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Economic, Environmental & Social Incentives to Recover
Hypersaline Concentrate via the Dual-salt (Na_2CO_3 & NH_4Cl)
Process at Desalination Plants in Latin America and the Caribbean

by

William Miller

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To qualify for the degree of

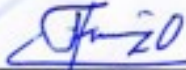
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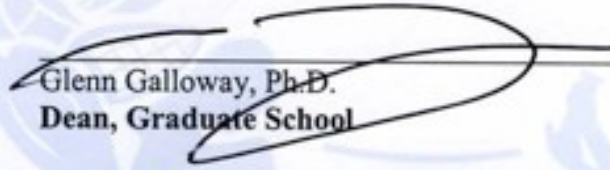


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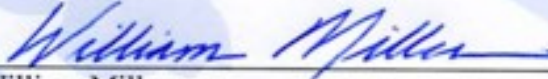


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DEDICATION

To my dog Mickey, who always kept me in good spirits.

To Laura Ayala Martinez, who I missed during my two years at CATIE.

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I am happy to thank Luci Mora for her Spanish editing on the presentation slides. Also, thanks to Adam Herbert for his advice and loaning his book on writing scientific papers. Finally, thanks to the staff at the CATIE library for all their help.

BIOGRAPHY

The author was born on the East coast of the United States in New Jersey, on October 1, 1964. In 1989, he graduated from the University of Colorado at Boulder with a BA degree in environmental, population and organismic biology. After graduation, he traveled to Europe, Asia and Africa visiting forty countries including sailing the Baltic Sea and snorkeling in the Red Sea. He has worked in research at the Johns Hopkins School of Medicine working with scanning electron microscopy for a project on micro-dental wear analysis of mantled howler monkeys, *Alouatta palliata* in Cañas, Costa Rica. Also, he has worked as a veterinarian technician for large and small animals even working part-time as a blacksmith forging horse shoes from stock metal. He has lived on a small sailboat and has sailed the Chesapeake Bay and the Atlantic Ocean. The author has taught high school chemistry and physics for the last four years in Costa Rica. He enjoys traveling, sailing, digital photography, bicycling, studying Spanish and spending time with his dog Mickey.

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SUMMARY

Commercial desalination produces desirable fresh water while reducing fresh water demand from local aquifers and surface tributaries which may decrease salt-water intrusion, reduce potential subsidence (such as sink-holes) by reducing withdrawals and allow overdrawn aquifers to recharge. However, desalination also produces undesirable hypersaline concentrate that can be injected into deep wells or discharged via an outfall pipe to coastal areas adversely affecting the coastal flora and fauna. This thesis will focus on reducing the hypersaline concentrate by converting a percentage of it to revenue generating products: sodium bicarbonate (baking soda, NaHCO_3), sodium carbonate (soda ash, Na_2CO_3) and ammonium chloride (rice and palm fertilizer, NH_4Cl) via the dual-salt (DS) process. The dual-salt process utilizes the following consumables (inputs): hypersaline concentrate, sequestered CO_2 , crystallized NaCl and ammonia (NH_3) which limits the desalination/dual-salt plant to be collocated with an ammonia production facility. An ammonia plant will also allow the production of anhydrous ammonia and urea for additional revenue. Latin American and Caribbean ammonia exporters include Venezuela, Mexico, Argentina, Brazil and Colombia with Trinidad and Tobago as the world's largest ammonia exporter (ICIS 2009). This thesis will emphasize the economic, environmental abatement and social incentives to employ the dual-salt process at the Point Lisas, Trinidad and Tobago desalination plant because it is the site of the largest sea water reverse osmosis (SWRO) desalination plant in the western hemisphere (GE Water 2009) and is collocated with ammonia production facilities (Caribbean Nitrogen Co.) built to take advantage of the abundant natural gas found off the East coast of Trinidad and Tobago.

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RESUMEN

La desalinización comercial, además de producir agua dulce, reduce la demanda de este recurso desde los acuíferos y manantiales, lo que a su vez, puede reducir la intrusión de agua salada y reducir procesos potenciales de subsidencia (tales como sumideros) por retractación y por permitir la recarga de acuíferos libres. Sin embargo, la desalinización también produce concentrados hipersalinos indeseables que puede ser inyectados en los pozos profundos o descargarse, a través de una tubería de desagüe, a las zonas costeras, afectando negativamente la flora y fauna.

Esta tesis se enfoca en la reducción de concentrados hipersalinos mediante la conversión de una parte de estos, a productos que generan ingresos: bicarbonato de sodio (NaHCO_3), carbonato de sodio (Na_2CO_3) y cloruro de amonio (fertilizante para arroz y palma, NH_4Cl) a través del proceso llamado doble sal (“dual salt”, DS).

El proceso de doble sal utiliza los siguientes insumos: concentrados hipersalinos, CO_2 , secuestrado, NaCl cristalizado y amoníaco (NH_3), los cuales limitan para que plantas de desalinización/doble sal puedan ser adecuadas para producir amoníaco con facilidad. Una planta de amoníaco también permitiría ingresos adicionales mediante la producción de amoníaco anhidro y urea.

Los principales países de América Latina y el Caribe exportadores de amoníaco son Venezuela, México, Argentina, Brasil, Colombia y Trinidad y Tobago, siendo este último, el mayor exportador de amoníaco del mundo (ICIS 2009).

Esta tesis enfatiza en los incentivos económicos y sociales, así como la reducción de efectos ambientales por el uso del proceso de doble sal, en la planta de desalinización Point Lisas en Trinidad y Tobago, que es el sitio donde está la planta de desalinización más grande del hemisferio Occidental (Caribe Nitrogen Co.) que utiliza el proceso de ósmosis inversa (SWRO) (GE Water 2009) y que tiene facilidades para la producción de amoníaco, y para aprovechar la abundante disponibilidad de este gas natural en la costa este de Trinidad y Tobago.

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ABBREVIATIONS AND SYMBOLS

AB: Ammonia borane (form of hydrogen storage synthesized from NH_4Cl)

ANSAC: American Natural Soda Ash Corporation

aq: aqueous

CATIE: Centro Agronómico Tropical de Investigación y Enseñanza

CH_4 : methane

DESALCOTT: Desalination Company of Trinidad and Tobago Ltd.

DS: Dual-salt process

ESAPA: European Soda Ash Producers Association

g: gas

l: liquid

MGD: million gallons per day

NaCl : sodium chloride

NaHCO_3 : sodium bicarbonate (baking soda)

Na_2CO_3 : sodium carbonate (soda ash)

$(\text{NH}_2)_2\text{CO}$: urea fertilizer (47% N)

NH_3 : ammonia

NH_4^+ : ammonium ion

NH_4Cl : ammonium chloride (“rice fertilizer”, 25% N)

NH_4HCO_3 : ammonium bicarbonate (hartshorn)

NH_4OH : ammonium hydroxide (aqueous ammonia)

PSA: Pressure Swing Adsorption (separation of N_2 from air)

PSS: Practical Salinity Scale (dimensionless: open ocean PSS between 32-37)

SMR: Steam Methane Reforming

SWRO: Sea Water Reverse Osmosis

WASA: Water and Sewage Authority of Trinidad & Tobago

WGS: Water Gas Shift reaction

ZLD: Zero Liquid Discharge

1. INTRODUCTION

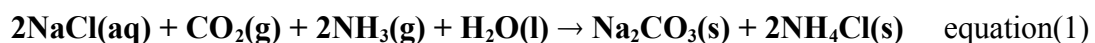
The island of Curaçao in the Netherlands Antilles (a Caribbean island just north of Venezuela) was the first place to make a major commitment to desalination, and plants have operated there since 1928 (Zander 2008).

Future coastal water planners will include desalination as part of their water portfolio for providing reliable freshwater for drinking, irrigation and industry. Desalination offers more than an opportunity for an unlimited source of freshwater and has many hidden and indirect benefits such as:

- Provide a drought-resistant freshwater supply.
- Reduce sub-surface water withdrawals, allowing aquifers to recharge.
- Reduce surface water withdrawals.
- Reduce salt-water intrusion into coastal aquifers.
- Reduce subsidence (sink-holes) caused by overdrawn aquifers.
- Alleviate water scarcity problems.
- Allow coastal communities, agriculture and industry to expand where natural freshwater resources are limited or nonexistent.
- Restore wetlands to increase habitat of ecologically sensitive species.
- Allow coastal watersheds to recover and improve as more surface and ground water becomes available.

With the many benefits desalination delivers, it unfortunately produces copious amounts of hypersaline concentrate as a by-product of fresh water production. The hypersaline concentrate discharge to coastal waters may adversely affect the coastal flora and fauna, posing a severe environmental challenge; it is for this reason some desalination plants are being opposed (Miller 2003). Instead of discharging the concentrate, it may be converted to valuable products via the dual-salt (DS) process which was developed in 1933 by Hou Debang, who modified the ammonia-soda (Solvay) process to convert brine into the products sodium bicarbonate (NaHCO_3), sodium carbonate (Na_2CO_3) and ammonium chloride (NH_4Cl). Equation (1) demonstrates the overall reaction:

Overall equation of dual-salt (DS) process



1.1 Justification and importance

As populations increase and the world's freshwater resources remain fixed, one solution to increase potable water after conservation of freshwater and reuse has been exhausted, is desalination to alleviate water scarcity, and provide reliable and drought-resistant freshwater. Desalination has many advantages to society but water planners need to consider the environmental aspects of concentrate management to mitigate harm to the flora and fauna of the coastal discharge zones.

If the concentrate can be chemically converted to yield products of economic potential and show a profit, then the process would be viable. If the products have useful value to society then the process would be valuable. The DS process may be a solution that is economically justified by increasing revenue to help offset desalination energy costs, ecologically important by abating concentrate discharge and sequestering CO₂, and socially important because new jobs would be created as well as producing needed soda ash and valuable fertilizer for rice and palm cultivation in Latin America and the Caribbean.

