海水淡化技术应用研究及发展现状

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摘要 当前淡水资源短缺已成为全球性的环境问题, 海水淡化被认为是一种最具前景的解决方法. 目前已开发出了不同的海水淡化技术. 本文首先介绍了海水淡化技术的分类和概况, 其次对传统海水淡化技术进行了评述, 简单介绍了各技术的基本工艺流程和工作原理, 对其性能和技术特点进行了总结, 最后从已有技术的改进、不同技术之间的融合、结合新能源的海水淡化技术和发展新型海水淡化技术等4个方面对海水淡化技术的发展进行了分析和展望. 重点对海水淡化技术的能耗进行了分析.

关键词 海水淡化, 热方法, 膜方法, 新能源

当前淡水资源匮乏日益严重, 已成为全球性的环境问题. 而全球水资源总量中近97.5%的水为海水等咸水资源, 且数据显示世界上超过70%的人口居住在距海边70 km的范围内, 因此20世纪后半叶以来, 海水淡化被认为是最实用的能持续提供淡水来源的方法. 相比另外两种常用淡水取用方式——地下取水和远程调水, 海水淡化能耗低, 原水资源丰富, 因而进入新世纪后被世界各国认为是最可行和最经济的淡水取用方式.

海水淡化是指将海水里面的溶解性矿物质盐分、有机物、细菌和病毒以及固体分离出来从而获得淡水的过程. 从能量转换角度来讲, 海水淡化是将其他能源(如热能、机械能、电能等)转化为盐水分离能的过程. 水质通常用总溶解固体(total dissolved solids, TDS)这一术语来衡量, 用于表征水中盐分和矿物质含量, 从而对原水进行分类和对获得的淡水的质量进行评价. TDS又可称为溶解性固体总量或矿化度, 单位为mg/L或ppm, 即每升水中盐分或矿物质的毫克量. 一般将TDS≤1000 mg/L的水定义为淡水, 而世

界卫生组织(World Health Organization, WHO)也以此范围作为饮用水标准, 美国环境保护部(US EPA)则将饮用水标准设定为TDS≤500 mg/L. 一般将TDS在1000~10000 mg/L的水定义为苦咸水, TDS在10000~45000 mg/L的水定义为海水, 而海水的平均标准为35000 mg/L.

根据盐水分离过程的不同, 海水淡化技术的分类如图1所示. 当盐水分离过程中有新物质生成时, 则该海水淡化方法属于化学方法, 反之则属于物理方法. 在物理方法中, 利用热能作为驱动力, 盐水分离过程中涉及相变的归类为热方法, 主要包括多级闪蒸、多效蒸馏、压汽蒸馏、冷冻法和增湿除湿等方法; 利用膜(半透膜或离子交换膜等)进行盐水分离且不涉及相变的则归类为膜方法, 主要包括反渗透和电渗析等方法; 此外, 物理方法中还包括溶剂萃取法. 而化学方法主要包括水合物法和离子交换法. 若将图1中的海水淡化技术按照从海水中分离出的物质(水或盐分)的标准进行分类, 则除电渗析和离子交换法属于从海水中分离出盐分外, 其他方法均属于从

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图1 海水淡化技术分类

Figure 1 Classification of desalination technologies

海水中分离出水,而冷冻法和水合物法的分离过程都涉及结晶,因此二者通常又被归类为结晶法。值得注意的是,大多数海水淡化技术都适用于废(污)水净化,尤其是反渗透法。

当前在工业上大规模应用的海水淡化技术有多级闪蒸、多效蒸馏和反渗透法。截至2011年,全球有近16000家海水淡化厂,总装机容量达 $7.48 \times 10^7 \text{ m}^3/\text{d}$,其中反渗透法的装机容量占63%,多级闪蒸和多效蒸馏分别占23%和8%^[1]。当前由海水(苦咸水)淡化技术生产的淡水总量中,市政部门的消耗占62%,主要供给人们的生活用水;工业和电力用户(电厂)所占比例分别为26%和6%;剩下的6%用于农业灌溉、旅游和军事等方面^[1]。正如上文所述,大部分海水淡化过程也能用于废(污)水净化,因而淡化过程的原水可以为废(污)水,但是废(污)水在淡化过程原水总用量中只占6%,而主要的原水来源仍然是海水和苦咸水,所占比例分别为59%和21%^[1]。而且,由于各海水淡化技术特点的不同,各技术以较高经济性运行时对原水TDS范围的要求也不一样,具体范围如图2所示^[2]。由于水蒸发所需要的能量与水的盐度无关,因此热蒸馏法(包括多级闪蒸、多效蒸馏和压汽蒸馏等)适用于高盐度原水的淡化。

经过多年的发展,目前已开发了多种基于不同

图2 各海水淡化技术以较高经济性运行时原水的TDS范围

Figure 2 TDS range of raw water for each desalination technology in cost-efficient operation

原理的海水淡化技术。本文首先对海水淡化技术的分类和概况进行了简单的介绍,其次从基本工艺流程和工作原理以及性能和技术特点等方面对传统海水淡化技术进行了详细的评述,最后从已有技术的改进、不同技术之间的结合、结合新能源的海水淡化技术和发展新型海水淡化技术等4个方面对海水淡化技术的发展进行了分析。此外,能耗是评价海水淡化技术经济性的重要参数,因而本文对海水淡化技术的能耗进行了重点分析。

1 主要传统海水淡化技术及其特点

传统海水淡化技术的提出相对较早,经过多年的发展,在商业上的应用更为成熟。本节对图1所示的常见的海水淡化方法进行了介绍,重点对各方法的基本原理、工艺流程和主要特点进行了阐述。

1.1 多效蒸馏

多效蒸馏法(multi-effect distillation, MED)的起源可追溯到19世纪30年代。但早期MED一直受换热表面容易结垢(水垢)的制约,直至20世纪60年代,低温多效蒸馏(low temperature MED, LT-MED)技术的开发才使得结垢和腐蚀问题得到缓解。LT-MED系统中采用水平管降膜蒸发器,可以消除蒸发表面上的静压影响,从而增大总换热系数,在低温(最高盐水温度(top brine temperature, TBT)为65~70℃)下运行也可限制管壁上水垢的形成。当前水平管降膜蒸发器已成为业界标准。

MED系统由多个蒸发容器串联而成,蒸发容器的个数称为效数(effect),多效蒸馏法的命名也由此而来。MED工艺流程按照进料海水和蒸汽流动方向

的异同可以分为逆流(backward feed)、顺流(forward feed)和平流(parallel feed), 其中海水淡化工业上广泛应用的MED系统为平流式结构, 图3给出了平流式LT-MED工艺流程的示意图. 当海水在冷凝器内预热后被分成两股, 一股作为冷却海水被排放回海中, 用于排出加入到系统中的过多的热量; 另一股作为进料海水被分配到各效蒸发容器中. 在每一效蒸发容器中, 进料海水通过喷嘴被喷洒在水平布置的换热管上. 第一效内水平管上的液膜通过吸收管内加热蒸汽冷凝释放的潜热而蒸发, 由此产生的二次蒸汽进入第二效的水平管内驱动管外液膜的蒸发. 第一效的加热蒸汽由外部蒸汽发生器(如锅炉, 电厂汽轮机等)提供, 加热蒸汽在管内冷凝后产生的冷凝水返回到外部蒸汽发生器. 此后每一效内水平管外液膜的蒸发都由上一效提供的二次蒸汽驱动, 而二次蒸汽则在管内凝结成淡水, 并被收集到淡水罐中. 由于每一效蒸发容器内的压力依次降低, 因而可以实现海水在每一效内的连续蒸发而不需要再提供热量. 最后一效产生的二次蒸汽被引入到冷凝器中对海水进行预热. 每一效内未蒸发的剩余海水则作为浓盐水被排出. 每一效蒸发容器内产生的二次蒸汽都需要经过除雾器以去除夹带在二次蒸汽中的海水液滴, 从而提高生产的淡水的质量. 系统内的每一效均需要与真空排气系统连接以除去不凝气, 不凝气的存在会阻碍传热过程, 降低传热系数.

