a filtered salt solution, which is a saturated ammonium chloride solution and is then sent into a thermostatic tank for storage;

(3) production of a calcium chloride solution: the saturated ammonium chloride solution is sent into a reactor, in which the solution reacts with the condensate produced by ammonia evaporation in the ammonia condenser I and the lime powder, and the decomposed reaction solution is fed to a sand separator together with the calcium chloride solution partially recycled from a hydrocyclone separator and is fed to a fixed ammonia distillation tower after the separation of large sands, in which the solution is brought into contact countercurrently with vapor from top to bottom for heat exchange, thereby evaporating all the ammonia and discharging a calcium solution from the bottom of the tower to a first flash evaporator, and the waste liquid after flashing is fed to a second flash evaporator, and the calcium solution after the second flashing is fed to the hydrocyclone separator, in which a controlled amount of top flow is returned to the sand separator for sand separation and the bottom flow is sent to a purifier for calcium solution; the gas produced in the reactor and the gas produced in the fixed ammonia distillation tower are sent to a low vacuum absorption tower after passing through the ammonia condenser I and an ammonia cooler for heat exchange; the sand slurry from the sand separator is sent to a slag discharge pump;

(4) purification of the calcium chloride solution: the calcium solution from the hydrocyclone separator is fed to a clarification tank, in which the solution is settled down by gravity, and a clear top flow flows into a tank for thick calcium solution and then is pumped by a pump for thick calcium solution to a calcium chloride production device; a bottom flow of thickened slurry is sent by a pressurizing charging pump into a plate-and-frame filter press for pressure filtration, and the filter cake is sent by a belt conveyor to a basic slag dump site, and the qualified filtrate flows into the tank for thick calcium solution.

2. The processing method for preparing calcium chloride solution using filtered mother liquor in ammonia-soda process according to claim 1, wherein during the deammoniation of the filtered mother liquor, the free ammonia and carbon dioxide evaporated from the free ammonia distillation tower are sent to an ammonia condenser II for heat exchange with recycled cooling water and then to a high vacuum absorption system; the heat source of the reboiler at the bottom of the free ammonia distillation tower is the water vapor from the system and the vapor that is formed by compressing secondary vapor discharged from a first-effect evaporator by means of a vapor injection heat pump; the gauge pressure of the water vapor from the system is 0.6 MPa; the distillation gas, into which the small amount of carbon dioxide gas generated by flashing in the ammonia condenser I is guided, comprises the gas produced in the reactor during the generation of the calcium chloride solution and the gas produced in the fixed

ammonia distillation tower after passing through the ammonia condenser I and the ammonia cooler.

3. The processing method for preparing calcium chloride solution using filtered mother liquor in ammonia-soda process according to claim 1, wherein during the evaporation and separation of the deammoniated mother liquor, the gas produced in the flash tank and the gas produced in a third-effect evaporator are sent to the condenser, in which the water vapor is directly condensed and the incondensable gas is discharged by a vacuum pump; the heat source for the heating chamber of a second-effect evaporator is waste vapor at a temperature of 95°C from the procedure for dense soda ash production; the secondary vapor from the second-effect evaporator is fed to the heating chamber of the third-effect evaporator; the water vapor from the system and the secondary vapor discharged from the first-effect evaporator are compressed by means of a vapor injection heat pump and fed to the heating chamber of the first-effect evaporator; the gauge pressure of the water vapor from the system is 0.6 MPa.

4. The processing method for preparing calcium chloride solution using filtered mother liquor in ammonia-soda process according to claim 1, wherein during the evaporation and separation of the deammoniated mother liquor, the condensed water discharged from the heating chamber of the first-effect evaporator and from the reboiler of the free ammonia distillation tower are guided into the flash evaporator, wherein the flashed vapor is fed to the triple effect evaporator and the condensed water is partially sent into an apparatus for temperature maintenance and partially discharged, collected and sent together into a preheater for preheating the mother liquor of raw materials from the second-effect evaporator; the condensed water from the preheater and the condensed water discharged from the heating chamber of the second-effect evaporator are collected in a flash container, the collected condensed water and the condensed water discharged from the heating chamber of the third-effect evaporator are collected in the flash container, and finally the condensed water is sent into a device for producing soda ash or calcium compound by means of a pump for condensed water.