1.2 Research objectives

1.2.1 General objective

To demonstrate that hypersaline concentrate recovery via the dual-salt process will have economic, environmental and social incentives when deployed at desalination plants in Latin America and the Caribbean with a special emphasis at the SWRO desalination plant at Point Lisas, Trinidad.

1.2.2 Specific objectives

1.2.2.1 Economic incentives: To demonstrate that the dual-salt process will produce products with market value.

1.2.2.2 Environmental incentives: To demonstrate that the dual-salt process will abate the discharge of hypersaline concentrate and sequester CO₂.

1.2.2.3 Social incentives: To demonstrate that the dual-salt process will provide jobs and products with social value.

1.3 Expected results and implications

- A market should exist for the fertilizer ammonium chloride for rice and palm

cultivation in Latin America and the Caribbean.

- The dual-salt method will require collaboration between the desalination plant and the ammonia production facility or to integrate the DS plant with an ammonia production facility as part of the desalination plant overall design.

1.4 Research questions

- What will be some of the economic, environmental and social incentives of incorporating the DS process at the Point Lisas, Trinidad and Tobago SWRO desalination plant?
- What will be the principal conditions and requirements to employ the DS process at other locations in Latin America and the Caribbean?

2. LITERATURE REVIEW

The marriage of a desalination plant with an ammonia plant is a synergistic coupling. The hypersaline concentrate, an environmental concern, can now be utilized for the production of sodium carbonate and ammonium chloride, thus providing revenue. The ammonium chloride can be used for rice and palm cultivation. In addition, the ammonium chloride can be reacted with sodium borohydride to yield ammonia borane (AB), a promising candidate for safe hydrogen storage for fuel cells. Producing AB also produces NaCl salt which can be recycled back to the dual-salt process. Hydrogen gas is also produced as an intermediary which can be recycled back into the Haber-Bosch ammonia process.

The chemistry of the dual-salt process is fairly straightforward, yet it involves ammonia derived from the Haber-Bosch process, which requires hydrogen from methane gas through a process called steam methane reforming or SMR. CO₂ is produced in the SMR process as a by-product and is required in copious amounts for the dual-salt process. There are many steps involved and many may seem unrelated at first because it is not apparent that ammonia generates CO₂ when one considers it is just a reaction between hydrogen and nitrogen. The topics in the literature review are mentioned because of their importance in the dual-salt process. An attempt will be made to explain various literature reviews with their role in the dual-salt process.

The dual-salt process requires large amounts of ammonia, carbon dioxide and NaCl salt. Ammonia requires hydrogen and nitrogen. Nitrogen is easily obtained from the atmosphere in the pressure swing adsorption (PSA) process and hydrogen is obtained by cracking the four hydrogen atoms in methane (CH₄) in a process known as steam methane reforming (SMR). This process also creates the needed CO₂ as water vapor and methane gas are passed over a catalyst producing syngas (H₂ & CO). Then the H₂ is separated and the CO is passed with water vapor in the water gas shift reaction (WGS) producing H₂ and CO₂. Crystallized NaCl salt is purchased and not evaporated due to costs. If ammonia borane is produced with sodium borohydride, then little NaCl is required after the initial start of the process and only NaCl is required to replenish small losses over time.

Solar and wind energy will be incorporated at all costs to ensure sustainability and maintain a low-carbon footprint. Solar thermal energy can produce heat needed to

crystallize the ammonium chloride and solar photovoltaic and wind energy can help supplement electricity costs.

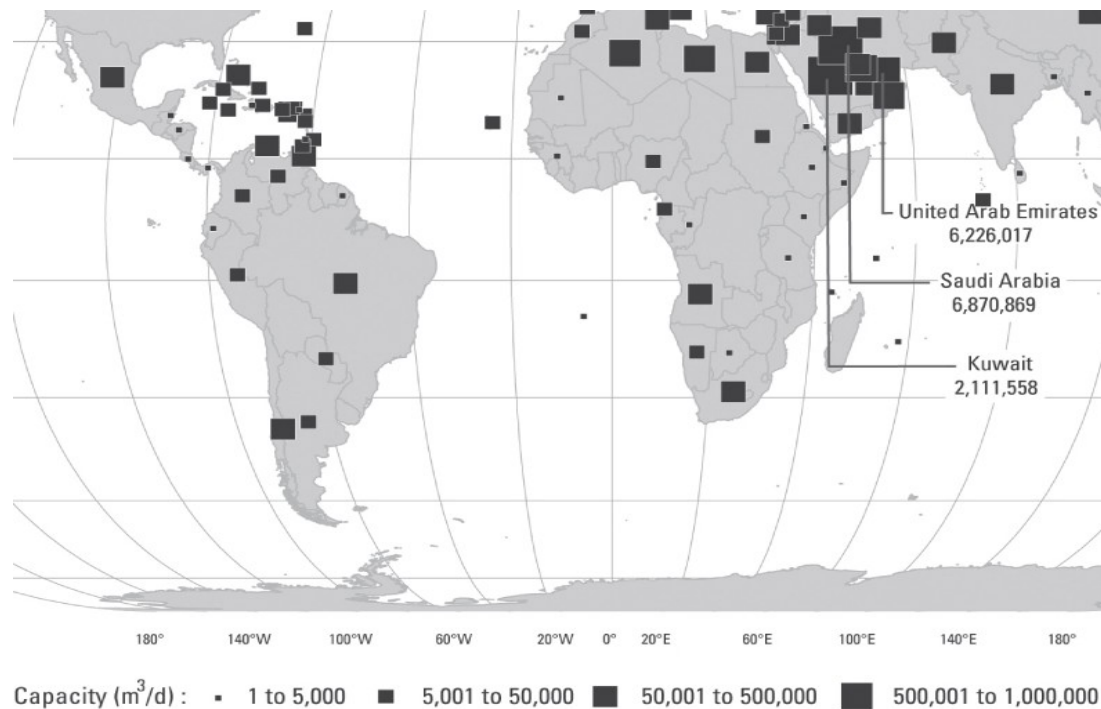


Figure 2.1 Desalination by capacity (source: Zander 2008)

2.1 Desalination, ammonia production and salt production in Latin America & the Caribbean

2.1.1 Desalination

Figure 2.1 shows Argentina and Colombia having a desalination capacity between 5,001 to 50,000 m³/day and Venezuela, Mexico, Brazil and Trinidad & Tobago having a desalination capacity between 50,001 to 500,000 m³/day (Zander 2008). Trinidad and Tobago are also the home of the largest SWRO desalination plant in the western hemisphere coming online in 2002 with a production of 29 MGD (GE Water 2009).

2.1.2 Ammonia production

Venezuela, Mexico, Argentina, Brazil, Colombia and Trinidad & Tobago are the major ammonia exporters of Latin America and the Caribbean (ICIS 2009). Since the DS process requires ammonia production, these countries would be candidates for employing the DS process at desalination plants, especially Venezuela, Mexico, Brazil and Trinidad & Tobago

because of their high desalination capacity.

Table 2.1 shows the world's top ten ammonia exporters with Trinidad & Tobago as number 1, Venezuela as number 5 and Colombia as number 9.

Table 2.1 Major supply countries of anhydrous ammonia 2005-2009 (source: TradeData international analysis report 2009)

Major Supply Countries	Anhydrous Ammonia 2005-2009 (Metric Tons)				
	2005	2006	2007	2008	2009 up to August
Trinidad & Tobago	4,493,478	4,070,623	4,354,542	3,809,753	2,461,214
Canada	1,337,683	1,010,383	920,269	932,602	547,497
Russia	425,971	670,210	1,642,208	1,427,882	288,411
Ukraine	1,163,197	975,975	347,374	553,482	15,494
Venezuela	148,329	252,447	271,617	213,479	157,560
Qatar	51,007	35,451	48,692	75,077	11,000
Latvia	117,740	0	748,117	226,862	0
Saudi Arabia	24,870	18,579	0	84,138	27,800
Colombia	35,985	31,174	21,360	19,852	17,508
Oman	23,459	4,409	48,852	48,196	0

The price of ammonia is correlated to the price of natural gas, since the hydrogen in NH_3 is obtained from methane (CH_4) in a process known as steam methane reforming (SMR). Figure 2.2 indicates a price hike in September of 2008 when fuel prices (natural gas) were also at or near record highs.

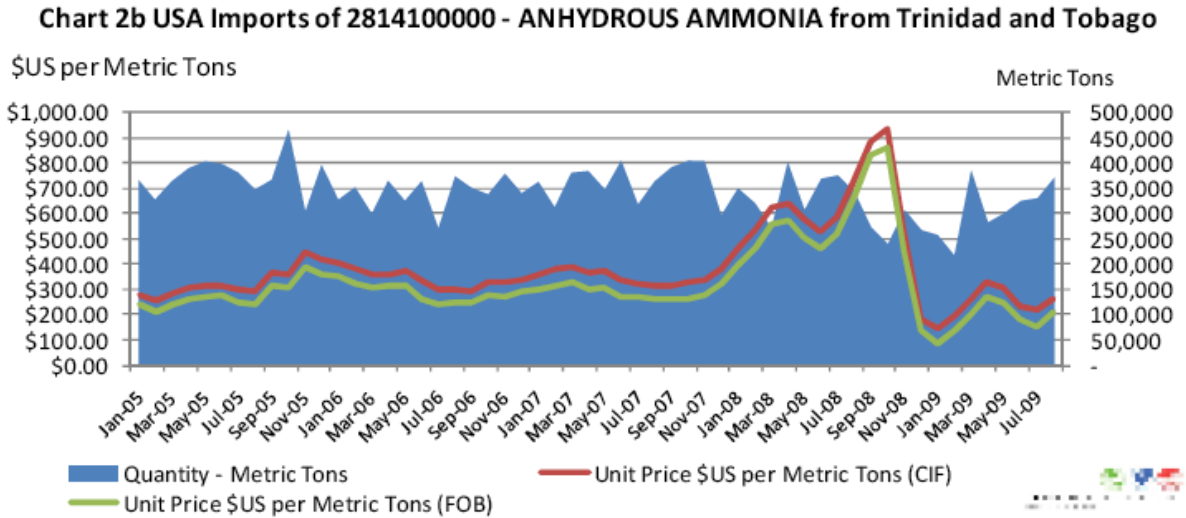


Figure 2.2 Anhydrous ammonia US imports from Trinidad & Tobago 2005-2009 (source: TradeData international analysis report 2009)

2.1.3 Salt production

Besides rich underground salt deposits around the globe, there's enough salt in the oceans of the world to make a full-scale relief map of Mexico and all of Central and South America—including the Andes! - Richard Hanneman (from Latin America's salt industry).