LT-MED技术的主要特点有: (1) 海水温度越低, 对金属材料的腐蚀性越轻, 导致水垢生成的无机盐的溶解度也越高, 因此LT-MED系统中较低的TBT可减缓腐蚀和水垢的生成; (2) 海水预处理工艺简单, 只需要进行简单的筛分和加入阻垢剂即可; (3) 系统

操作弹性大, 可在设计的产水量额定值的40%~110%范围内运行; (4) MED与多级闪蒸不同, 不需要大量的海水在系统内循环, 因而输送海水所需要的动力消耗小; (5) 换热管的内外两侧都存在相变换热, 传热系数高; (6) 换热管内蒸汽压力大于管外压力, 当换热管发生腐蚀穿孔时, 只会导致蒸汽向管外的少量泄漏损失而不会影响产品水的质量, 因此MED系统的操作安全可靠; (7) 产品水质量高, TDS通常低于20 mg/L, 特殊应用场合下可低至5 mg/L以下^[3]; (8) 由于相变传热系数随温度的升高而增大, 因此较低的TBT虽然可以减缓腐蚀和结垢, 但是也限制了热效率的提高; (9) 由于海水在换热管外壁蒸发, 因而即使结垢得以减缓, 还是有钙类无机盐在管外壁析出, 从而导致水垢的生成, 需要定期清洗换热管外壁去除水垢, 以维持系统的高效稳定运行.

1.2 多级闪蒸

为了克服早期MED系统结垢严重的问题, 多级闪蒸法(multi-stage flash, MSF)于20世纪50年代被提出并开始发展. 由于MSF具有结垢倾向小等优点, 因此在被提出后就得以快速发展, 成为当前技术最成熟, 应用最广泛的大规模工业海水淡化技术.

MSF系统同样是由多个蒸发容器(闪蒸室)串联而成, 闪蒸室的个数通常称为级数(stage). 按照工艺流程的不同, MSF系统可分为直流式(once-through MSF, 又称贯流式)和海水循环式(brine circulation MSF), 其中, 海水循环式MSF是当前的业界标准, 其工艺流程示意图如图4所示. 各级闪蒸室分为两个部分: 排热段和热回收段. 海水首先被引入排热段的冷凝管中, 在吸收蒸汽冷凝释放的潜热后, 海水被预

图3 平流式LT-MED工艺流程示意图

Figure 3 Schematic diagram of LT-MED process with parallel feed

MSF技术的主要特点有: (1) 海水在冷凝管内被加热且不发生相变, 而闪蒸过程发生在各级闪蒸室底部的盐水池的表面, 因此加热和蒸发过程分开进

RO的基本原理是一个通过压力驱动从而克服自然渗透这一现象的过程。自然状态下浓度梯度的存在将驱使溶剂(例如水)从稀溶液通过半透膜向浓溶液输运,达到新的化学平衡时半透膜两侧溶液的液位差产生的压力即为渗透压。当在浓溶液一侧施加大于渗透压的压力时,溶剂将从浓溶液向稀溶液输运,与自然渗透方向相反,因而该海水淡化方法被称为反渗透法。图5给出了RO工艺流程的示意图。经过预处理后的海水在高压泵的作用下,海水中的水通过半透膜而迁移到淡水侧,盐分和其他成分则遗留在海水侧。而水通过半透膜的机理是水分子通过亲水性半透膜而扩散的能力要远强于盐分和海水中的

图5 RO工艺流程示意图

Figure 5 Schematic diagram of RO process

其他成分，这也是半透膜半透性的本质所在。由于RO系统中大部分的能量损失来源于排放的海水的压力，因而商业RO系统通常配置了能量回收装置以回收排放的浓盐水中的机械压缩能，从而提高系统的能量使用效率。

RO技术的主要特点有：(1) 盐水分离过程中不涉及相变，能耗低；(2) 工艺流程简单，结构紧凑；(3) RO系统中的半透膜对海水的pH，以及海水中含有的氧化剂、有机物、藻类、细菌、颗粒和其他污染物很敏感，因此需要对海水进行严格的预处理；(4) 半透膜上容易生成水垢和污垢，从而导致脱盐率衰减，水质不稳定，需要定期对半透膜进行清洗和更换。

1.4 压汽蒸馏

压汽蒸馏法(vapor compression, VC)与LT-MED类似，不同的是VC结合了热泵，通过压缩蒸汽来驱动盐水分离过程。图6给出了VC工艺流程示意图。海水分成两股，在热交换器内分别被排放的浓盐水和产品淡水预热，然后合成一股并与从蒸发器底部排出的浓盐水的一部分混合。混合后的海水通过喷嘴喷洒在换热管束上，管束外的海水吸收管内蒸汽冷凝释放的潜热而蒸发，产生的蒸汽通过除雾器除掉夹带在其中的海水液滴后，被蒸汽压缩机压缩至具有更高的压力和温度。此后压缩蒸汽被送回至换热管束内，在管内压缩蒸汽将释放的潜热传递给管外的海水使其蒸发，而其自身则冷凝形成淡水。系统内的不凝气同样需要通过真空排气系统排出，以消除其不利影响。根据蒸汽压缩机分别采用压缩机、蒸汽引射器、吸收式热泵和吸附-解吸热泵的不同，VC又可以分为机械压汽蒸馏(mechanical vapor compression, MVC)、热力压汽蒸馏(thermal vapor compression, TVC)、吸收式压汽蒸馏(absorption vapor compression, ABVC)和吸附式压汽蒸馏(Adsorption vapor compression, ADVC)，其中，商业上采用较多的为MVC

图6 VC工艺流程示意图

Figure 6 Schematic diagram of VC process

和TVC。

VC技术的主要特点有：(1) 相比MED和MSF，VC系统只需提供动力源，不需要提供额外的外部蒸汽热源，而且也不需要提供冷却水；(2) 海水预处理工艺简单，对海水污染不敏感；(3) 结构简单紧凑，易于模块化构造，可设计成舰载、车载等便携式装置^[6]；(4) 整个系统构成闭合循环，蒸汽潜热在系统内循环使用，能量利用率高，经济性好；(5) 产品淡水质量高，TDS低于10 mg/L；(6) 海水在换热管束外壁蒸发，容易引起管壁的腐蚀和水垢的生成。

1.5 电渗析

电渗析法(electrodialysis, ED)与RO同属于膜方法，不同的是ED中是由于海水中的盐分通过离子交换膜迁移而产生盐水分离。图7给出了ED的工艺流程示意图。ED系统中交替排列了一系列的阴、阳离子交换膜，相邻的阴、阳离子交换膜之间形成通道，在膜的两端布置了正负电极。当海水流入膜之间的通道内时，处在海水内的正负电极通以直流电，海水内的带电离子(如 Na^+ 和 Cl^-)在直流电场的作用下向带有与其相反电荷的电极移动，即阳离子(如 Na^+)向负极移动，阴离子(如 Cl^-)向正极移动，阴离子可以自由

图7 ED工艺流程示意图

Figure 7 Schematic diagram of ED process

通过离其最近的阴离子交换膜,而在进一步向正极移动的过程中会被阳离子交换膜阻挡,同样,阳离子可以通过最近的阳离子交换膜,但在进一步向负极移动的过程中被阴离子交换膜阻挡.最终的效果是浓缩的海水和稀释的海水(即淡水)在膜的两侧通道内分别形成,而后分别被引出ED系统.

ED技术的主要特点有: (1) 盐水分离过程中无相变; (2) 相比RO中的半透膜,离子交换膜具有更高的化学和机械稳定性,也可以在更宽的温度范围内运行,对不同的水质有较好的灵活性,预处理工艺简单; (3) 水回收率高; (4) 结构简单紧凑; (5) 耗电量与海水的浓度成正比,从能量经济性的角度考虑一般适用于苦咸水淡化; (6) 只能去除海水中的带电离子,对中性的有机物、细菌和非离子成分等物质则无法处理,也无法改变残余浊度,因此需要进行额外的处理才能达到饮用水标准; (7) 离子会在电极和离子交换膜表面聚集,随着时间的推移会导致污垢的生成,因而需要定期进行清洗.

为了解决结垢的问题,发展了频繁倒极电渗析(electrodialysis reversal, EDR)方法,在EDR中电极极性周期性地反转,从而浓盐水通道变为淡水通道,而淡水通道变为浓盐水通道,离子反向迁移. EDR有利于破坏和冲洗水垢、污泥和其他沉积物,从而减少预处理时化学品的使用和污垢的生成.

上述5种海水淡化技术在工业海水(苦咸水)淡化中的应用最为广泛,特别是MED, MSF和RO,这3种海水淡化技术的装机容量之和在全球总装机容量当中的占比达94%.然而经过多年发展,热蒸馏法仍然受限于结构材料的腐蚀和水垢的生成,而RO和ED存在膜上污垢生成,需要对原水进行严格的预处理等问题.

1.6 其他方法

除了上述5种技术外,传统的海水淡化技术还包括冷冻法、水合物法、溶剂萃取法、离子交换法和增湿除湿法等.这些方法由于各自特点的不同,在商业海水淡化中未有大规模应用,而是更多地应用于海水淡化的预处理和后处理工艺、淡水资源需求较少的场合或其他工业场合中.