5. The processing method for preparing calcium chloride solution using filtered mother liquor in ammonia-soda process according to claim 1, wherein during the production of the calcium chloride solution, the temperature of the calcium solution after the second flashing is 85°C and the content of calcium chloride in percentage by weight is not less than 30%; fresh vapor with a gauge pressure of 0.25 MPa is used as working vapor and is compressed together with the vapor flashed from the first flash evaporator by means of a vapor injection heat pump and is collected and fed to a bottom ring of the fixed ammonia distillation tower together with vapor having a gauge pressure of 0.07 MPa, where the vapor is guided upwards through a gas separation cap and is brought into contact countercurrently with the reaction flow through tower plates for heat and mass exchange, the evaporated ammonia exits the tower from the top and is collected together with the gas output from the reactor and fed to the condenser I for heat exchange with the filtered mother liquor, the condensed gas is fed to the low vacuum absorption system after cooling through a cooler, and the condensate is sent to the reactor.

6. The processing method for preparing calcium chloride solution using filtered mother liquor in ammonia-soda process according to claim 1, wherein during the production of the calcium chloride solution, lime powder produced by grinding in a lime procedure is pneumatically conveyed into a lime powder storage, and the lime powder is weighed by a material dispenser at the bottom of the storage and sent into the reactor by a screw conveyor for the reaction with the saturated ammonium chloride solution; and the content of active calcium oxide in the lime powder is $\geq 75\%$.

Processing method for preparing calcium chloride solution using filtered mother liquor in ammonia-soda process

Technical Field

[0001] The present invention relates to the field of methods for producing calcium chloride, in particular a processing method for preparing calcium chloride using filtered mother liquor in ammonia-soda process, namely a processing method for preparing calcium chloride solution using the filtered mother liquor in ammonia-soda process.

Background Art

[0002] China is the world's largest producer of soda ash. The ammonia-soda process, the joint production process for ammonium chloride and sodium carbonate, and the trona process are developed and applied with various technologies, which promotes the transition of the role of China from a major producer to a creator of new techniques. The joint production process for soda ash makes up a large proportion in the production of soda ash in China and possesses the advantage of solving the problem of waste liquid disposal in the ammonia-soda process. However, the chloride-based chemical fertilizer as side product has limited suitability, which causes an increasingly serious problem of marketing with the increase of its production. In 1970s, a new method was developed by Asahi Glass Company from Japan, by which the production of ammonium chloride can be adjusted by decomposing the side product of ammonium chloride. Because of the above-mentioned shortcoming of the joint production process, the ammonia-soda process remains the dominant method for soda ash domestic and abroad, but its waste liquid problem is still crucial. The ammonia-soda process generates 9 - 10 m³ distillation waste per ton of soda ash, which contains about 3% of solid slag and about 10% of calcium chloride and about 5% of sodium chloride in the waste liquid. Due to its enormous amount of production, the waste is also discharged in massive quantity, which is difficult to be handled completely. Therefore, the improvement of technologies in ammonia-soda process has become a worldwide challenge.

[0003] In the traditional ammonia-soda process for soda ash production, the procedure for using the filtered mother liquor from the soda ash production consists in:

1. Refinement of the salt solution: The sodium chloride solution used contains impurities such as Ca^{2+} , Mg^{2+} and the like, which will produce insoluble complex salts, such as calcium carbonate, during ammoniation or carbonatization, thereby blocking the equipment and pipelines and influencing heat transfer and the quality of the finished products. Therefore, these impurities must be removed before the salt solution is fed to an ammonia absorption tower. The refinement method therefor lies in the addition of basic substances, such as calcium hydroxide and sodium carbonate, so that Ca^{2+} and Mg^{2+} are removed by precipitation.

[0004] 2. Ammoniation of the refined salt solution: Since the aqueous solution of sodium chloride cannot absorb carbon dioxide, in the ammonia absorption tower, the ammonia must be absorbed first with the sodium chloride solution before the absorption of carbon dioxide, so as to facilitate the reaction and the production of soda ash.

[0005] 3. Carbonatization of the ammoniated salt solution: The refined salt solution which has been ammoniated in step 2 is fed to a carbonatization tower, where solid sodium bicarbonate and a filtered mother liquor are formed after the reaction.

[0006] 4. Separation of sodium bicarbonate: The solid sodium bicarbonate and the filtered mother liquor are separated from each other.

[0007] 5. Calcination of sodium bicarbonate: The separated sodium bicarbonate is calcined into soda ash.