Fifty-eight percent of crystallized sodium chloride is used as a major feedstock for chemistry producing among other chemicals (Hanneman 2003):

- NaOH (caustic soda, sodium hydroxide)
- Cl₂ (chlorine)
- Na₂CO₃ (soda ash, sodium carbonate)

NaCl salt is required in the DS process to create a saturated salt solution of almost 300 g/l (Detournay et al. 2004). It is also required to precipitate ammonium chloride in Hou Debang's modified Solvay process. Concentrate is approximately twice as saline as feedwater (~7.0 g/l or practical salinity scale (PSS) ~70), and to reach the 300 g/l saturation required means large quantities of additional salt will be required to be purchased for the DS process (unless ammonia borane is produced, then no salt is required).

Salt production is led by the US/Puerto Rico (46 million tons in 2000), followed by Mexico, Brazil and Chile (USGS 2001). Other producers in the region include: Bahamas, Venezuela, Netherland Antilles, Colombia, Guadalupe, Martinique and Cuba.

2.2 Concentrate management

There are a few options for concentrate management and figure 2.3 demonstrates examples of concentrate disposal methods in the US in 2006. The largest US desalination plant is a BWRO plant located in Tampa Bay, Florida that became operational in 2008 with a freshwater production of 25 MGD and a concentrate production of 19 MGD (see figure 2.4). The concentrate is diluted by the adjoining power company cooling water to a ratio of 70:1 before discharge to surface waters of the Tampa Bay.

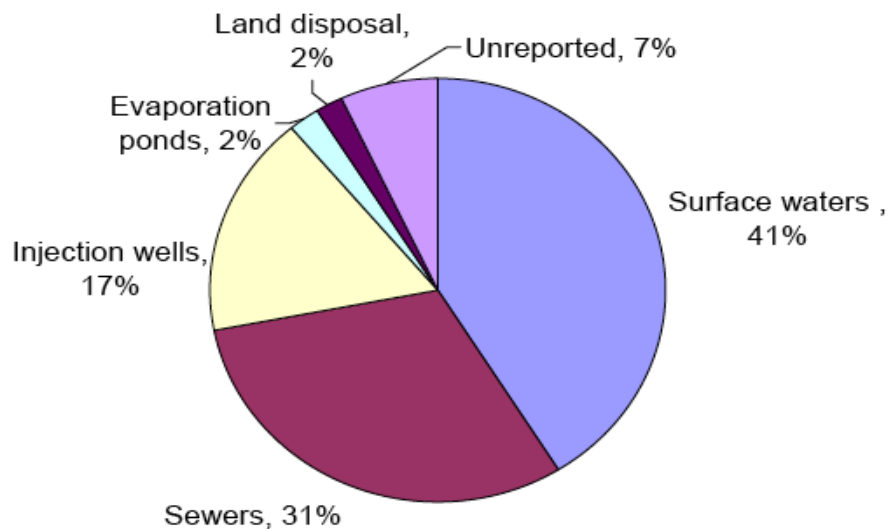


Figure 2.3 Concentrate disposal methods at US desalination plants (source: Mickley 2006)

Consolidated Water Corporation's North Shore, Grand Cayman Island's SWRO desalination plant disposes their concentrate in an 800 foot deep well (and their intake wells are at 300 feet deep with a 500 foot separation zone) thus eliminating any concentrate discharge concerns for the coastal flora and fauna (personal tour of the plant June of 2010). Proactiva's Lox Bight SWRO desalination plant located in San Andrés, Colombia discharges their concentrate along with untreated sewage through an outfall pipe located 1.5 km from the shoreline situated in currents that sweeps the sewage and concentrate away from the island and towards the East coast of Nicaragua (personal tour of the plant, July of 2009).

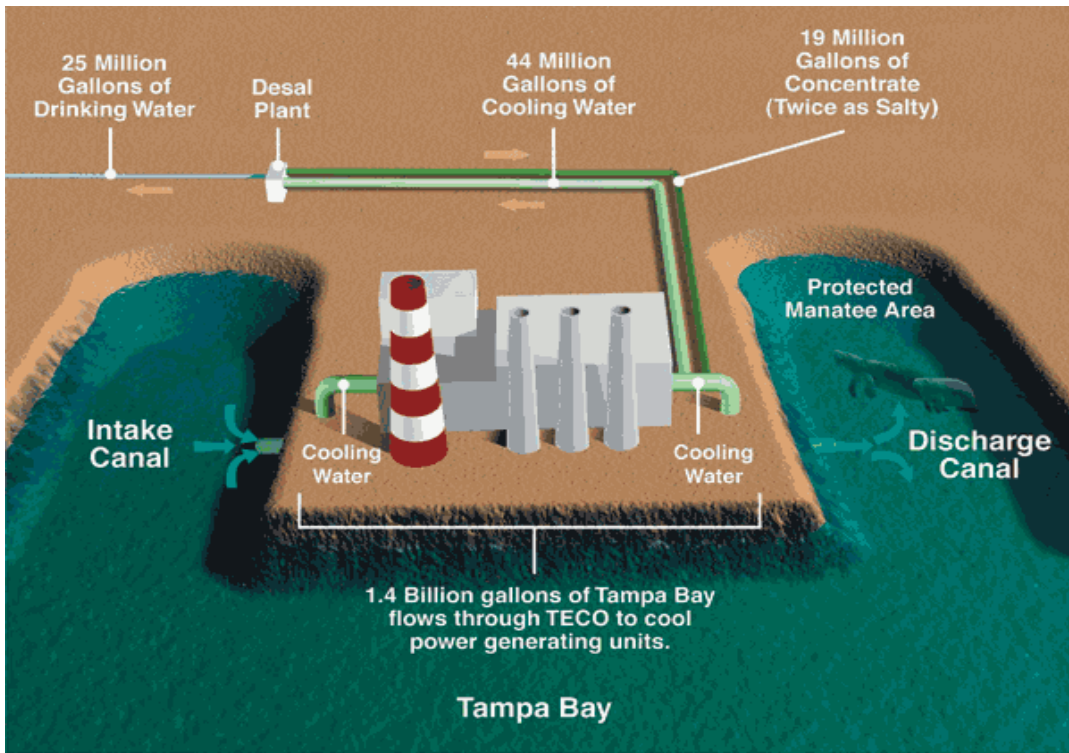


Figure 2.4 Tampa Bay, FL collocation of BWRO desalination plant with once-through cooling to dilute concentrate to 70:1 (source: Tampa Bay Water Authority/TECO, Tampa, FL 2009)

2.3 Dual-salt process

2.3.1 Overview

In 1811, the French scientist A. J. Fresnel had shown that sodium bicarbonate could be precipitated from a salt solution containing ammonium bicarbonate, but it was not until the early 1880s that the Belgian Ernest Solvay commercialized this to produce soda ash and the name, Solvay process stuck (Tutorvista 2009).

In the 1930s, Hou Debang developed the dual-salt process by modifying the Solvay or ammonia-soda process. The DS process eliminated the calcium chloride by-product formed in the ammonia-soda process and instead added more ammonia and dry NaCl salt to the ammonium chloride mother liquor to produce crystallized ammonium chloride, having value as a fertilizer for rice and palm cultivation especially important in Asia (SEVAS 2007).

The dual-salt process inputs are: water, salt, ammonia, carbon dioxide and lime. The dual-salt outputs are: sodium bicarbonate (calcined to sodium carbonate) and ammonium

chloride. Before the dual-salt process begins, the brine will need to be purified with the addition of quick lime (CaO) and soda ash which will precipitate the calcium and magnesium cations. This will produce calcium carbonate and magnesium hydroxide, which can be added to the ammonium chloride fertilizer or sold separately. An ammonia production plant collocated with the desalination plant makes economic sense by allowing the desalination plant to increase its revenues with the additional products of anhydrous ammonia and urea.

Ammonia is synthesized from nitrogen and hydrogen. Nitrogen gas is easily obtained from air extraction (air being comprised of approximately 78% N₂) by pressure swing adsorption (PSA), which is a gas separation process relying on the principle that at high pressures, gases adsorb differently to certain surfaces such as carbon molecular sieves. At high pressures, nitrogen gas adsorbs more strongly than oxygen gas allowing the oxygen gas to pass out of the system leaving high purity nitrogen gas.

Hydrogen gas is economically obtained from cracking the four hydrogen atoms in methane gas (CH₄) in the steam methane reforming (SMR) process which produces syngas (H₂ & CO). The carbon monoxide (CO) is separated from the hydrogen and then combined with steam in the water gas shift (WGS) reaction producing more hydrogen and carbon dioxide in an approximate ratio of 1:2.5 (H₂:CO₂). The CO₂ gas is utilized as a reactant along with ammonia in the Bosch-Meiser urea reaction to produce urea, a fertilizer with the highest nitrogen content (46% nitrogen). The dual-salt process also requires CO₂ and the water gas shift (WGS) reaction will provide the required CO₂ gas.