(i) 冷冻法. 冷冻法(freezing-melting)同样通过相变(由液体变固体)来实现盐水分离,其基本原理为:海水在结冰时,水首先被冷冻从而生成冰晶,而盐分被排除在冰晶之外存在于剩余的浓海水中,将冰晶从浓海水中分离出来,经过清洗和融化后即可得到淡水.按照冰晶生成方式的不同,冷冻法可以分为天然冷冻法和人工冷冻法,其中人工冷冻法又可以分为直接接触冷冻法、间接接触冷冻法、真空冷冻法和共晶分离冷冻法.目前,冷冻法在海水淡化上还没有得到商业应用,而主要应用于以下3个方面:处

理有害废物,浓缩果汁和有机化学物质提纯^[7]. 冷冻法的主要特点有: (1) 冰融化的潜热为水汽化潜热的1/7, 因此相比热蒸馏法, 冷冻法能耗较低; (2) 操作温度较低, 可减少水垢和腐蚀问题, 能够采用廉价的结构材料; (3) 预处理工艺简单, 甚至可以不需要; (4) 对污垢和海水水质不敏感; (5) 工艺繁琐复杂, 投资和运营成本较高; (6) 清洗冰晶的过程中需要用到部分产品水; (7) 结晶过程中冰晶中会残留有部分盐分; (8) 相比热蒸馏法可以利用低品位热源, 结晶过程需要利用高品位能源.

(ii) 水合物法. 水合物法(gas hydrate)的基本原理为: 海水中的水分子与较易生成水合物的水合剂结晶聚合形成笼状水合物晶体, 通过物理方法将水合物晶体从剩下的海水中分离后, 经过清洗和升高温度而融化, 水合物晶体分解即可得到淡水, 挥发出来的气体可以回收并被再利用. 笼状水合物晶体通常在中等高压下形成, 但是其凝固温度可高达12℃. 已知的水合剂包括轻烃(如C₃H₈)、氯氟烃制冷剂(如CHClF₂)和CO₂. 水合物的主要特点有: (1) 能耗低、设备简单紧凑、成本低、无毒、无爆炸危险^[8-11]; (2) 初级淡化水水质低, 需二次或多级淡化才能达到生活用水标准; (3) 操作温度稍高于冷冻法, 但是操作压力较高.

(iii) 溶剂萃取法. 溶剂萃取法(solvent extraction)有两种途径, 一是利用萃取剂除去海水中的盐而得到淡水, 但由于海水的成分复杂, 需要采用能同时萃取多种成分的萃取剂或多种萃取剂, 因此工艺流程较为复杂和困难, 一般不予采用. 另一种途径是利用萃取剂(一般为聚合物)在低温下萃取出海水中的水, 然后升高温度使溶剂与水分离. 在这个方法中, 需要海水与萃取剂接触以形成两相, 一相为能溶解水的聚合物萃取相, 另一相为盐水, 当海水与萃取剂充分接触后, 聚合物萃取相里面不含有盐分, 对萃取相进行加热后可将萃取剂和水分离开来, 分离得到的水即为产品水, 而萃取剂则被回收以循环使用. 溶剂萃取法的主要特点有: 液-液转化过程, 操作温度接近室温, 且不涉及蒸发过程, 因而耗能少、腐蚀轻, 但其萃取性能随海水含氧量的增大而降低, 而且溶剂在水中有一定的溶解度, 会影响产品质量^[12-14].

(iv) 离子交换法. 离子交换法(ion exchange)的基本原理是: 利用某些有机或无机固体(离子交换剂)

本身所具有的离子与海水中带同性电荷的离子相互交换, 比如海水中的Na⁺和Cl⁻分别与阳离子交换剂中的H⁺和阴离子交换剂中的OH⁻相互交换, 从而实现盐分离. 上述过程可以通过用酸再生阳离子交换剂和用碱再生阴离子交换剂从而实现可逆, 具体的过程可参见文献[15]. 离子交换法的主要特点有: 成本较高, 主要用于苦咸水淡化和应急状况下的海水淡化, 在工业海水淡化中主要应用在预处理的软化工艺和后处理的选择性去除污染物(如硼)工艺中.

(v) 增湿除湿法. 增湿除湿法(humidification-dehumidification, HDH)基于自然界中的雨水循环, HDH系统可以被视为一个人造雨水循环, 其基本工艺流程为: 流动空气在增湿器(蒸发器)内与加热后的海水充分接触, 在此过程中一定量的蒸汽被空气提取出来, 被加湿后的空气被输送到除湿器(冷凝器)内, 在流经换热管时湿空气中的部分蒸汽在管外壁冷凝形成淡水, 冷凝过程释放的潜热传递给管内流动的海水对其进行预热, 从除湿器流出的湿度降低的空气被输送回增湿器内. HDH的主要特点有: 可利用低品位热源(如太阳能和地热), 设备腐蚀轻, 适用于对水需求较为分散的干旱地区.

1.7 不同海水淡化方法的性能对比

表1给出了在商业上有较大规模应用的5种主要海水淡化方法的性能对比. 其中, 造水比(gained output ratio, GOR)是指给MSF、MED或TVC系统提供每单位质量的蒸汽所能产生的淡水的质量. 表2详细给出了各方法的能耗, 其中的能耗单位是指生产单位体积的淡水所需要的电能或等效电能. 从表1和2中可以看出, 基于蒸发相变原理的热蒸馏法的原水预处理工艺简单, 生产的淡水具有更高的质量, 但能耗也相对较大; 而RO和ED等膜方法对原水的预处理要求较高, 生产的淡水质量不及热蒸馏法, 但RO的能耗比热蒸馏法的能耗小.

2 海水淡化技术发展现状

近年来, 为了克服和改善传统海水淡化技术的缺点和不足, 进一步降低海水淡化能耗, 已提出了很多旨在优化传统方法海水淡化性能的改进方法, 并开发了不同的新型海水淡化技术. 总体上来说, 当前海水淡化技术的发展主要从以下四个方面着手: (1) 就当前现有海水淡化方法中的关键技术或设备进行

表1 海水淡化方法性能对比

Table 1 Performance comparison of different desalination methods

海水淡化方法	预处理要求	造水比(GOR)	产品水TDS (mg/L)	消耗能量形式	操作温度(TBT) (°C)	腐蚀倾向	水垢倾向	污垢倾向
LT-MED	低	8~16	<20	热能、电能	65~70	小	较小	小
MSF	低	8~10	<20	热能、电能	<120	较小	小	小
MVC	低	—	<10	电能	<70	小	较小	小
RO	高	—	<500	电能	<45	无	大	大
ED	高	—	<500	电能	—	无	大	大

表2 海水淡化方法能耗对比^[2,4,16,17]

Table 2 Comparison of energy consumption of different desalination methods

海水淡化方法	热能消耗的等效电能 (kW h/m ³)	电能 (kW h/m ³)	总能耗 (kW h/m ³)
LT-MED	4.5~6.0	1.2~1.8	5.7~7.8
MSF	9.5~11.0	3.2~4.0	12.7~15.0
MVC	—	8.5	8.5
RO	—	2.5~4.0	2.5~4.0
ED	—	16~20	16~20

改进; (2) 发展不同海水淡化技术之间相互结合的混合海水淡化方法; (3) 开发利用可再生能源或新能源的海水淡化方法; (4) 基于先前未曾利用过的物理现象, 发展新型海水淡化技术. 下面将分别进行详细阐述.

2.1 技术改进

热蒸馏法的性能主要受限于结垢和腐蚀, 因而针对热蒸馏法的改进主要集中在这两方面. Galal等人^[18]通过对MSF中的换热管束的研究发现, 对于铝-黄铜材料的换热管, 波纹管比光滑管具有更高的淡水产量和更小的结垢热阻, 对于实验中选定的管内海水流速范围内, 波纹管的传热性能要优于光滑管. 为了提高防腐性能, Peultier等人^[19]采用新型的双相不锈钢替代传统的奥氏体不锈钢(如316L)作为结构材料. 研究表明, 双相不锈钢具有更高的耐腐蚀性和更长的使用寿命^[16]. 而相比传统的铜镍合金管, 钛管同样具有更加优越的防腐性能^[16]. Zarkadas等人^[20]对聚合物中空纤维换热器进行了测试, 发现相比常见的金属换热器, 聚合物中空纤维换热器具有相同甚至更好的换热性能, 而且还具有体积小、压降小和耐腐蚀等特点. Christmann等人^[21]同样利用聚合

物材料为MED系统开发了一种厚度仅为25 μm的降膜板式蒸发器, 通过实验测试发现其具有足够的机械稳定性, 且其热阻仅相当于厚度为1.5 mm的不锈钢板的热阻. Larché和Dézerville^[22]通过比较碳钢、铜合金、不锈钢、镍基合金、钛合金以及塑料等RO海水淡化系统中采用的结构材料指出, 抗腐蚀能力最强的结构材料为镍基合金和钛合金, 但其成本也最高, 从成本和技术可行性的角度考虑, 通常首选不锈钢, 而铜镍合金在合适的设计下可以作为良好的管道系统的结构材料.