[0008] 6. Utilization of the filtered mother liquor: The filtered mother liquor contains mainly ammonium chloride as well as unconverted sodium chloride and ammonium bicarbonate. Firstly, the mother liquor from sodium carbonate production is fed to a heater, so that the unconverted ammonium bicarbonate is decomposed into ammonia, carbon dioxide and water, which exit in the gas phase. The filtered mother liquor is fed from the heater to a mixing tank, where calcium hydroxide is added to react with ammonium chloride, so as to give ammonia, water and calcium chloride. The solution from the outlet of the mixing tank is fed to an ash distillation tower, where the ammonia is evaporated while heating for recovery. The solution discharged from the bottom of the ash distillation tower contains in addition to calcium chloride and sodium chloride also a large amount of water-insoluble substances from the calcium hydroxide, which is referred to as waste liquid from the distillation tower and is usually directly disposed.

[0009] Traditionally, the waste liquid from the distillation tower should be disposed. However, for each ton of the product of soda ash produced by the ammonia-soda process, 10 cubic meters of waste liquid and slag need to be disposed. With such a high quantity, the waste liquid and slag do not only cause pollution to the environment, but also lead to the waste of substances in the waste liquid, such as a certain amount of calcium chloride, sodium chloride, etc. With the improvement in terms of the awareness of the importance of environment protection and with the increase in requirements for environment protection, the waste liquid should be treated. One of the methods for treating consists in the preparation of calcium chloride using the waste liquid. In the method for recovering the waste liquid from production of soda ash and producing calcium chloride, waste distillation liquid or waste distillation liquid which has been concentrated by solar drying is usually used as raw material, which is then evaporated and concentrated for obtaining the product of calcium chloride. In for example Chinese patent application (with the application number of 200710139304.6) "Method for direct production of calcium chloride from waste liquid in ammonia-soda process", the method disclosed is to prepare calcium chloride using waste liquid which has been dried under the sun. In for example Chinese patent application (with the application number of 200710139305.0) "Method for direct production of spherical anhydrous calcium chloride from waste liquid in ammonia-soda process", the method disclosed is to prepare calcium chloride using waste distillation liquid. For a person skilled in the art, the second way of treating waste liquid consists in the recycling of the waste liquid back to the sodium carbonate production system itself. In for example Chinese patent application (with the application number of 00130228.0) "Process for soda ash production", the method disclosed is to carry out a reaction of calcium chloride in the mother liquor after ammonia evaporation (which is referred to the mother liquor acquired after feeding the filtered mother liquor through the distillation tower) with water vapor, so as to give HCl and

CaO, wherein HCl is separated as a joint product and the pure calcium oxide is returned to the ammonia evaporation system.

[0010] Although in the second way of treating waste liquid for a person skilled in the art, where the waste liquid is utilized by recycling back to the sodium carbonate production system itself, the problem of the utilization of the waste liquid is solved, calcium chloride cannot be prepared thereby. The preparation of calcium chloride in the prior art is thus mainly effected by the recovery of the waste liquid in ammonia-soda process. However, this method relies on the direct evaporation of purified waste distillation liquid, which leads to a large vapor consumption and high costs, owing to the low concentration of calcium chloride. Although the concentration of calcium chloride in the waste distillation liquid can be increased to 20% by solar drying, this requires a large field for solar drying and transportation of the waste liquid from/to the field. As the available area gradually decreases, it would be more and more difficult to obtain a raw material of highly concentrated calcium solution by solar drying.

Summary of the Invention

[0011] The object of the present invention is to solve the above-mentioned technical problems by providing a method for preparing calcium chloride solution using filtered mother liquor in ammonia-soda process, in which the joint production of soda ash and calcium compound can be achieved by modifying the distillation process for the mother liquor without changing the main procedure for producing soda ash in ammonia-soda process, while guaranteeing the recycling of ammonia and carbon dioxide and achieving a concentration of calcium chloride being 30% (wt) or higher.