Figure 2.5 shows the overall dual-salt process with inputs and outputs and the various processes required such as tank mixers, centrifuges, dryers and conveyers. The heart of the process lies in the carbonating tower (refer to C-12 in fig. 2.5) where precipitation of sodium bicarbonate takes place. The soda ash calciner (refer to V-16 in fig. 2.5) heats the sodium bicarbonate releasing CO₂ and water vapor. The CO₂ can be recycled to the carbonating tower and the water vapor can be used for heating the mother liquor in another step before it condenses back to liquid where it can be recycled as an input to the desalination plant feedwater.

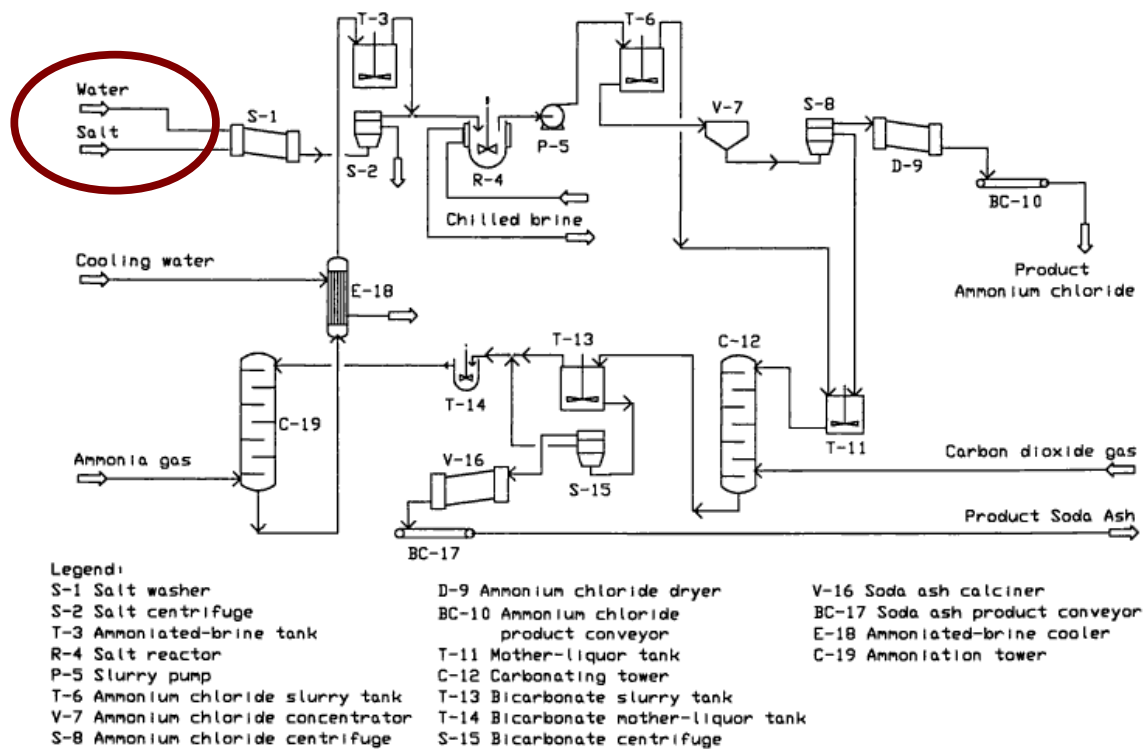


Figure 2.5 Dual-salt process (source: Fertilizer manual - UN Industrial Development Organization 1998) Oval indicates concentrate and salt inputs.

2.3.2 Sodium bicarbonate (baking soda, NaHCO_3)

Sodium bicarbonate has many uses, but is usually calcined (heated) to form sodium carbonate, a more desired product which will also yield CO_2 in the process which will be used in the carbonation process of ammoniated brine (SEVAS 2007). Figure 2.6 illustrates some applications of sodium bicarbonate in the EU in 2002; the most environmentally important being flue gas desulfurization (11%) which eliminates upwards to 97% of sulfur dioxide emissions thus eliminating acid rain.

Consumption of Sodium Bicarbonate in EU

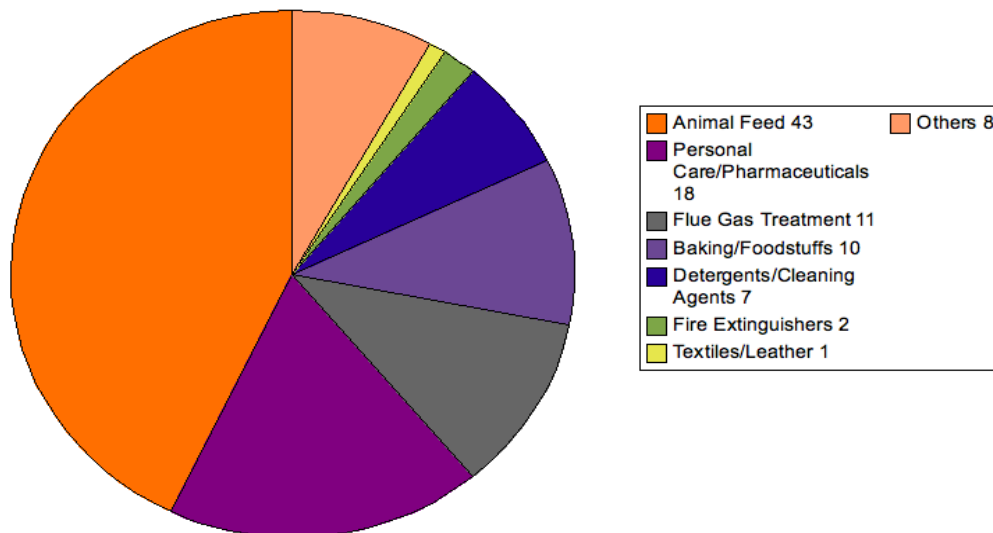


Figure 2.6 Consumption of sodium bicarbonate in EU 2002 (source: Detournay et al. 2004; graph: author)

2.3.3 Sodium carbonate (soda ash, Na_2CO_3)

Soda ash made from ashes of certain plants such as *salsola soda* or seaweed has been known since antiquity. Sodium carbonate is a white crystalline solid, which can exist as:

- Anhydrous salt (Na_2CO_3 - soda ash).
- Monohydrate salt ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$).
- Heptahydrate salt ($\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$).
- Decahydrate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ - washing soda).

Sodium carbonate is readily soluble in water. On heating, the decahydrate salt gradually loses water to, finally give anhydrous salt (Na_2CO_3 - soda ash) (Tutorvista 2009).

Uses of soda ash include glass making, chemicals and even water treatment (see figure 2.7). Soda ash in addition to sodium bicarbonate, is also used for flue gas desulfurization, which prevents the release of sulfur into the atmosphere preventing acid rain formation (dilute sulfuric acid, H_2SO_4).

Uses of soda ash

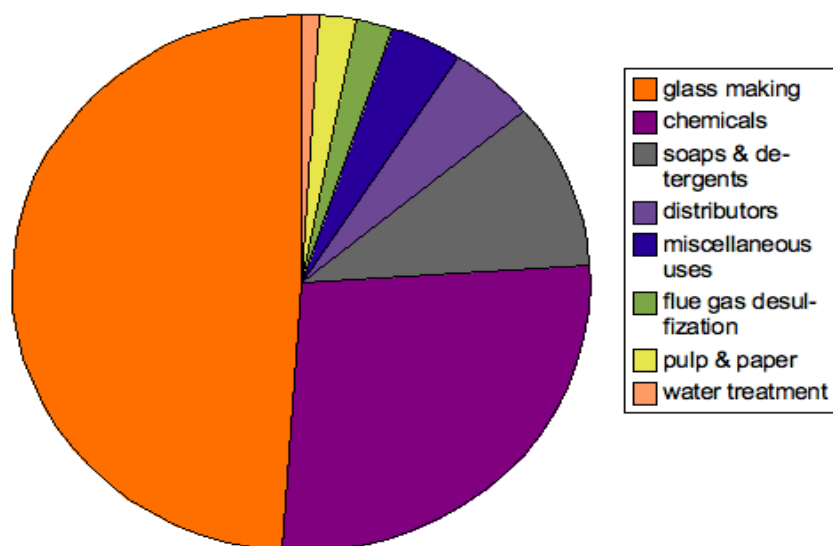


Figure 2.7 Based on final 2005 reported data estimated 2006 distribution of soda ash by end use (source: ANSAC, graph: author)

According to Detournay et al. (2004), Latin America only produced about 0.5 million tons/year of soda ash in 2000 from a worldwide total production of 42.3 million tons/year constituting only 1.18% of total worldwide production (see table 2.2).