RO系统中能耗占据了约70%的运行成本^[23], 因此系统中能量回收装置的高效性和可靠性显得尤为重要. 传统的能量回收装置有冲击式和混流式透平^[24]. Bermudez-Contreras和Thomson^[25]对Clark泵进行改进, 将两对工作腔的作用反转, 在初步的实验中获得了3.5~4.5 kW h/m³的能耗. Sun等人^[26]开发了一种流体切换器(fluid switcher)的能量回收装置, 在以水作为工质进行实验的情况下, 流体切换器的水力回收效率可达76.83%, 而在仿真RO海水淡化系统上的初步实验表明其能量回收率高达95.9%^[27]. Song等人^[28,29]开发了活塞式往复切换器, 在6.5 MPa和30 m³/h的RO系统的实验条件下得到了高达98%的能量回收率. Al-Hawaj^[30]对一种新型的能量回收装置——滑片式工作交换器(sliding vane work exchanger)进行了理论分析, 该装置以容积式泵和容积式透平结合的方式运行, 通过研究几何参数、物理参数和运行参数对装置性能的影响发现, 滑片式工作交换器的可行性十分依赖于叶片端部的摩擦和泄露. RO系统中的关键部件是RO半透膜, 因此开发具有持续的高通量、低压力和低能耗的半透膜, 以及通过施加有机抗污染活性涂层以减少膜上污垢的生成是RO海水淡化方法发展所面临的挑战^[31]. McCloskey等人^[32,33]通过

在RO半透膜的表面施以聚多巴胺的沉积,实现了在不过大降低纯水渗透率的同时提高了膜的抗污垢性能. Azari和Zou^[34]通过把一种氧化还原功能性氨基酸合并到商业RO膜SW 30 XLE上,在RO膜上创建了可以抵抗污垢的两性离子表面. Fujiwara和Matsuyama^[35,36]采用耐氯性的三醋酸纤维素(CTA)RO膜,通过直接氯气灭菌和间歇氯气注入从而消除了生物污垢问题. Yang等人^[37]提出采用纳米银涂层对RO膜和隔板进行表面改性,并通过实验证明了该技术能有效地控制膜上的生物污垢. Kang和Cao^[38]从新起始单体的选择、界面聚合工艺的改进以及表面改性等方面对RO膜抗污垢方法的发展进行了评述. 近年来纳米技术的进步推动了RO膜的发展,通过利用纳米技术开发了多种具有亲水性、高通量和低渗透压的半透膜^[39~43]. 此外,有效的预处理方法也可以控制生物污垢. 在超滤(ultrafiltration)膜过滤之前布置溶气气浮可以提高RO的通量(水回收率),还能减少污垢^[44],气浮用作RO的预处理步骤可以有效地去除油和藻类^[45]. 为了提高RO膜的回收率,日本开发了一套高回收率海水RO系统,主要通过提高RO膜和模块的耐压性以及控制膜表面的浓差极化来实现,通过在日本和沙特的RO海水淡化厂对不同TDS的海水进行测试发现,对于标准海水(TDS为35000 mg/L),该系统可将回收率由40%提升至60%,而对于中东地区的海水(TDS为43000 mg/L),回收率可由35%升高到50%^[46].

2.2 技术结合

通过结合不同的海水淡化技术,可以利用各自的优势,弥补不足,从而达到优化海水淡化性能,以及降低能耗和成本的目的.

(i) MED与VC的结合. El-Dessouky和Ettouney^[47]对平流式MED与TVC和MVC的结合以及顺流式MED与TVC, MVC, ABVC和ADVC的结合等多种海水淡化系统的性能分别进行了分析和评估. 在MED与TVC结合的系统(MED-TVC)中, MED最后一效中产生的蒸汽的一部分被蒸汽引射器压缩后输送到MED的第一效中驱动海水的蒸发. 而对于MED与MVC结合的系统(MED-MVC), 则是MED最后一效产生的全部蒸汽被压缩机压缩后输送到第一效中驱动海水的蒸发,而且未使用MED中的冷凝器(图3)对海水进行预热,而是使用VC中的两个热交换器(图6)

进行预热. 在MED与ABVC和ADVC结合的系统(MED-ABVC和MED-ADVC)中, MED中的第一效和最后一效替代了热泵中的冷凝器单元和蒸发器单元,这样可以减少热泵的设备成本,同时MED-ABVC和MED-ADVC系统还可以用于加热工业应用中的公共用水,这些特点是MED, MED-TVC和MED-MVC系统所不具备的. 相比单独的MED系统, MED与VC结合的混合系统具有更好的性能和更大的造水比,还可以在更高的操作温度下运行,从而使得蒸发器面积可以大幅减小,系统的建设成本也由此可以大大降低.

(ii) 膜蒸馏. 膜蒸馏(membrane distillation, MD)是一种将膜方法和热蒸馏法结合起来的混合方法,其基本工艺流程是:海水加热后被输送到疏水性微孔膜的表面,由于疏水性微孔膜的表面张力大,因而只允许海水蒸发得到的蒸汽通过膜上的微孔,而液态水则被阻止通过,通过疏水性微孔膜的蒸汽被冷凝而形成淡水. MD中盐水分离过程的驱动力为膜两侧的蒸汽压力差^[48]. 增大MD的膜通量和热效率是当前的研究热点, Zhang等人^[49]分析了不同因素对MD热效率的影响,针对在MD中广泛应用的几种热回收技术进行了评述. Hitsov等人^[50]总结了针对MD内传热传质过程的不同建模方法,评价了各方法的优缺点,且进一步指出合适的CFD方法是设计MD模块的关键,但目前仍缺少可靠的CFD方法. Drioli等人^[51]则从膜的制备、传热传质过程、非传统污垢、模块制造以及MD的应用等方面对MD的发展进行了总结. 根据蒸汽收集方式和冷凝机理的不同, MD可以分为以下4类: 直接接触式(direct contact MD)^[52~55]、气隙式(air gap MD)^[56~61]、气体吹扫式(sweeping gas MD)^[62~64]和真空式(vacuum MD)^[65~69]. Koo等人^[70]比较了直接接触式、气隙式和真空式3种不同的MD模块,针对3种MD分别建立了实验室规模的MD模块测试系统,建立了一个简单的考虑多种不同传质机理的模型,并对实验结果进行了理论分析,发现3种MD的最佳原水温度是不同的. MD的主要特点有: (1) 操作温度低(60~90℃^[71]), 可利用低品位废热或太阳能等可再生能源, 从而对远离海洋的偏远地区供水; (2) 结构简单、紧凑, 采用聚合物作为结构材料可防止腐蚀并大大降低建设成本; (3) 蒸汽空间需求比热蒸馏法小, 操作压力低于RO^[72]; (4) 疏水膜对结垢和沉淀不敏感, 预处理需求小; (5) 不论原水

质量如何都能获得高纯度水,理论上脱盐率可达100%^[73]; (6) 随着时间的推移,膜上污垢的生成和疏水性的损失会造成膜退化。

(iii) 填充床电渗析. 填充床电渗析^[74~76] (electrodeionization, EDI) 又被称为电去离子, 是ED与离子交换法结合的混合方法, 其基本工艺流程是: 在淡水通道内填充了离子交换树脂等电活性介质, 淡水通道内的盐离子与离子交换树脂上的氢离子和氢氧根离子相互交换并附着到离子交换树脂上, 由于淡水通道内盐分浓度的下降会导致盐水电导率的减小, 从而削弱盐离子通过盐水向离子交换膜的迁移, 因此盐离子在直流电的作用下会沿着电导率更大的离子交换树脂迁移到离子交换膜的表面, 并通过离子交换膜进入到相邻的浓盐水通道中. 同时, 在淡水通道内的离子交换膜的表面和离子交换树脂的周围会发生水解反应, 产生氢离子和氢氧根离子, 从而可以实现离子交换树脂的再生. 因此, EDI是一个连续的盐水分离过程, 具有很高的水回收率, 可用于制备高纯度的淡水, 还可以用于去除金属离子^[76]. 此外, 相比于ED, 离子交换树脂的存在会加强淡水通道内盐离子的迁移, 而相比于离子交换法, 离子交换树脂的再生过程不需要相应的酸和碱等化学品。