[0012] In order to achieve the above-mentioned object, the technical solution used in the present invention is: providing a processing method for preparing calcium chloride solution using filtered mother liquor in ammonia-soda process, which consists in:

(1) deammoniation of the filtered mother liquor: the filtered mother liquor from a plant for sodium bicarbonate is heated by an ammonia condenser I to 75 - 80°C, and the small amount of carbon dioxide gas, which is generated by flashing in the ammonia condenser I, is guided into a distillation gas; the heated filtered mother liquor is fed to an upper part of a free ammonia distillation tower through a pump for hot mother liquor and is brought into contact countercurrently with vapor from a reboiler at the bottom of the tower for heat exchange, evaporating all the free ammonia and carbon dioxide and the liquid discharged from the bottom of the tower being the deammoniated mother liquor;

(2) evaporation and separation of the deammoniated mother liquor: the deammoniated mother liquor is fed to a flash tank through a heat exchanger and then is sent into a triple effect evaporator, the concentrated mother liquor from the triple effect evaporator is fed to a thickener, and the thickened salt slurry is sent into a separator for separation, thus obtaining solid sodium chloride and a filtered salt solution, which is a saturated ammonium chloride solution and is then sent into a thermostatic tank for storage;

(3) production of a calcium chloride solution: the saturated ammonium chloride solution is sent into a reactor, in which the solution reacts with the condensate produced by ammonia evaporation in the ammonia condenser I and the lime powder, and the decomposed reaction solution is fed to a sand separator together with the calcium chloride solution partially recycled

from a hydrocyclone separator and is fed to a fixed ammonia distillation tower after the separation of large sands, in which the solution is brought into contact countercurrently with vapor from top to bottom for heat exchange, thereby evaporating all the ammonia and discharging a calcium solution from the bottom of the tower to a first flash evaporator, and the calcium solution after flashing is fed to a second flash evaporator, and the calcium solution after the second flashing is fed to the hydrocyclone separator, in which a controlled amount of top flow is returned to the sand separator for sand separation and the bottom flow is sent to a purifier for calcium solution; the gas produced in the reactor and the gas produced in the fixed ammonia distillation tower are sent to a low vacuum absorption tower after passing through the ammonia condenser I and an ammonia cooler for heat exchange; the sand slurry from the sand separator is sent to a slag discharge pump;

(4) purification of the calcium chloride solution: the calcium solution from the hydrocyclone separator is fed to a clarification tank, in which the solution is settled down by gravity, and a clear top flow flows into a tank for thick calcium solution and then is pumped by a pump for thick calcium solution to a calcium chloride production device; a bottom flow of thickened slurry is sent by a pressurizing charging pump into a plate-and-frame filter press for pressure filtration, and the filter cake is sent by a belt conveyor to a basic slag dump site, and the qualified filtrate flows into the tank for thick calcium solution.

[0013] During the deammoniation of the filtered mother liquor, the vapor, which contains ammonia and carbon dioxide and is evaporated from the free ammonia distillation tower, is sent to an ammonia condenser II for heat exchange with recycled cooling water and then to a high vacuum absorption system; the heat source of the reboiler at the bottom of the free ammonia distillation tower is the water vapor from the system and the vapor that is formed by compressing secondary vapor discharged from a first-effect evaporator by means of a vapor injection heat pump; the gauge pressure of the water vapor from the system is 0.6 MPa; the distillation gas, into which the small amount of carbon dioxide gas generated by flashing in the ammonia condenser I is guided, comprises the gas produced in the reactor during the generation of the calcium chloride solution and the gas produced in the fixed ammonia distillation tower after passing through the ammonia condenser I and the ammonia cooler.

[0014] During the evaporation and separation of the deammoniated mother liquor, the gas produced in the flash tank and the gas produced in a third-effect evaporator are sent to the condenser, in which the water vapor is directly condensed and the incondensable gas is discharged by a vacuum pump; the heat source for the heating chamber of a second-effect evaporator is waste vapor at a temperature of 95°C from the procedure for dense soda ash production; the secondary vapor from the second-effect evaporator is fed to the heating chamber of the third-effect evaporator; the water vapor from the system and secondary vapor processed by the first-effect evaporator are compressed by means of a vapor injection heat pump and fed respectively to the reboiler of the free ammonia distillation tower and the heating chamber of the first-effect evaporator; the gauge pressure of the water vapor pressure from the system is 0.6 MPa.

[0015] During the evaporation and separation of the deammoniated mother liquor, the condensed water discharged from the heating chamber of the first-effect evaporator and from the reboiler of the free ammonia distillation tower are guided into the flash evaporator, wherein

the flashed vapor is fed to the triple effect evaporator and the condensed water is partially sent into an apparatus for temperature maintenance and partially discharged, collected and sent together into a preheater for preheating the mother liquor of raw materials from the second-effect evaporator; the condensed water from the preheater and the condensed water discharged from the heating chamber of the second-effect evaporator are collected in a flash container, the collected condensed water and the condensed water discharged from the heating chamber of the third-effect evaporator are collected in the flash container, and finally the condensed water is sent into a device for producing soda ash or calcium compound by means of a pump for condensed water.