Table 2.2 Worldwide soda ash production (source: Detournay et al. 2004)

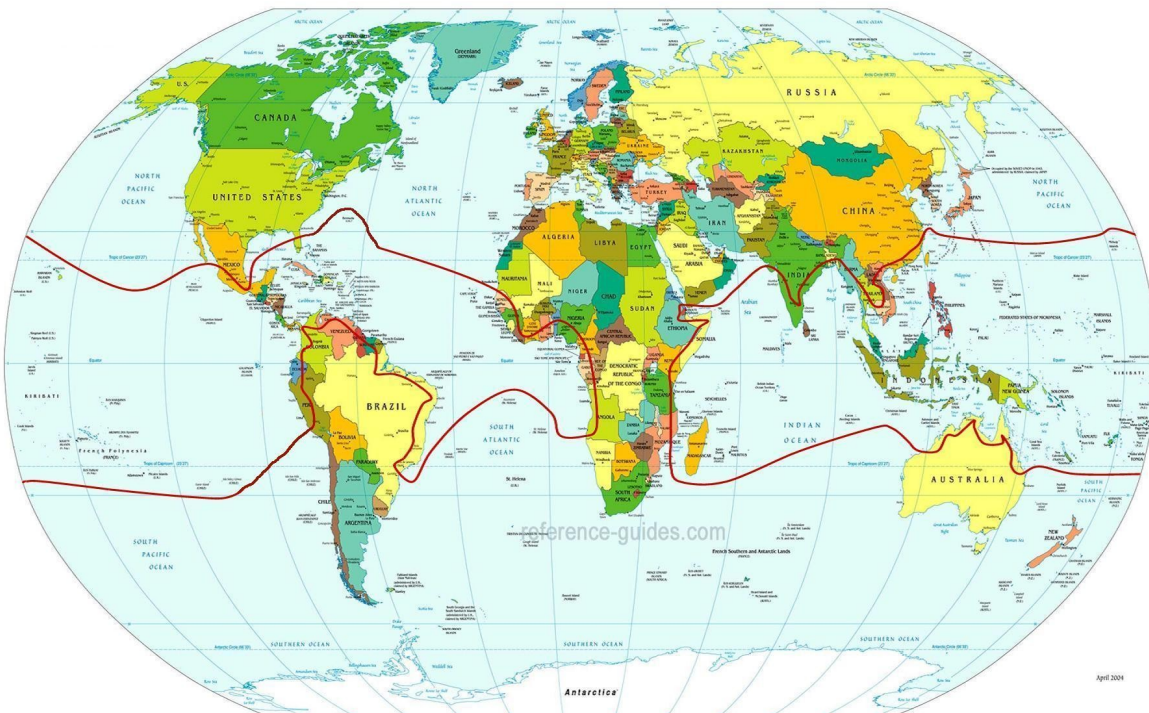
Production Capacity	EU A	Rest of Europe	North America	Latin America	Asia	Africa	Oceania	Total
Solvay process	7.7	6.6	-	0.5	9.7	0.1	0.4	25
Na minerals process	-	-	11.6	-	0.5	0.6	-	12.7
Others	0.1	0.8	-	-	3.7	-	-	4.6
Total	7.8	7.4	11.6	0.5	13.9	0.7	0.4	42.3

2.3.4 Ammonium chloride (rice & palm fertilizer, NH_4Cl)

Fertilizer-grade NH_4Cl usually contains 25% N. About two-thirds of the world capacity for manufacture of this material is located in Japan, with the remaining one-third situated in India and China. Most of it is produced by the dual-salt process, in which NH_4Cl and Na_2CO_3 are formed simultaneously. Some of its advantages include a higher N concentration than $(\text{NH}_4)_2\text{SO}_4$ and superiority over $(\text{NH}_4)_2\text{SO}_4$ for rice. Ammonium chloride is an excellent source of both N and Cl^- for coconut, oil palm, and kiwifruit, which are Cl responsive crops. Ammonium chloride is as acid forming as $(\text{NH}_4)_2\text{SO}_4$ per unit of N, and this effect is undesirable in acidic soil, especially if liming costs are excessive. Other shortcomings are its low N analysis in comparison to urea or NH_4NO_3 , and its high Cl-content limits its use to tolerant crops (Havlin et al. 2005).

Figure 2.8 is presented to approximate the geographic zone where ammonium chloride has potential as a fertilizer in regards to palms, such as coconut palms. All of Central America, the Caribbean and the northern coasts of South America would benefit.

Figure 2.8 Coconut palm distribution (source: Niklas Jonsson)



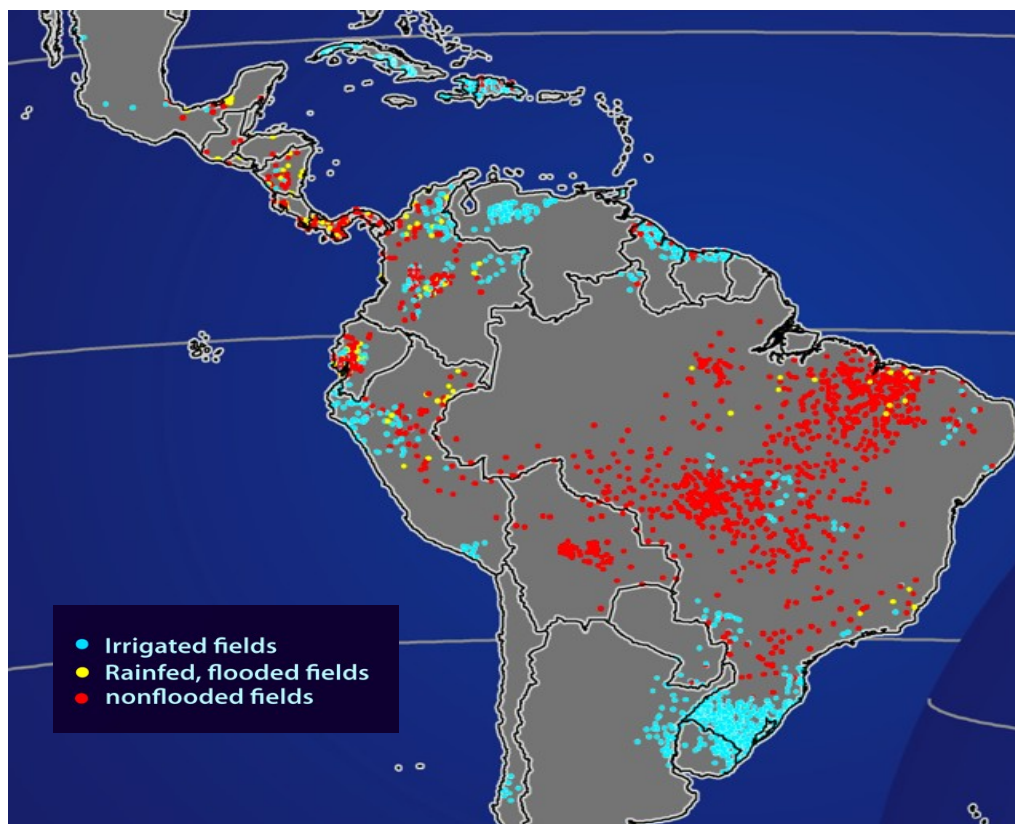


Figure 2.9 Rice production in Latin America & the Caribbean, where each small circle represents 5,000 hectares (source: IRRI 2005 RJ Hijmans)

Ammonium chloride is a widely used fertilizer for rice in Asia and is also known as the rice fertilizer. Ammonium chloride has produced maximum rice yield in a study comparing urea, calcium ammonium nitrate and ammonium chloride (see table 2.3).

Table 2.3 Effect of N levels and sources on grain yield of rice variety IR8, Punjab, India (source: IRR Newsletter 1983)

N (kg/ha)	Rice Yield (t/ha)			
	Calcium ammonium nitrate	Ammonium chloride	Urea	Mean
60	4.3	4.7	4.8	4.6
120	6.3	7	6.9	6.7
180	6.9	7.8	7.3	7.3
Mean	5.9	6.5	6.3	-

2.4 CO₂ & H₂ production

Since the Solvay process obtained its CO₂ from the calcination of limestone to lime and the DS process lacks this step, CO₂ needs to be obtained from another source. A complimentary source is from the production of hydrogen from methane gas known as steam methane reforming (SMR). SMR provides hydrogen (H₂) for ammonia production as it is currently cheaper than other methods such as electrolysis of water.

SMR consists of two steps (from HFS 2010):

Step 1: Hydrogen is obtained from methane, CH₄ by passing steam and methane over nickel catalysts at 750-800 °C to produce syngas, a mixture of H₂ gas and CO.

Step 2: This step is known as the water gas shift (WGS) reaction and reacts CO with H₂O (steam) to produce CO₂ and H₂. There are two stages: 1st stage: high temperature shift (HTS) occurring at 350 °C and 2nd stage: low temperature shift (LTS) occurring at 200 °C.

The SMR process (specifically the WGS reaction mentioned above) produces more than twice (2.51X) the volume of CO₂ than H₂ which is normally not desirable, but ammonia and CO₂ react to produce urea (NH₂)₂CO, yielding one of the highest nitrogen fertilizers available (46.7% N) (HFS 2010). Because the DS process requires NH₃ and CO₂, the SMR supplies the DS process with the necessary CO₂ and is a complimentary process. If the desalination plant is a DS plant as well, then of course ammonia and urea can be produced in addition to ammonium chloride.

2.5 N₂ generation

Nitrogen is generated by separating nitrogen (air ~ 78% N₂) from air using pressure swing adsorption (PSA) technology which has been around since the 1960s. Gases bind differently to certain solids at high pressures and carbon molecular sieves (CMS) bind oxygen preferentially to nitrogen, allowing separation of nitrogen to occur. Oxygen is vented to the atmosphere (or could be reused in other applications) and the non-binding nitrogen produced is very pure and can reach 99.9995% purity (Peak Scientific Instruments 2010).

2.6 NH₃ & urea synthesis

Chemical fertilizers contribute about half of the nitrogen input into global agriculture, while biological nitrogen-fixation taking place in leguminous plants contributes the other half. That means about half of the nitrogen atoms in the body of an average person living in a developed country once passed through a chemical plant and participated in the nitrogen-to-ammonia Haber-Bosch reaction. Perhaps no other human invention has had a more dramatic impact on Earth than Haber-Bosch chemistry (Ritter 2008).

Ammonia production consumes approximately 5% of the world's natural gas supply and 2% of the world's energy (Ritter 2008). The rise of industrial ammonia production had other repercussions. For one thing, it caused the Chilean saltpeter industry to eventually collapse, leaving ghost towns in the Atacama Desert in northern Chile (Ritter 2008).

2.6.1 Haber-Bosch NH₃ synthesis

The Haber-Bosch process reacts hydrogen gas, H₂ and nitrogen gas, N₂ over iron catalysts to produce ammonia, NH₃. High temperatures and pressures are required. Nitrogen is obtained from the separation of air (78% N₂) by pressure swing adsorption (PSA) and hydrogen is obtained from methane by steam methane reforming (although it could be obtained from sea water electrolysis or brine electrolysis at a higher energy cost).