2.3 可再生能源/新能源海水淡化技术

随着淡水资源的短缺以及传统化石能源的减少和成本的上升, 以可再生能源作为驱动力的海水淡化技术受到了越来越多的关注. 特别是对于水和电供应不足的偏远地区或小型社区, 可再生能源作为一种环境友好型清洁能源在小规模海水淡化装置上的应用潜力近年来受到越来越多的重视^[77]. 此外, 由于传统化石能源的燃烧会带来温室气体和有害物质的排放, 可再生能源海水淡化因而也被认为是解决气候变化问题的潜在的可行方案^[78]. 目前应用于海水淡化的可再生能源的主要有太阳能、风能、地热能、海洋能等. 除可再生能源之外, 核能作为一种可持续能源在海水淡化上的应用同样被认为具有能够安全、经济、可持续地供应大量淡水的潜力。

(i) 利用太阳能的海水淡化技术. Al-Karaghoul等人^[79]认为太阳能海水淡化对于偏远地区淡水产量为10 m³/d的小型海水淡化装置是适合的, 同时也可能是唯一一种在技术上和经济上具有竞争力的海水淡化技术. Sharon和Reddy^[80]对不同太阳能海水淡化

技术的工作原理、优势和局限性, 以及相关进展进行了详细的综述。

太阳能海水淡化可以分为直接法和间接法. 直接法中太阳能以热能被收集的过程和脱盐过程在同一个装置内进行. 直接法主要有太阳能蒸馏^[81~86], 即太阳能直接对海水加热产生蒸汽, 冷凝后获得淡水. 根据加热原理的不同, 太阳能蒸馏又可以分为被动式和主动式. 被动式太阳能蒸馏不需要额外的辅助设备, 单纯依赖于太阳能照射产生的热量对海水加热; 而主动式太阳能蒸馏则在被动式的基础上增加了辅助设备, 将太阳能间接地引入系统中以强化传热传质, 并对冷凝潜热进行回收. 目前已经开发了多种主动式太阳能蒸馏用于克服被动式太阳能蒸馏中产水量低的问题, Sampathkumar等人^[87]对主动式太阳能蒸馏方面的研究进行了详细的评述. 此外, 还有不同文献对不同的太阳能蒸馏系统以及相关进展进行了综述^[88~90], Velmurugan和Srithar^[91]分析了不同参数对太阳能蒸馏系统性能的影响, Kabeel等人^[92]建立了简化模型对17种不同类型的太阳能蒸馏法进行了成本分析。

间接法中太阳能收集的过程和脱盐过程是分开的, 其中太阳能可通过太阳能集热器转换为热能, 也可以通过光伏(PV)发电转换为电能, 从而用于驱动脱盐过程. 根据不同海水淡化方法中盐水分离过程所需的驱动能量形式的不同, 间接太阳能海水淡化主要包括太阳能转换为热能驱动MSF^[93,94], MED^[95~97], MD^[98~105], HDH^[106,107], 以及转换为电能驱动RO^[108~111], ED^[112~115]. 此外, 热能还可以通过有机朗肯循环(ORC)转换为机械能用于驱动RO中的高压泵^[116~121]. Ali等人^[122]对不同的间接太阳能海水淡化方法进行了综述, 并分析了每种方法的技术经济性。

(ii) 利用风能的海水淡化技术. 风能海水淡化主要是利用风力发电机将风的动能转换为电能用于驱动消耗电能的海水淡化方法, 主要有两种实施方式: 一种是风力发电机与海水淡化系统均与电网系统连接; 另一种是风力发电机直接与海水淡化系统连接^[123], 利用产生的电能或转子叶片转动产生的轴功, 此种方法中海水淡化系统的性能会受到风力发电机发电功率不恒定(由风能的不连续性和不稳定性引起)的影响, 因而整个系统中需要加入蓄电池、柴油发电机或飞轮等备用供电系统. 虽然风能可以用于驱动ED^[124]或MVC^[125]等不同海水淡化系统, 但从

经济性和低能耗等角度考虑,风能主要还是和RO结合^[126-135].此外,风能还可以与PV结合驱动RO和MVC等系统^[136-140],与ORC结合驱动RO系统^[141],以此削弱风能利用上的缺点,获得更规律的能源利用方式.

(iii) 利用地热能的海水淡化技术. 地热能是由地球内部放射性元素衰变产生的热能. 根据温度的不同,可以分为低温地热(<100℃)、中温地热(100~150℃)和高温地热(>150℃)^[142]. 地热能与海水淡化系统的结合主要有3种方式:一是直接利用中高温地热以蒸汽的方式驱动热蒸馏法^[143,144];二是利用高温地热发电驱动RO和ED等海水淡化系统;三是利用高压地热驱动RO和MVC等需要机械能驱动的海水淡化系统. 此外,随着膜技术的发展,已开发出可以承受温度高达60℃的商业RO膜,可直接应用于地热苦咸水淡化,且有助于RO中淡水产量的增加^[145,146]. 地热能海水淡化的主要优势在于系统中不需要蓄热.

(iv) 利用海洋能的海水淡化技术. 将海洋能应用到海水淡化的方式有4种:潮汐能、波浪能、深海静压和温差能. 潮汐能是潮水受太阳和月亮引力的影响而发生周期性的涨落,从而形成的势能. 当前潮汐能在海水淡化中的应用主要集中在潮汐能直驱式海水淡化系统^[147-151],即通过水轮机等水力机械将潮汐能转换为轴功,轴功驱动泵对海水增压,然后将压力足够高的海水送入半透膜单元产生淡水. 此外,刘业凤等人^[152-154]结合潮汐能和太阳能开发了MED海水淡化装置.

波浪能主要是通过开发不同的装置收集或转化波浪运动的动能和势能. Davies^[155]对不同的利用波浪能的海水淡化技术及其研究进展进行了详细的评述. 不同的研究人员开发了不同的波浪能泵送系统用于驱动RO海水淡化,如McCabe装置^[156], DELBOUY装置^[157], WaveCatcher装置^[158], AaltoRO系统^[159]. 水锤是一种发生在非定常不可压管内流动中液体流速突然变化的现象,液体流速的突变是由阀门的突然关闭或其他外界因素引起的,且流速的突变会形成压力波, Sawyer和Maratos^[160,161]利用水锤效应收集压力波的能量用于驱动RO系统. Salter^[162]开发了“Nodding Duck”装置收集波浪能用于驱动VC海水淡化, Crerar等人^[163,164]对该装置进行了改进,但该装置只进行过模型实验,未在实际海水淡化当中实施. Sharmila等人^[165]开发了振荡水柱式(OWC)海水淡化

装置,随波浪的升降,空气柱不断压缩和膨胀,冲击式透平从空气柱中提取能量并转换为电能后驱动RO海水淡化装置. Whittaker和Folley等人^[166,167]报道了一种独立的波浪能驱动的海水淡化系统,通过利用波浪能转换器Oyster将波浪能最终转换为电能驱动RO海水淡化,此系统中波浪能的收集和转换装置实质上是一个波浪能驱动的水力发电装置. 孙业山等人^[168]和林润生等人^[169]分别开发了不同的振荡浮子式波浪能转换装置驱动RO海水淡化.

深海静压主要是利用深层海水具有较大的静压,从而克服半透膜的渗透压驱动RO海水淡化. Levenspiel和de Nevers^[170]曾提出渗透泵的概念,该装置在理论上不需要人为提供能量即可从海水中获得淡水,其基本原理是将一端由RO半透膜封盖住的管道垂直沉入海水中,当海水的静压大于渗透压时,水便会通过半透膜流入管道中,当下沉深度足够大时,淡水水柱会上升到海面从而获得淡水,但通过分析发现,渗透泵只在理论上存在可能. 在欧盟的主持下,多国研究机构联合开发了反渗透深海系统(RODDS)^[171],并且进行了原型机实验^[172],该系统在深度为500 m左右的海底运行,利用海水的静压取代高压泵作为驱动力,因此其所需的电能的绝大部分都用于将生产的淡水从海底泵送到岸边,能耗约为1.88 kW h/m³^[171].