[0016] During the production of the calcium chloride solution, the temperature of the calcium solution after the second flashing is 85°C and the content of calcium chloride in percentage by weight is not lower than 30%; fresh vapor with a gauge pressure of 0.25 MPa is used as working vapor and is fed to a bottom ring of the fixed ammonia distillation tower together with the vapor, which is flashed from the first flash evaporator and injected by a vapor injection heat pump, and vapor having a gauge pressure of 0.07 MPa, where the vapor is guided upwards through a gas separation cap and is brought into contact countercurrently with the reaction flow through tower plates for heat and mass exchange, the evaporated ammonia exits the tower from the top and is collected together with the gas output from the reactor and fed to the condenser I for heat exchange with the filtered mother liquor, the condensed gas is fed to the low vacuum absorption system through a cooler, and the condensate is sent to the reactor.

[0017] During the production of the calcium chloride solution, lime powder produced by grinding in a lime procedure is pneumatically conveyed into a lime powder storage, and the lime powder is weighed by a material dispenser at the bottom of the storage and sent into the reactor by a screw conveyor for the reaction with the saturated ammonium chloride solution; and the content of active calcium oxide in the lime powder is $\geq 75\%$.

[0018] The processing method for preparing calcium chloride solution using filtered mother liquor in ammonia-soda process according to the present invention has the following beneficial effects: The processing method for preparing calcium chloride solution using filtered mother liquor in ammonia-soda process according to the present invention can produce calcium chloride solution by merely changing the post-processing procedure of the filtered mother liquor rather without modification to the conventional soda ash production procedure in ammonia-soda process. In the processing method for preparing calcium chloride solution using filtered mother liquor in ammonia-soda process according to the present invention, the deammoniation of the filtered mother liquor is performed by decomposing the ammonium bicarbonate and ammonium carbonate that have not been decomposed and discharging the resultant ammonia and carbon dioxide in gaseous form. The evaporation and separation of the deammoniated mother liquor are intended to increase the concentration of the solute in the filtered mother liquor, which facilitates not only the separation of sodium chloride in high quality, but also the preparation of the saturated solution of ammonium chloride. The production of the calcium chloride solution is carried out by the reaction of the saturated ammonium chloride solution with lime powder, whereby the amount of lime powder is compliant with those conventional for industry. The purification of the calcium chloride solution aims to clarify the produced calcium chloride solution, and to filter under pressure for removal of slag.

[0019] In comparison to conventional methods for recovering waste liquid in ammonia-soda process for calcium chloride production, the processing method for preparing calcium chloride solution using filtered mother liquor in ammonia-soda process according to the present invention can save a large amount of field for solar drying of the waste liquid. The recovery yield is 150 kg of high quality raw salt per ton of sodium carbonate, at the consumption of fresh vapor for distillation and evaporation of the mother liquor of 1.6 ton per ton of sodium carbonate, which is comparable to that of conventional distillation technologies. For the joint production of calcium chloride dihydrate by the inventive method, the consumption of vapor for evaporation, concentration and drying is about 1.8 - 2.0 t per ton of calcium, while the consumption of vapor for evaporation of waste liquid with solar drying and without solar drying in ammonia-soda process is respectively 3.0 - 3.8 t per ton of calcium and 5.2 - 6.0 t per ton of calcium. The consumption of vapor by the inventive method is reduced by 3.4 - 4.0 t per ton of calcium and by 1.2 - 1.8 t per ton of calcium respectively in comparison to that in conventional method without solar drying and with solar drying.

[0020] In the processing method for preparing calcium chloride solution using filtered mother liquor in ammonia-soda process, the joint production of the soda ash and calcium compound with a concentration of the calcium chloride solution of 30% or more by weight is realized, while guaranteeing the recovery and recycling of ammonia and carbon dioxide. The whole procedure makes full use of the vapor and heat generated by the system. For example, the heating of the filtered mother liquor utilizes the gas produced in the reactor and the fixed ammonia distillation tower, and the vapor discharged from the first-effect evaporator is utilized in the indirect distillation and the first-effect evaporation of free ammonia. In addition, the system also exploits waste vapor from other procedures of the soda ash production, which is generally difficult to utilize. For example, the heating chamber of the second-effect evaporator exploits waste vapor from the drying of the sodium carbonate monohydrate in the procedure for dense soda ash production.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] The figure depicts a simple procedure of the processing method for preparing calcium chloride solution using filtered mother liquor in ammonia-soda process according to the present invention.