2.6.2 Bosch-Meiser urea synthesis

The Bosch-Meiser process reacts ammonia, NH₃ with CO₂ to produce urea, (NH₂)₂CO and the process also generates water, which could be used for steam in the DS process (see equation (2)). Integrating a desalination plant, DS plant, ammonia plant and a urea plant would be a synergistic opportunity, especially if the desalination plant were a FO NH₃/CO₂ desalination plant.

Bosch-Meiser urea process



where, 2NH₃=34.08g, (NH₂)₂CO=60.07g/mol

1 tonne of ammonia will yield 1.76 tonnes of urea (theoretical)

2.7 Dual purpose chemical desalination

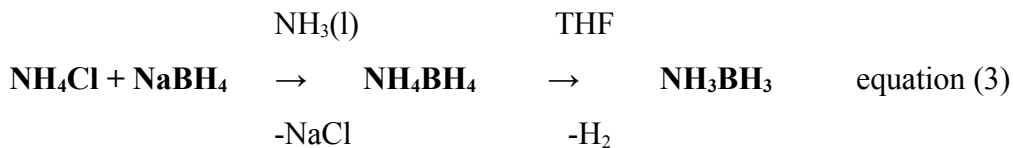
This research performed in Saudi Arabia in 1997 (Abdel-Aal et al.) was examining desalting sabkha water with a salt concentration of 25% to produce freshwater, soda ash

and ammonium chloride. This research mentions the utilization of brine concentrate from a MSF (multi-stage flash) thermal desalination plant as an alternate approach to using sabkha water to produce soda ash and ammonium chloride.

2.8 Ammonia borane synthesis

Because ammonium chloride is a product in the dual-salt process, it has immediate use in rice and palm cultivation as a fertilizer, but another application may be in store for ammonium chloride in the future as it is a reactant to manufacture ammonia borane. Ammonia borane with a gravimetric density *ca.* 194 gm H₂ kg⁻¹ and a volumetric density *ca.* 146 H₂ liter⁻¹, is a potential hydrogen storage material for fuel cell powered applications (Heldebrant et al. 2008). Table 2.5 lists ammonia borane as the second highest hydrogen content by formula weight after methane. Equation (3) shows NH₄Cl as a reactant and NaCl precipitated in the metathesis synthesis. The NaCl can be recycled back into the dual-salt process instead of acquiring NaCl salt as an added bonus.

Ammonium chloride and sodium borohydride react in liquid ammonia to yield ammonium borohydride and NaCl precipitate. Ammonium borohydride in the presence of the ether solvent, tetrahydrofuran (THF) yields 99% ammonia borane (NH₃BH₃).



Ammonia borane fuel cells are commercially available and provide continuous low power at 20 Watts of power for 72 hours (1440 W-h) and are sold by Jadoo power systems. These fuel cells are used in broadcast cameras, portable power units for soldiers, portable power for unmanned aerial vehicles and other applications (Jadoo Power 2010).

Table 2.4 High hydrogen content of various formulas by wt % (Heldebrant *et al.* 2010)

Formula	Formula Wt% Hydrogen
CH ₄	25
NH ₃ BH ₃	19.6
LiBH ₄	18.3
(CH ₃) ₄ NBH ₄	18
NH ₃	17.7
Al(BH ₄) ₃	16.8
Mg(BH ₄) ₂	14.8
LiH	12.6
CH ₃ OH	12.5
H ₂ O	11.2
LiAlH ₄	10.6
NaBH ₄	10.6
AlH ₃	10
MgH ₂	7.6
NaAlH ₄	7.4

It should be noted that many SWRO desalination plants have to limit their boron levels in their product water which normally requires a second pass thus increasing expenses. If boron can be selectively extracted and combined on-site, efficiently and inexpensively with sodium and hydrogen (borohydride complex), then this process would be a complimentary one.

3. MATERIALS AND METHODS

3.1 Point Lisas, Trinidad and Tobago

Point Lisas, Trinidad and Tobago (see figure 3.1) is host to the largest RO desalination plant in the Western hemisphere with a capacity of 29 MGD that became operational in 2002 (GE Water 2005) (see figure 3.2). In comparison, the largest US RO desalination plant only produces 25 MGD (see figure 2.1 TECO/Tampa Bay, FL) and the world's largest RO desalination plant in Ashkelon, Israel produces 87 MGD (Water-Technology.net 2009).

Point Lisas, Trinidad and Tobago is also the site of ammonia production (Caribbean Nitrogen Company, CNC) to take advantage of the low-cost methane derived from Trinidad's abundant natural gas reserves on the East coast. Because of this unusual combination of a large desalination plant coupled with a large ammonia production facility, this unique collocation offers the opportunity to investigate a hypothetical DS process utilizing the concentrate from the desalination plant.

Because the feedwater (see figure 3.4) to the Point Lisas, Trinidad and Tobago SWRO desalination plant is high in total solids (TS) due to the proximity of the Orinoco river mouth south of the plant, intensive pre-treatment is required to prepare the feed water for the RO trains hosting the osmotic membranes.

Figure 3.3 shows five different processes to pre-filter the ocean water prior to entering the SWRO membranes. It is for this reason that the concentrate has intrinsic value and should not be discarded. The Paria Gulf waters have high silt due to the Orinoco delta waters (see figure 3.5) located to the southwest and as a result, the gulf water needs to be pre-treated extensively to prolong RO membrane life and reduce membrane maintenance.



Figure 3.1 Point Lisas, Trinidad & Tobago



Figure 3.2 Point Lisas, Trinidad & Tobago SWRO Desalination plant (source: Google Earth February 26, 2006)

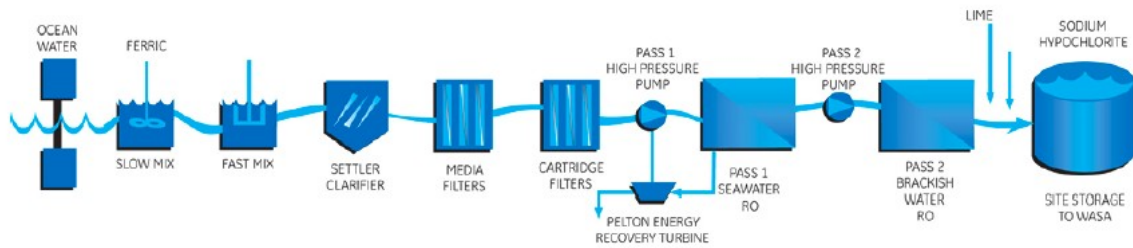


Figure 3.3 Point Lisas, Trinidad & Tobago SWRO desalination plant process start to finish (source: GE Water 2005)



Figure 3.4 Water intake for the Point Lisas, Trinidad & Tobago SWRO desalination plant (source: GE Water)

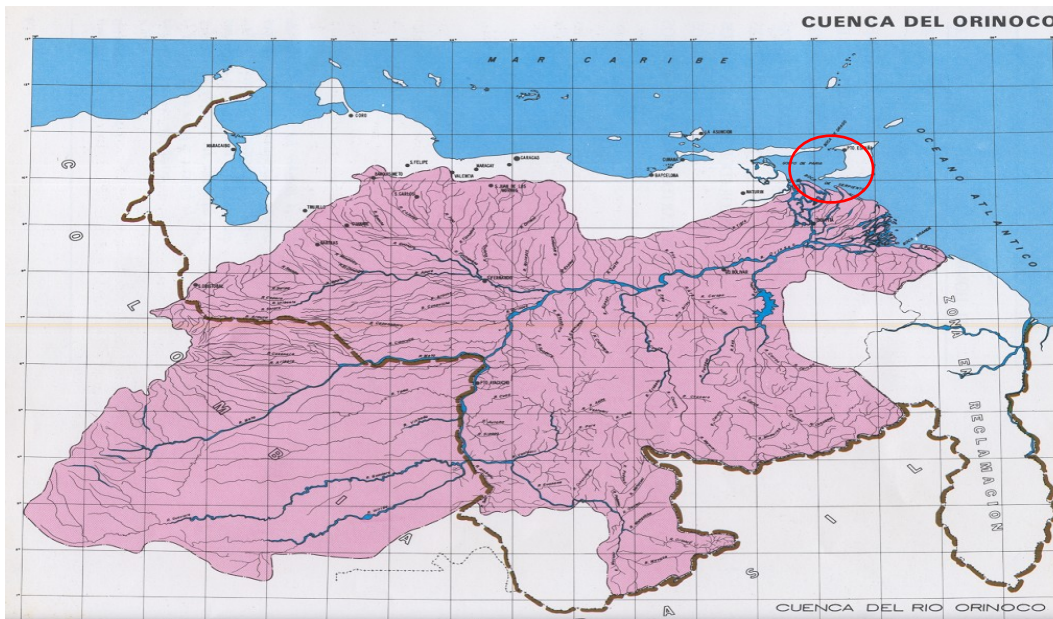


Figure 3.5 Orinoco Watershed and Orinoco River delta just south of Trinidad & Tobago (circle at delta and Trinidad)

3.2 Methods to determine economic incentives

A balanced equation of the process is the first step (equations 3 & 4), followed by molar masses (see table 3.1) and then a scaled-up stoichiometric ratio to compare masses on a ton basis (see table 3.2) because all the products are sold based on a ton price (or tonne price). Table 3.2 shows that 1 ton of ammonia will yield approximately 3 tons of sodium carbonate and 3 tons of ammonium chloride.