温差能海水淡化主要是利用海洋不同深度处海水温度的不同引起热交换而产生的热能. 基于此主要开发有海洋热能转换(ocean thermal energy conversion)技术用于海水淡化^[173-176],其基本原理是:低纬度海面具有较高温度的海水在真空室内闪蒸,产生的蒸汽被海洋深层较冷的海水冷凝,从而获得淡水. 海洋热能转换技术成本较高,因此限制了其在商业上的发展,然而近期的研究表明通过优化设计其能耗可达5.5 kW h/m³,与现存的海水淡化技术相近^[177]. 而基于上述原理,浙江大学金志江教授课题组也开发了类似的温差能海水淡化系统^[178-181].

(v) 利用核能的海水淡化技术. 核能作为一种安全、可靠、清洁的可持续能源,在发电和区域供热中的应用已成为成熟的技术. 核能海水淡化是利用核反应堆释放出的热能或者转化后的电能作为驱动能量进行海水淡化. 核能海水淡化的研究始于20世纪60年代,此后国际原子能机构(IAEA)对核能海水淡化的发展起到了重要的推动作用^[182],对核能海水

淡化进行了定义^[183],开发了用于评价海水淡化系统经济性的软件——DEEP (desalination economic evaluation program),适用于不同的能源形式和不同的海水淡化方法^[184,185],其后又开发了海水淡化热力学评价软件——DE-TOP (desalination thermodynamic optimization program)^[186].核能与海水淡化技术结合的方式主要有两种:一种是利用核电站产生的电能驱动RO和MVC等海水淡化方法,此方式中海水淡化装置消耗的电能仅占核电站生产电能的一小部分,且两个系统不需要在同一个空间内建立;另一种结合方式是利用低温供热用核反应堆中的低品位余热驱动MSF和MED等热蒸馏法,此方式中低温供热堆和海水淡化装置直接连接,因而两个系统需要在同一个空间内建立,同时直接连接也会带来产品水受放射性污染的风险,因此需要采取一定的措施,但是由于相比核电站,低温供热堆投资成本低,也更安全,因而此种结合方式受到越来越多的关注.核能与海水淡化的结合必须考虑核电站或核反应堆的安全性,保证产品水不受放射性污染以及停堆时淡水的稳定供应,同时还需要考虑经济性以及对周围环境带来的影响.截止2010年,核能海水淡化的运行已超过200堆年^[187,188].多年来哈萨克斯坦和日本的核能海水淡化的成功运行证明了核能海水淡化的技术可行性、安全性和可靠性^[189].哈萨克斯坦利用MSF和MED工艺开发了淡水产量为 $8 \times 10^4 \text{ m}^3/\text{d}$ 的核能海水淡化,运行了26堆年^[190].日本基于MSF, MED和RO等不同工艺开发了多个核能海水淡化系统,产量从1000到 $3900 \text{ m}^3/\text{d}$ 不等^[182],截止2007年运行经验已超过150堆年^[191].俄罗斯正在筹建一个安装在驳船上的漂浮核能海水淡化系统,相比于陆地海水淡化系统,漂浮海水淡化装置灵活性大,适用于区域供热、发电以及对饮用水有紧急需求的场合^[192,193].中国设计开发了利用200 MW供热用核反应堆NHR-200^[194,195]和MED工艺的核能海水淡化系统,目前已实施并完成了可行性研究,同时清华大学正在建立一套测试系统用于验证MED工艺的热工水力参数^[190,191].此外,印度、韩国、美国、巴基斯坦、阿根廷、科威特、法国、荷兰和南非等国也开发和运行或正在研究建设核能海水淡化系统^[187,191,196,197].由于核能海水淡化的未来完全取决于不同类型的反应堆的设计、开发和利用^[187],因而近年来已经提出了很多结合不同反应堆和海水淡化技术的核能海水淡

化系统,如高温气冷堆(HTGR)与MED的结合^[198]、先进重水堆(AHWR)与MED-TVC的结合^[199]、汽轮机—模块化氦反应堆(GT-MHR)^[200], NuScale小型模块化反应堆^[201]、基于水冷堆的低压散热器核能海水淡化(low-pressure inherent heat sink nuclear desalination plant, LIND)^[202]、固定床反应堆(FBNR)^[203]等.对于核能海水淡化技术经济性的不同研究结果表明,核能海水淡化生产淡水的成本与传统化石燃料驱动的海水淡化技术生产淡水的成本相近^[189,204~206],有的甚至要低于化石能源海水淡化的成本^[207],同时发电成本大大降低^[208].综上所述,核能海水淡化已成为技术上可行,经济上可与传统化石能源海水淡化竞争的成熟海水淡化技术,甚至可能是能满足未来淡水需求和实现可持续海水淡化的唯一途径^[209].

2.4 新型海水淡化技术

为了减少结垢,降低能耗、建筑成本和人力成本以及对环境的影响,通过利用未曾利用的物理过程,已开发了不同的新型海水淡化技术.下面将对各新型海水淡化技术的基本原理、包括能耗在内的特点以及研究进展进行详细介绍.

(i) 正渗透. 正渗透(forward osmosis, FO)海水淡化与RO相同,采用半透膜将淡水和海水分隔开,但不同于利用外加压力作为驱动力实现淡水通过半透膜,FO利用的是由高盐度汲取液(draw solution,又称驱动液)产生的自然的压力梯度,与另一侧的海水相比,汲取液具有更高的渗透压和更低的化学势,从而使海水内的水通过半透膜向汲取液一侧移动.汲取液中的淡水通过其他分离方式进行分离,而分离方式依赖于汲取液的特性,分离出来的汲取液可以回收再利用于FO工艺中.FO具有低能耗($0.25 \text{ kW h}/\text{m}^3$ ^[210])、膜污染倾向小^[211,212]和低成本等优势.但是当前FO海水淡化仍面临浓差极化、膜污染、溶质逆向扩散^[213,214]、膜的选择和开发、以及汲取液的选择和发展等问题.浓差极化包括发生在FO膜多孔支撑层内的内部浓差极化和发生在FO膜活性层表面的外部浓差极化^[213].外部浓差极化会减小驱动力,可通过增大流动速度或湍流度以及优化水通量来减轻外部浓差极化对FO膜通量的不良影响^[215,216],但造成膜通量下降的主要原因不是外部浓差极化,而是内部浓差极化,内部浓差极化可使膜通量下降80%以上^[217,218],由于内部浓差极化发生在多孔支撑层的内

部,因此无法通过增加流动速度或湍流度等改变水动力学条件的方法来缓解内部浓差极化.也正是由于内部浓差极化的存在,RO膜不适用于FO海水淡化.研究表明在多孔支撑层涂覆聚多巴胺可以增加FO膜的亲水性并削弱内部浓差极化^[219].此外,通过膜表面改性可以有效抑制膜污染^[220].而溶质逆向扩散只与FO膜活性层的选择性有关^[221],改善活性层的选择性即可减轻溶质逆向扩散.由此可见,FO膜是FO海水淡化的关键部件,合理地选择FO膜可以有效地解决浓差极化、膜污染和溶质逆向扩散等问题,当前FO膜材料开发与发展的相关研究可参考文献[213~215,222~225].汲取液对于FO同样至关重要,其选择关系到膜通量和FO的经济性.理想的汲取液应满足以下特征^[226]:(1)高渗透效率,即溶解度高且分子量小;(2)保证最小的溶质逆向扩散以维持驱动力和避免污染进料海水;(3)与FO膜具有化学相容性;(4)无毒;(5)从水中分离出来的方法简单、廉价,且能够重复使用;(6)成本低廉.当前用于FO的汲取液(或汲取液溶质)有CO₂和氨气溶液^[227]、聚电解质^[228]、化肥^[229]、无机类^[230]、磁性纳米颗粒/凝胶^[231~234]等,汲取液的发展和相关研究进展可参考文献[213,214,222~225,235~237].Kim等人^[238]基于OLI电解质化学模拟软件和ASPEN化学数据库建立了汲取液选用方法,以辅助设计商业上可行的FO海水淡化系统.