Detailed Description of Embodiments

[0022] The processing method for preparing calcium chloride solution using filtered mother liquor in ammonia-soda process according to the present invention will be described in detail below in conjunction with the particular embodiments.

[0023] The processing method for preparing calcium chloride solution using filtered mother liquor in ammonia-soda process according to the present invention forms an improvement to the preparation of calcium chloride using waste distillation liquid in a traditional soda ash production procedure in ammonia-soda process. The production of sodium carbonate is identical to the conventional procedure:

1. Refinement of the salt solution: The sodium chloride solution used contains impurities such as Ca^{2+} , Mg^{2+} and the like, which will produce insoluble complex salts, such as

calcium carbonate, during ammoniation or carbonatization, thereby blocking the equipment and pipelines and influencing heat transfer and the quality of the finished products. Therefore, these impurities must be removed before the salt solution is fed to an ammonia absorption tower. The refinement method therefor lies in the addition of basic substances, such as sodium carbonate and sodium hydroxide, so that Ca^{2+} and Mg^{2+} are removed by precipitation.

[0024] 2. Ammoniation of the refined salt solution: Since the aqueous solution of sodium chloride cannot absorb carbon dioxide directly, in the ammonia absorption tower, the ammonia must be absorbed first with the sodium chloride solution before the absorption of carbon dioxide, so as to facilitate the reaction and the production of soda ash.

[0025] 3. Carbonatization of the ammoniated salt solution: The refined salt solution which has been ammoniated in step 2 is fed to a carbonatization tower, where solid sodium bicarbonate and a filtered mother liquor are formed after the reaction.

[0026] 4. Separation of sodium bicarbonate: The solid sodium bicarbonate and the filtered mother liquor are separated from each other.

[0027] 5. Calcination of sodium bicarbonate: The separated sodium bicarbonate is calcined into soda ash.

[0028] 6. Utilization of the filtered mother liquor: The processing method for preparing calcium chloride solution using filtered mother liquor in ammonia-soda process according to the present invention, i. e. the process for utilizing the filtered mother liquor, is different to that in the prior art.

[0029] The processing method for preparing calcium chloride solution using filtered mother liquor in ammonia-soda process consists in the following steps:

(1) deammoniation of the filtered mother liquor: the filtered mother liquor from a plant for sodium bicarbonate is heated by an ammonia condenser I to 75 - 80°C, and the small amount of carbon dioxide gas, which is generated by flashing in the ammonia condenser I, is guided into a distillation gas; the heated filtered mother liquor is fed to an upper part of a free ammonia distillation tower through a pump for hot mother liquor and is brought into contact countercurrently with vapor from a reboiler at the bottom of the tower for heat exchange, evaporating all the free ammonia and carbon dioxide and the liquid discharged from the bottom of the tower being the deammoniated mother liquor.

[0030] (2) evaporation and separation of the deammoniated mother liquor: the deammoniated mother liquor is fed to a flash tank through a heat exchanger and then is sent into a triple effect evaporator, the concentrated mother liquor from the triple effect evaporator is fed to a thickener, and the thickened salt slurry is sent into a separator for separation, thus obtaining solid sodium chloride and a filtered salt solution, which is a saturated ammonium chloride solution and is then sent into a thermostatic tank for storage.

[0031] (3) production of a calcium chloride solution: the saturated ammonium chloride solution is sent into a reactor, in which the solution reacts with the condensate produced by ammonia evaporation in the ammonia condenser I and the lime powder, and the decomposed reaction solution is fed to a sand separator together with the calcium chloride solution partially recycled from a hydrocyclone separator and is fed to a fixed ammonia distillation tower after the separation of large sands, in which the solution is brought into contact countercurrently with vapor from top to bottom for heat exchange, thereby evaporating all the ammonia and

discharging a calcium solution from the bottom of the tower to a first flash evaporator, and the waste liquid after flashing is fed to a second flash evaporator, and the calcium solution after the second flashing is fed to the hydrocyclone separator, in which a controlled amount of top flow is returned to the sand separator for sand separation and the bottom flow is sent to a purifier for calcium solution; the gas produced in the reactor and the gas produced in the fixed ammonia distillation tower are sent to a low vacuum absorption tower after passing through the ammonia condenser I and an ammonia cooler for heat exchange; the sand slurry from the sand separator is sent to a slag discharge pump.