Balanced equations of the dual-salt (DS) process

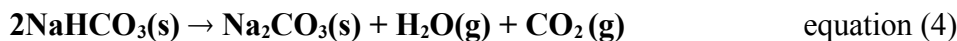
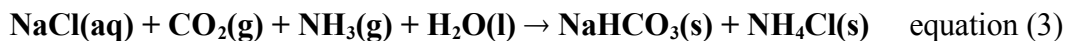


Table 3.1 Molar masses of reactants and products of the DS process

Molar masses (g/l)						
NaCl	CO ₂	NH ₃	H ₂ O	NaHCO ₃	0.5 Na ₂ CO ₃	NH ₄ Cl
58.44	44.01	17.04	18.02	84.01	52.99	53.05
where Na=22.99, Cl=35.45, C=12.01, H=1.01, O=16.00, N=14.01 IUPAC periodic table						

Table 3.2 Stoichiometric ratios (theoretical yield)

Reactants/ Products	REACTANTS				PRODUCTS	
Chemical	NaCl	CO₂	NH₃	H₂O	Na₂CO₃	NH₄Cl
Weight (tonnes)	3.43	2.58	1	1.06	3.11	3.14

Note: based on 1 tonne of ammonia

Materials will be assessed for the most current prices available to determine the profitability of the DS process. Prices for salt, ammonia, sodium bicarbonate, sodium carbonate and ammonium chloride will be determined (see table 3.3). Calculations based upon theoretical molar masses (at ton or tonne levels) will be performed to give approximate gross profit.

In addition, information obtained from SEVA (2007) and Detournay et al. (2004) will provide hard data to work out material and process costs on a qualitative basis (table 3.4).

Table 3.3 Dual-salt process raw material consumption per ton of co-product (source: SEVA 2007)

Raw material consumption	Quantity
Salt	1.3 ton
Ammonia (NH ₃)	335 kg
Power	250 kWh
Fuel oil	18 liter
Steam (including refrigeration)	5.2 ton

Table 3.4 Soda ash produced via the Solvay process (source: Detournay et al. 2004)

Soda Ash Manufacturing Costs	
Item	Cost (Euros/t Soda ash)
Raw materials	25
Energy	40
Labor	35
Maintenance	20
Total (cash costs)	120

Table 3.5 demonstrates the different areas of operation of a typical DS plant which includes the steam methane reforming (SMR) process from methane, pressure swing adsorption (PSA) to separate nitrogen from air and the Haber-Bosch ammonia synthesis process.

Table 3.5 Area & Operations of a DS plant (source: Detournay et al. 2004 & adapted by author to fit DS)

AREA	OPERATION
Brine purification	Brine preparation (addition of CaO & Na ₂ CO ₃) This will form precipitates of CaCO ₃ & Mg(OH) ₂ which are removed by flocculation or filtration
NH ₃ production	NH ₃ synthesis <ol style="list-style-type: none"> 1. Steam methane reforming (SMR) to generate H₂ from methane, CH₄ 2. PSA separation of air to obtain N₂ 3. Haber-Bosch ammonia synthesis
Absorption	Absorption of NH ₃
Columns (Carbonation Towers)	Precipitation of NaHCO ₃
Filtration	Separation of NaHCO ₃ crystals from mother liquor
Calcination	Decomposition of NaHCO ₃ to Na ₂ CO ₃ <ol style="list-style-type: none"> 1. Calcination produces CO₂ & H₂O which is sent to the carbonation towers
Densification	Production of dense soda ash
Crystallization of NH ₄ Cl	Separation of NH ₄ Cl crystals from mother liquor (steps #1-3, performed @40 °C) <ol style="list-style-type: none"> 1. Addition of NaCl(s) until saturation 2. Addition of NH₃ 3. Addition of CO₂ 4. Collect NH₄Cl precipitate cooled at 5-10°C

3.3 Methods to determine environmental (pollution abatement) incentives

There is a direct environmental or pollution abatement consequence by diverting a small percentage of concentrate to the DS process and away from surface discharge or deep well injection. To determine this incentive one would have to place a value on the flora and fauna of the coastal discharge zone and subtract the diverted concentrate. This could be

measured in tons of salt sequestered per year utilized in the DS process. Another way to say this would be the “salt footprint” reduction of the desalination plant measured in percentage of concentrate output.

Most likely the greatest pollution abatement (environmental incentive) would be the indirect effect of the DS product sodium bicarbonate used to desulfurize the flue gas at coal burning plants thus preventing the formation of sulfuric acid rain. This method of injecting sodium bicarbonate into flue gas stacks is already being utilized and lowers sulfur emissions greatly (97% or higher). This could be measured in tons of SO₂ sequestered per year.

Other indirect environmental incentives would be less subtle, such as reduced shipping costs for the ammonium chloride fertilizer and sodium bicarbonate used locally within the Latin American & Caribbean region instead of shipping from Asia or North America for example.

3.4 Methods to determine social incentives

The primary social incentives would be the amount of jobs created by the design, construction and operation the DS plant. The secondary social incentives would be the social value of the:

- 1) Conservation of the coastal flora and fauna (if surface discharge of concentrate is deployed).
- 2) Social value of the ammonium chloride fertilizer.
- 3) Social value of the sodium bicarbonate & sodium carbonate used for pollution abatement and glass making in the Latin America & Caribbean region.

4. RESULTS AND DISCUSSION

Why has the dual-salt (DS) process not been incorporated at a desalination plant before, especially since the chemistry is straightforward and the DS process is a mature industry in Japan, China and India? The DS process requires an investment in an ammonia synthesis plant. This adds cost, but also allows increased revenue from of course anhydrous ammonia, the production of urea (an automatic bonus, as it is a complimentary process deriving CO₂ from SMR) and of course ammonium chloride. The addition of an ammonia plant also limits the DS to sites where natural gas is cheap and abundant. Electrolysis is of course possible with sea water to obtain H₂, but is not cost competitive with H₂ cracking from SMR. If a breakthrough in ammonia synthesis occurs, then the DS process may not necessarily be required to be located in an area where natural gas is cheap and abundant, such as Trinidad, Colombia and Venezuela for example.

There are a few reasons for not considering incorporating a DS process plant:

- Trona mining in the state of Wyoming, US offers inexpensive naturally available soda ash, but this advantage diminishes relative to synthetic soda ash when transportation & shipping costs are considered. International tariffs may also be a factor depending on country and trade agreements. (**Note:** The discovery of Trona deposits during oil exploration in Wyoming in the late 1930s eventually replaced the Solvay synthetic soda ash industry in the US, although Solvay plants are still operational in Europe and Asia (Trona 2010)).
- Desalination plants are focusing on a short-term economic outlook.
- Financing a larger dual-purpose desalination plant /DS process plant may be perceived to be long-term financing and a faster ROI is desired.
- Engineering of desalination plants is task-specific and not holistic or integrated to take advantage of complimentary technologies.

On the other-hand, there are more reasons for incorporating a DS process plant with a desalination plant such as:

- Economic (revenue from products, carbon credits, integrating desalination with ammonia production, DS process -sodium carbonate & ammonium chloride, and urea production).
- Environmental abatement (concentrate discharge is reduced or eliminated to be reused to yield valuable products, CO₂ is sequestered and sodium carbonate & sodium

bicarbonate can be used to desulfurize flue gas).

- Social (increased jobs, social value of products especially ammonium chloride which is a fertilizer for rice and palm cultivation, important in Latin America & the Caribbean).

If it can be demonstrated that collocating a desalination plant with an ammonia facility can turn a profit by producing the many products that this combination of technologies can offer, than maybe if the return on the investment (ROI) can be managed in a short-time span, investors would be willing to consider implementing a DS plant with a desalination plant.

Point Lisas, Trinidad and Tobago offers a proving ground because of its unique position of being the world's largest ammonia exporter and having the western hemisphere's largest SWRO desalination plant in close proximity to ammonia production.

4.1 Economic incentives at Point Lisas, Trinidad and Tobago

Table 4.1 reflects the current actual prices of raw materials as of the first quarter of 2010. The largest expense is ammonia, which can fluctuate from \$120/ton to almost \$800/ton (ICIS 2009) depending on natural gas price fluctuations. Table 4.2 reflects actual costs of products obtained by the DS process and an ammonia plant.

Table 4.1 Raw material consumption per ton of co-product (source: SEVAS 2004, prices researched as current as possible and are not from SEVAS)

Raw Material	Consumption	Unit Price	Price (USD)
Salt	1.3 tons	@\$30-50/ton (average=\$40/ton)	52
Ammonia	335 kg	@\$250/metric tonne (August 2009)	83.75
Power	250 kWh	@\$0.10/kWh	25.00
Fuel Oil	18 liters (=4.76 gallons*145,000 BTUs=6.9E5 BTUs)	@\$36.20/1E6 BTUs (Wikipedia 2008)	25.00
Steam (including refrigeration)	5.2 tons (=10.4 Kips)	@\$1/Kip (US DOE 2003 Steam costs)	10.4
Total (USD)			196.15

Note: Kips=kilopounds, prices are a rough estimate-most likely, Point Lisas, Trinidad & Tobago would produce ammonia and substitute natural gas for fuel oil thus lowering costs substantially

Table 4.2 Chemical prices

Chemical	Price	Notes
NaHCO ₃ (baking soda)	\$22.50/100 lbs. \$450/ton (converted)	Industrial grade 100-lb. bgs, t.l., works, frt. equald. (from ICIS.com 2006)
NaCl (salt)	\$30-50/ton \$33-55/tonne (converted)	Puerto Rico (from CS Group 2010)
Na ₂ CO ₃ (soda ash)	\$165/ton \$182/tonne (converted)	dense, US Gulf, f.o.b. bulk (from ICIS.com 2006)
NH ₃ (ammonia)	\$250/tonne	price as of August 2009 (from TradeData International Analysis Report 2009)
NH ₄ Cl (ammonium chloride)	\$185~200/tonne	FOB TIANJIN (July 2008 price China)
(NH ₂) ₂ CO (urea) 1 tonne NH ₃ yields 1.76 tonnes of urea (theoretical)	\$360.00-820.00/short ton \$346.00-795.00/short ton	granular, US Gulf, spot f.o.b. USG (from ICIS.com 2006) Prill, US Gulf, spot f.o.b. USG (from ICIS.com 2006)

Note: NH₃ prices would be lower in Point Lisas, Trinidad & Tobago due to local production and no shipping fees.

Terms: Short ton=2000 lbs., long ton =2,240 lbs., tonne=1000 kg, 1 ton [short, US] = 0.907 metric ton.