(ii) 电容去离子. 电容去离子(capacitive deionization, CDI)的实质是一个电吸附过程,在此过程中离子在电场作用下被吸附到多孔电极的表面.当海水在多孔电极之间流动时,带正电的阳离子会吸附到带负电的负极的双电层上,而带负电的阴离子则会吸附到带正电的正极的双电层上,其主要机理是物理吸附、化学吸附、电沉积和电泳.当电极的离子吸附容量达到饱和时,吸附的离子可以通过撤除或反转电场从电极表面解吸,从而实现电极的再生,再生阶段可回收50%~70%消耗的能量^[4].离子吸附和解吸的过程是电容充放电的过程,在此过程中海水的淡化和浓缩交替进行,因此CDI不是一个连续海水淡化工艺.与ED类似,CDI的能耗正比于移除的离子的数量,因而CDI更适合于苦咸水淡化.Porada和Suss等人^[239,240]对CDI技术在海水淡化方面的应用以及发展现状和趋势进行了详细的综述.在CDI中,电极是其关键组件,CDI的效率强烈依赖于电极的表

面特性,如表面积和吸附特性,因而开发了不同的电极材料以提高电极的性能和CDI的效率,当前主要的电极材料有活性炭^[241,242]、活性炭纤维^[243]、炭气凝胶^[244]、碳纳米管^[245]、碳纳米纤维^[246]、石墨烯^[247]、多孔碳球^[248]、介孔碳^[249]、有序介孔碳^[250]、氧化石墨烯^[251]、活性介孔碳、氧化铝和二氧化硅纳米复合材料、硬质合金衍生碳、炭黑和不同材料的掺杂混合,具体的材料性能和相关研究文献可参考综述文献[239,252,253].离子交换膜电容去离子^[254~262](MCDI)是对CDI的改进,结合了离子交换膜,即在正极的前面布置阴离子交换膜,在负极的前面布置阳离子交换膜,以此阻止解吸过程中离子吸附到相反电极上,实现电极的完全再生,从而增加脱盐率,因此MCDI可以提高海水淡化效率.Welgemoed和Shutte^[263]开发了第一台用于苦咸水淡化的工业CDI样机,并对其性能进行了评测,结果表明对于TDS为1000 mg/L的苦咸水其能耗仅为0.594 kW h/m³.

(iii) 离子浓差极化. Kim等人^[264]基于离子浓差极化(ion concentration polarization, ICP)设计了微流体装置用于海水淡化.其基本工艺流程是:海水在外部压力的驱动下在微通道内流动,同时在流场中施以直流电场;在流向上的某一位置处微通道分叉为两个微通道,在分叉点处布置纳米多孔膜或连接纳米通道,纳米多孔膜和纳米通道均具有离子选择性,将在膜或通道的两侧触发ICP,从而导致阴离子和阳离子在膜或通道的正极侧减少,在负极侧增加,则与离子减少的一侧连通的微通道内流动的为淡水,另一侧微通道内流动的为浓盐水,从而实现海水淡化.最初的研究结果表明该微流体装置的能耗为3.5 kW h/m³,其后发现其能耗要更高^[265].随后, Kim等人^[266]利用创新设计的网格开发了一个低成本、小规模ICP淡化/净化装置,相比原来的ICP装置,其淡水产量增加了约1000倍,而ICP装置成本却降到只需0.33美元,此外新的网格结构允许的流量为0.7 mL/(min cm²),远大于RO膜的典型流量(0.05 mL/(min cm²)),而且新型ICP装置淡化TDS为30000 mg/L的原水的能耗不到5 kW h/m³,与当前大规模应用的海水淡化方法的能耗相当.Ouyang和Wang^[267]基于Nafion膜引起的ICP开发了用于小规模淡化的纳流体装置,相比Kim等人开发的ICP装置,该装置淡化浓度小于10 mmol/L的海水所需的电压更低,但其能耗更大,为33.3 kW h/m³. MacDonald等人^[268]基于ICP设计了微尺度和常规尺

度下的出平面(out-of-plane)海水淡化装置,出平面的设计方法可以增加海水淡化的功能密度,从而达到降低成本的目的.针对微尺度装置研究了纳米多孔膜的尺寸和流量对能耗的影响,发现对于宽度为125~200 μm 的纳米多孔膜,当施加电压为5 V时,淡化浓度为20 mmol/L的溶液所需的能耗为4.6 kW h/m^3 ,对于浓度为200 mmol/L的溶液其能耗为13.8 kW h/m^3 ,而流量则对能耗没有影响.通过对常规尺度装置(进口宽度为2 cm)的研究发现,常规尺寸装置可淡化浓度高达500 mmol/L的盐溶液,且其功能密度为平面型装置的3倍.ICP装置可以将盐分等带电粒子从膜上驱离,因而可以消除污垢的生成,此外ICP还能有效去除对人体有害的重金属污染物.

(iv) 电化学介导海水淡化. Knust等人^[269,270]基于法拉第反应开发了电化学介导海水淡化(electrochemically mediated desalination, EMD)的微流体装置,该装置具有与ICP海水淡化装置类似的几何结构,不同点在于分叉点处布置的为铂电极,在铂电极和微通道末端布置的导线之间施加合适的电压,使得海水中的 Cl^- 失去电子发生氧化反应生成 Cl_2 ,氧化反应的发生会减少铂电极附近 Cl^- 的数量,从而产生离子消耗区(ion depletion zone),离子消耗区的形成会导致在该区域形成局部电场,局部电场将海水中的离子重新导向浓盐水通道,从而实现海水淡化.EMD是一种无膜海水淡化,因而不会有膜上结垢的问题,也不用对海水进行严格的预处理,相比CDI,EMD具有更高的效率^[270],在50%的回收率和25%±5%的脱盐率下其能耗为0.025 kW h/m^3 (接近海水淡化理论最小能耗0.017 kW h/m^3)^[269].

(v) 碳纳米管. 近年来,碳纳米管(carbon nanotube, CNT)在海水淡化方面的应用发展迅速^[271~273],主要涉及的海水淡化方法包括RO, MD, CDI和FO等^[274,275]. Gethard等人^[276~278]将CNT固定在MD疏水膜的孔隙, CNT为蒸汽分子通过疏水膜提供了额外的通道,从而提高了蒸汽的渗透率,同时阻止液态水堵塞孔隙.在结合碳纳米管后,对于80℃下TDS为34000 mg/L的盐水,蒸汽通量和脱盐率分别增加了1.85和15倍^[276]. Corry^[279]采用分子动力学模拟对水和离子通过结合了不同尺寸CNT的膜进行了研究,发现掺杂了CNT的半透膜在RO海水淡化中的应用前景广阔,在流量远超现有半透膜的情况下可实现高度脱盐. Tofighy等人^[280]采用化学气相沉积(CVD)合成了CNT

膜,经氧化后用于脱盐,通过研究原水浓度、温度、压力和流量等4个运行参数对CNT膜性能的影响发现,原水浓度、温度和流量的增大,以及压力的减小都可以优化CNT膜的脱盐率和渗透通量等性能.

(vi) 旋转离心力. 利用旋转产生的离心力提供RO所需的驱动压力可以减少RO的能耗^[281],此外还可以减少颗粒物污垢^[282,283]和浓差极化^[283,284](浓差极化的形成将导致半透膜水通量的降低).在该系统中RO半透膜被安装在转子的外周,经过预处理的海水沿转轴进入系统中,随着转子的加速旋转,海水受离心力作用被甩到外周的半透膜上并受压通过半透膜,由此产生的淡水被包围系统的外壳收集,而浓缩盐水则沿转轴排出,由于海水沿转轴的流进和流出均在低压下进行,因而不需要辅助的能量回收装置.此系统的原型机已在加拿大海军舰船上安装试用,能耗为3.89 kW h/m^3 ^[281].李楠等人^[285]基于旋转电磁效应和旋转离心力提出了旋转电磁离心式海水淡化器,利用旋转电磁效应产生的电磁和热对海水进行预处理,利用高速旋转产生的离心力驱使海水通过半透膜,该方法可以抑制污垢、减缓腐蚀、延长膜使用寿命并降低能耗.类似地,离心力也被应用于VC^[286,287],在此系统中,海水从快速旋转的换热面的中心引入,旋转会使海水在换热面上形成一层薄液膜,从而大大提高换热速率,产生的蒸汽被提取出来并被鼓风机压缩,压缩后的蒸汽在换热面的另一侧冷凝,将释放的潜热用于加热液膜.这种方法适用于小型海水淡化,实验装置的能耗为18.6 kW h/m^3 ^[287].

(vii) 超临界海水淡化. Ingo等人^[288]提出超临界海水淡化(supercritical desalination, SCD),即利用水的超临界状态进行海水淡化.水在高温高压下可达到超临界状态,在此状态下,水的液相和气相共存且难以分辨.超临界水是无机盐的极不良溶剂,因而可以通过沉淀来实现盐分离,而产生的淡水的纯度则依赖于超临界流体的温度和压力. SCD已经被提出作为RO的预处理步骤,在压力为22 MPa和温度为350℃的状态下,利用SCD可产生TDS为3500 mg/L的水,此后即可将其视为苦咸水利用RO进行进一步的淡化,整个工艺的理论能耗与传统RO的能耗相近,但是具有更高的回收率(70%~80%). Odu等人^[289]进一步指出超临界海水淡化还具有无液体排放的优点,并设计了一个具有两级分离过程的超临界海水淡化实验装置,在300 bar和460℃的条件下对质量分数为

3.5%的NaCl溶液进行淡化得到了产量为10 kg/h, TDS为750 ppm的饮用水, 且排弃物仅为2~5 μm 的盐晶, 该实验装置消耗的热能约为450 MJ/m³. SCD目前仍处于实验研发阶段.