[0032] The controlled amount of top flow returned to the sand separator makes up 20 - 30% of the total weight.

[0033] (4) purification of the calcium chloride solution: the calcium solution from the hydrocyclone separator is fed to a clarification tank, in which the solution is settled down by gravity, and a clear top flow flows into a tank for thick calcium solution and then is pumped by a pump for thick calcium solution to a calcium chloride production device; a bottom flow of thickened slurry is sent by a pressurizing charging pump into a plate-and-frame filter press for pressure filtration, and the filter cake is sent by a belt conveyor to a basic slag dump site, and the qualified filtrate flows into the tank for thick calcium solution.

[0034] During the deammoniation of the filtered mother liquor, the free ammonia and carbon dioxide evaporated from the free ammonia distillation tower are sent to an ammonia condenser II for cooling by the recycled cooling water and then to a high vacuum absorption system; the heat source of the reboiler at the bottom of the free ammonia distillation tower is the water vapor from the system and the vapor that is formed by compressing secondary vapor discharged from a first-effect evaporator by means of a vapor injection heat pump; the gauge pressure of the water vapor pressure from the system is 0.6 MPa.

[0035] The distillation gas, into which the small amount of carbon dioxide gas generated by flashing in the ammonia condenser I is guided, comprises the gas produced in the reactor during the generation of the calcium chloride solution and the gas produced in the fixed ammonia distillation tower after passing through the ammonia condenser I and the ammonia cooler.

[0036] The gas produced in the reactor during the generation of the calcium chloride solution in the ammonia condenser I using the filtered mother liquor exchanges heat with the gas produced in the fixed ammonia distillation tower. During the heat exchange, the small amount of carbon dioxide flashed from the filtered mother liquor is collected together with the gas which has been subjected to heat exchange in the ammonia cooler and is sent to the low vacuum absorption tower.

[0037] During the evaporation and separation of the deammoniated mother liquor, the gas produced in the flash tank and the gas produced in a third-effect evaporator are sent to the condenser, in which the water vapor is directly condensed and the incondensable gas is discharged by a vacuum pump; The heat source for the heating chamber of a second-effect evaporator is waste vapor from the drying of the sodium carbonate monohydrate in the procedure for dense soda ash production, which has a temperature of 95°C; the secondary vapor from the second-effect evaporator is fed to the heating chamber of the third-effect evaporator; the water vapor from the system and secondary vapor discharged by the first-effect evaporator are compressed by means of a vapor injection heat pump and fed respectively to the reboiler of

the free ammonia distillation tower and the heating chamber of the first-effect evaporator; the gauge pressure of the water vapor pressure from the system is 0.6 MPa.

[0038] During the evaporation and separation of the deammoniated mother liquor, the condensed water discharged from the heating chamber of the first-effect evaporator and from the reboiler of the free ammonia distillation tower are guided into the flash evaporator, wherein the flashed vapor is fed to the triple effect evaporator and the condensed water is partially sent into an apparatus for temperature maintenance and partially discharged, collected and sent together into a preheater for preheating the mother liquor of raw materials from the second-effect evaporator; the condensed water from the preheater and the condensed water discharged from the heating chamber of the second-effect evaporator are collected in a flash container, the collected condensed water and the condensed water discharged from the heating chamber of the third-effect evaporator are collected in the flash container, and finally the condensed water is sent into a device for producing soda ash or calcium compound by means of a pump for condensed water.

[0039] During the production of the calcium chloride solution, the temperature of the calcium solution after the second flashing is 85°C and the content of calcium chloride by weight is not lower than 30%; fresh vapor with a gauge pressure of 0.25 MPa is used as working vapor and is fed to a bottom ring of the fixed ammonia distillation tower together with the vapor, which is flashed from the first flash evaporator and injected by a vapor injection heat pump, and vapor having a gauge pressure of 0.07 MPa, where the vapor is guided upwards through a gas separation cap and is brought into contact countercurrently with the mixed flow through tower plates for heat and mass exchange, the evaporated ammonia exits the tower from the top and is collected together with the gas output from the reactor and fed to the condenser I for heat exchange with the filtered mother liquor, the cooled gas is fed to the low vacuum absorption system, and the condensate is sent to the reactor.

[0040] During the production of the calcium chloride solution, lime powder produced by grinding in a lime procedure is pneumatically conveyed into a lime powder storage, and the lime powder is weighed by a material dispenser at the bottom of the storage and sent into the reactor by a screw conveyor for the reaction with the saturated ammonium chloride solution; and the content of active calcium oxide in the lime powder is $\geq 75\%$.