(viii) 磁流体. 在磁流体发电技术中采用海水代替高温电离气体可以降低对结构材料的技术要求, 与此同时, 海水中存在大量的Na⁺和Cl⁻等离子, 具有较好的电导率, 在磁场中高速流动时海水中的阴阳离子受Lorentz力的作用而相互分离, 在形成电流的同时也产生了去离子水, 从而达到发电和海水淡化的双重目的, 磁流体发电海水淡化有设备结构简单、能耗和成本低、效率高、以及综合利用性强等特点^[290,291]. Ballester和Garrido^[292]采用磁场代替ED中的直流电场来实现盐水中离子的迁移, 相比ED和RO, 此种方法预计分别能节省超过75%和超过45%的能量.

(ix) 超空化. 空化是液体在温度基本保持不变的情况下由于压力(或局部压力)降低到该温度所对应的饱和压力以下而发生汽化, 使液体内部的气核迅速膨胀, 形成含有水蒸气或其他气体的明显气(汽)泡, 从而造成液体破裂的现象. 通常采用空化数来描述空化流动, 流动中特征压力越低或特征速度越大, 则空化数越小, 空化程度越剧烈. 超空化(super-cavitation)即是小空化数下发生的剧烈空化现象, 此时空泡形态呈现一种完全发展的附着空泡, 其尾部在过流部件固体边界下游闭合, 长度大于过流部件的特征长度, 称为超空泡(supercavity). 超空泡汽液交界面处的液体蒸发汽化过程与固体壁面处液体沸腾过程类似, 其传热系数均由热流密度决定, 但是在超空泡蒸发过程中的汽液交界面具有更大的传热传质速率, 且能形成和维持相对稳定的空泡形态, 从而允许从空泡内抽取蒸汽, 对蒸汽进行收集和冷凝后即可得到淡水. 目前, 绝大部分对超空化现象在海水淡化中应用的研究主要集中在俄罗斯. 1984年Machinski^[293]将静止锥形超空化蒸发器引入到海水淡化中, 通过在超空泡内连接真空系统抽取超空泡内的蒸汽来获取淡水, 该系统包括多个级联的锥形超空化蒸发器, 蒸汽从每一级形成的超空泡内抽取, 然而以下问题限制了该系统的应用: 需要连续不断的大量原水在系统内循环, 系统的制造需要大量金属材料, 形成的超空泡的体积与循环水的总体积之比很小, 需采用能量密集型的水泵再循环系统. 近年

俄罗斯TJEROS-MIFI科技中心设计了淡水产量为1200 m³/d的商用空化海水淡化装置WATERFALL-1200^[294], 经过电磁处理的过热水流经特殊设计的固定障碍物后, 在其后方形成超空泡, 将从超空泡内抽取出的蒸汽冷凝得到淡水, 该装置可用于海水淡化和废/污水净化, 对于TDS为65000 mg/L的原水, 其能耗为3 kW h/m³, 污染物脱除率超过99%. 最近, 本研究小组提出了旋转超空泡蒸发器(rotational supercavitating evaporator, RSCE)的概念^[4], 并进行了初步的设计和研究^[295,296]. RSCE的核心部件是由两个出口边宽度随半径变化的楔形叶片组成的旋转空化器, 空化器在盐水中高速旋转形成超空泡, 在叶片根部的适当位置设置抽汽孔用于抽取空化形成的蒸汽, 经冷凝后生成淡水. 为了降低系统的能耗, 今后的改进工作集中在叶形优化、升高操作温度(温度的升高可降低饱和蒸汽压, 从而降低达到超空泡状态所需的叶片转速, 进而实现RSCE消耗的机械能的减少)和引入黏弹性流体(利用黏弹性流体具有的湍流减阻、降低表面张力以及促进沸腾和空化等特性减小RSCE的能耗)等方面^[297~299]. 由于超空化海水淡化中的汽化过程发生在汽液交界面, 因而不存在结垢的问题; 此外, RSCE系统中不需要对原水进行严格的预处理, 结构紧凑, 制造时所需的金属材料相对较少, 因而建造成本较低.

相比传统海水淡化技术, 上述新型海水淡化技术在防垢、能耗、淡化效率、成本等方面更具优势, 但是大多数方法目前仍处于实验研发阶段, 其在商业上的实际应用方式和场合还需要综合考虑其他因素并通过后续进一步的研究得以改进和发展.

3 结语

本文通过对传统海水淡化技术基本工艺流程和工作原理的介绍, 以及对其性能和技术特点的总结, 阐述了当前海水淡化技术的研究现状. 通过分析海水淡化技术的发展前景发现当前海水淡化技术向着低能耗、高效率、对环境影响小的方向发展, 具体的发展途径主要有以下四条: 一是弥补传统海水淡化技术中的不足, 对其关键技术或设备进行改进; 二是扬长补短, 将不同海水淡化技术结合起来; 三是利用可再生能源或新能源, 寻求可持续发展道路; 四是基于先前未曾利用过的物理现象, 发展新型低能耗海水淡化技术.

值得注意的是,虽然与传统海水淡化技术相比,新开发的海水淡化技术能耗普遍较低,但是新型海水淡化技术大多处于实验研发阶段,可靠性和稳定性还不能完全保证,使其在商业上的应用也处于探索阶段,而这也是传统海水淡化技术仍在市场上占领主要地位的原因。此外,除了能源成本以外,新型海水淡化技术转移到商业应用时其技术经济性还需考虑原水质量、系统建设成本、运行维护成本、劳动

力成本和排放物处置成本等因素。

综上所述,材料、能源和信息作为21世纪三大支柱产业,已经在海水淡化的发展中得到印证。新材料和新能源在提高性能、节约成本、环境友好等方面对海水淡化发展的推动作用不言而喻,新技术的出现使得海水淡化的应用场合呈现多样化,能源消耗呈现节约化。因此,在应对全球性淡水资源匮乏的危机上,海水淡化是最具前景的可持续淡水取用方式。

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State-of-the-art of R&D on seawater desalination technology

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Fresh water deficit has been an increasingly critical global environmental issue, and seawater desalination is considered as the most effective and promising solution, which promotes the development of different desalination technologies. In order to provide a comprehensive knowledge about the development of desalination technologies, state-of-the-art of research and development on the application of desalination technologies is reviewed in this paper. At first, the overview of desalination technologies is briefly introduced, including the definition of desalination, the evaluation index of water quality and the resulting classification of water resources, the overview of desalination industry, the usages of freshwater produced by desalination, and the sources of raw water. Besides, conventional desalination methods are categorized into physical method and chemical method according to whether there is new substance generated in the desalination process. In the following section conventional desalination methods are reviewed from the perspectives of basic processes and principles, the performances and technical characteristics. However, the shortcomings of conventional desalination technologies mainly lie in high energy consumption and complex treatment process, such as the decrease of heat transfer coefficient caused by the scaling and fouling generated on the solid heat transfer walls for multi-stage flash (MSF) and multiple effect distillation (MED), and rigorous pre-treatment and low recovery factor for reverse osmosis (RO). With the aims of overcoming these disadvantages and thus decreasing the energy consumption, different improvements have been put forward and new desalination methods have been developed. Therefore, the development of desalination technology is then exhaustively analyzed and forecasted in the following four aspects: improvement for the existing technology, combination of different technologies, desalination technology in combination with new energy, and development of new desalination technologies utilizing unemployed physical phenomena. The improvements mainly focus on the shortcomings of MSF, MED and RO, which are the current major large-scale industrial desalination technologies. The combination of different technologies can integrate their respective advantages to improve the desalination performance and decrease the energy consumption and the cost. The limitations of the decrease of traditional fossil energy and its increasing cost can be broken through the combination with solar, wind, geothermal, ocean and nuclear energies, which is also regarded as a potential solution for climate change. The newly developed desalination technologies have the advantages of lower energy consumption and cost, but most of which are still in lab-scale and need further improvement. Due to the important role in the assessment of the desalination efficient, special attention is paid to the analysis of energy consumption of each desalination technology.

seawater desalination, thermal method, membrane method, new energy

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