[0041] The contents disclosed above are only preferred embodiments of the present invention, and are not intended to limit the scope of protection of the present invention. Any person skilled in the art may conduct equivalent changes or modifications to the technical contents in the technical range disclosed in the present invention and according to the technical solutions as well as the inventive concepts of the present invention. These changes and modifications should all be included in the scope of protection of the present invention.

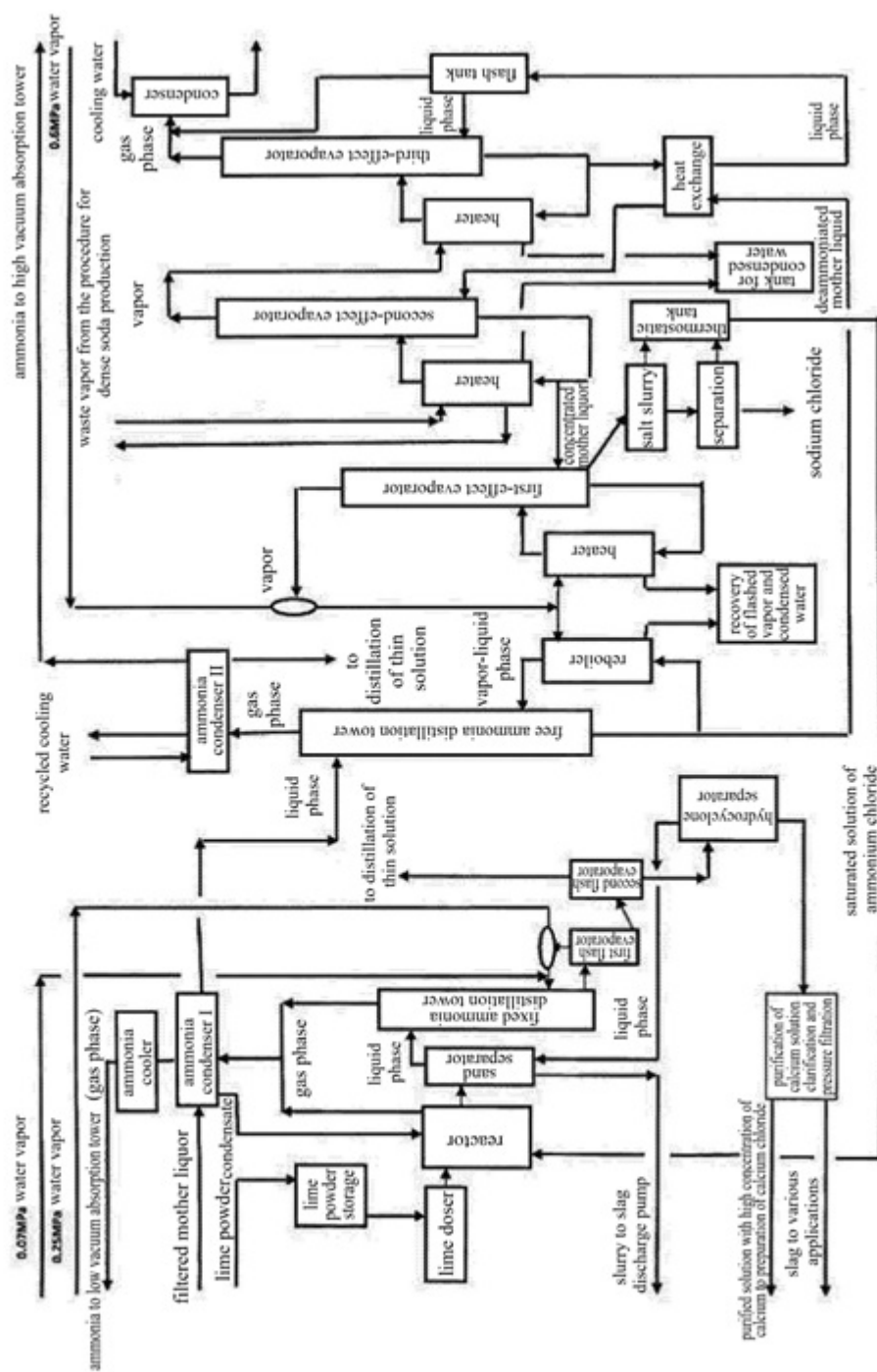


FIG. 1