The DS process will yield soda ash and ammonium chloride in approximate equal tonnage (see table 3.1). One tonne of NH₃ will yield approximately 3 tonnes of soda ash and 3 tonnes of ammonium chloride. The estimate of gross profit would equal revenues minus costs or:

Table 4.3 Material revenues & costs estimate *(salt costs would be less due to concentrate content of ~7+ g/l of NaCl) Data from Table 3.3

Revenues	Costs	Profit (not including energy costs & labor costs)
3 tonnes of soda ash 3 x \$182=+\$546	1 tonne NH ₃ 1 x \$250=-\$250	\$296.00
3 tonnes of NH ₄ Cl 3 x \$200=+\$600	3.43 tonnes of salt* 3.43 x \$33=-\$113	+\$487.00
Total material revenue = + \$1,146	Total material costs = -\$363	Total profit = +\$783- (energy)-(labor) per tonne of NH₃ used

From SEVAS data which includes energy, but not labor, the profit would be:

Table 4.4 SEVAS estimate

Revenues	Costs of material & energy	Profit					
<table border="1"> <tr> <td>1 tonne of soda ash 1 x \$182=+\$182</td> <td rowspan="2">\$382.00</td> <td rowspan="2">-\$196.15 from Table 4.1</td> <td rowspan="2"> Total profit = +\$185.85 per 0.335 tonne of NH₃ or +\$552.69 per tonne of NH₃ not including labor </td> </tr> <tr> <td>1 tonne of NH₄Cl 1 x \$200=+\$200</td> </tr> </table>	1 tonne of soda ash 1 x \$182=+\$182	\$382.00	-\$196.15 from Table 4.1	Total profit = +\$185.85 per 0.335 tonne of NH₃ or +\$552.69 per tonne of NH₃ not including labor	1 tonne of NH ₄ Cl 1 x \$200=+\$200		
1 tonne of soda ash 1 x \$182=+\$182	\$382.00				-\$196.15 from Table 4.1	Total profit = +\$185.85 per 0.335 tonne of NH₃ or +\$552.69 per tonne of NH₃ not including labor	
1 tonne of NH ₄ Cl 1 x \$200=+\$200							

If the SEVAS profit is \$553/tonne NH₃ (including materials & energy, but no labor) and the material profit is \$783/tonne NH₃ (no energy or labor), then labor and profit would estimate to about \$230/tonne NH₃ (\$783-\$553=\$230).

From Table 3.5, labor and maintenance is equivalent to about 46% of total costs (55/120=46% but this is based upon the Solvay process). Therefore, \$230 x 46% = \$106 leaving \$124/tonne NH₃ for profit and financing.

If the DS process owned and operated the ammonia production plant, then other revenues and costs would be considered such as anhydrous ammonia and urea production as well as additional financing for the Haber-Bosch ammonia synthesis facility, the SMR facilities and the liquefaction of nitrogen.

4.2 Environmental (pollution abatement) incentives at Point Lisas, Trinidad & Tobago

Table 4.5 shows the environmental incentives of collocating a DS and ammonia plant at desalination plant. The main advantage of the DS process is the reduction and possible elimination of concentrate discharge (ZLD) from desalination plants. Since the concentrate is usually about twice the salinity of the feedwater and the discharge is denser than feedwater, the concentrate sinks with little dispersion elevating salinity levels for benthic species, especially sessile plants and corals that must cope with osmoregulation. Mobile species such as fish and other vertebrates can swim to normal saline waters to escape the osmotic stress. It must be remembered that large desal plants can discharge upwards to tens of millions of gallons per day and this will have some type of impact on the flora and fauna. More studies are needed to quantify the effect, but in the meantime, prudence is recommended and if there is a profitable method to reduce or eliminate the concentrate, then by all means that method needs to be deployed.

Table 4.5 Environmental incentives of collocating a DS & ammonia plant at a desalination plant

DS & Ammonia plant collocated at desalination plant	Desalination benefits	ZLD/reduced concentrate discharge	NaHCO₃ Na₂CO₃ benefits	CO₂ sequestration
Environmental Incentives	Eliminate/reduce subsidence, reduce subsurface & surface freshwater withdrawals, allow aquifers to replenish	Less discharge, allows flora & fauna to osmoregulate normally or within a biological window of salinity	Desulfurization of flue gas in coal plants reducing acid rain (H ₂ SO ₄)	CO ₂ sequestration in DS process & urea process

Sodium bicarbonate (and sodium carbonate) are both candidates to reduce acid rain by reacting with sulfur in flue stacks of bituminous coal burning electric power plants. Sodium bicarbonate when heated (calcined), will release CO₂ and H₂O and desulphurize up to 90% or higher flue gas SO₂. It is one of the most effective methods to desulphurize flue gas and reduce acid rain from hydrosulfuric acid, H₂SO₄ (Detournay et al. 2004).

4.3 Social incentives at Point Lisas, Trinidad & Tobago

Table 4.6 shows the social incentives of collocating a DS & ammonia plant at a desalination plant. According to March 2002 Caribbean Update, an online news service, the Point Lisas, Trinidad & Tobago SWRO desalination plant (DESALCOTT Ltd.) employs 50 (1000 people were employed during construction) and has an annual revenue of \$6 million with a contract with WASA (Water & Sewage Authority of T&T) until 2022.

The DS plant addition will employ additional workers to process sodium bicarbonate, sodium carbonate and ammonium chloride and if the DS integrates the ammonia production facility, additional jobs may be created depending on fertilizer demands.

Locally produced fertilizer allows countries to be self-reliant and lowers costs due to shipping and handling. Rice and palm cultivation could benefit by fertilizing with lower costs thus lowering the cost of rice and palm production.

Sodium carbonate is needed in developing countries especially in glass production and detergents. When Latin America and Caribbean countries produce locally, they are more insulated from trade tariffs, currency fluctuations and in general have more control of other production reliant on soda ash for example.

Table 4.6 Social incentives of collocating a DS & ammonia plant at a desalination plant

DS & Ammonia plant collocated at desalination plant	Jobs created construction phase, operations & maintenance	Fertilizer ammonium chloride NH₄Cl	Soda Ash sodium carbonate Na₂CO₃
Social incentives	Construction would be the greatest, followed by operations, maintenance and increased shipping (longshoremen)	Locally produced fertilizer optimum for rice & palm cultivation	Latin America could increase its own production of soda ash

4.4 Criteria matrix for other locations in Latin America & the Caribbean

Table 4.7 Potential countries to deploy DS process (CH₄ data source: IEO 2009)

Countries with potential to deploy the DS process with desalination	Desalination Need	CH ₄ production	Crystallized NaCl	NH ₃ production	Rice & Palm Cultivation (NH ₄ Cl market potential)
Venezuela	√	Producer & importer from Colombia	√	√	√
Colombia	√	√	√	√	√
Brazil	Especially in the Northeast	Exporter & importer	√	√	√
Argentina	√	Exporter & importer	√	√	Rice cultivation only
Mexico	Mexico City was rationing water in 2009	√	√	√	√

4.5 Future prospects for DS process

4.5.1 Overview

If the DS process is employed at desalination plants in Latin America & the Caribbean and is profitable and successful with conventional RO equipment, then a breakthrough in economical ammonia synthesis would result in the DS process being deployed at desalination plants with access to economical crystallized salt. Also, the forward osmosis utilizing ammonia and CO₂ (FO NH₃/CO₂) desalination process is in its infancy and if it becomes the *de facto* standard in a short time, then the DS process will integrate beautifully because both the FO and DS utilize ammonia and CO₂, allowing for similar technology, training for personnel and equipment in plant design. In addition, the FO process recovers more freshwater from sea water than conventional RO desalination resulting in a concentrate with a higher salt content which benefits the DS process.

Steam methane reforming (SMR) produces 2.51 times the volume of CO₂ as a by-

product than the target H_2 (HFS 2010), and this CO_2 is necessary for the Bosch-Meiser urea production and the DS production, so a desalination plant integrated with an ammonia production facility will be able to generate revenue from desalinated water, ammonia, urea, sodium bicarbonate, sodium carbonate, and ammonium chloride in addition to possible carbon credits. Wind and solar thermal may allow some form of green energy credits and would reduce operating expenses.

4.5.2 Solar thermal steam

Since steam is required for the DS process for heating and cooling (steam jet-ejector), it may be possible to create steam via solar thermal to lower energy costs and make the plant more ecological and economical. Latin America and the Caribbean have many possibilities with high insolation year-round that could achieve a quick return on investment (ROI) of a solar thermal installation to generate steam for the DS process.

4.5.3 Wind energy for pumping/electricity

Many sea water desalination plants are located very close to the coast which lends itself to inshore and offshore breezes allowing for the possibility of wind energy to pump sea water to the plant, pump desalinated water to water tanks for storage, and assist in pumping required for the DS process such as pumping the ammoniated brine to the top of the carbonation towers. In addition, wind energy may also provide electricity to help power the desalination/DS plant.

In conclusion, sea water, air, sunlight, wind and waves offer the creative chemist many possibilities to produce freshwater, fertilizers, fuels and useful other chemicals such as chlorine and sodium hydroxide. The DS plant collocated with a desalination plant may be the start to further integrate desalination plants with other processes and future single-purpose large sea water desalination plants may become obsolete. Desalination of sea water may be a by-product of a large chemical processing plant subsidized by products obtained from sea water that are more profitable.

4.5.4 Ammonia borane synthesis

Ammonium chloride has immediate use as the tried and true "rice fertilizer" commonly used in Asia especially in Japan, India and China. Another use of ammonium chloride is the starting material (feedstock) for ammonia borane used as a lightweight and safe solid

storage form of hydrogen. Ammonia borane or AB is already being used in lightweight fuel cells for portable power. Jadoo power system has units that produce 20 Watts for 72 hours, or (1440 W-h).

If the market for AB increases, then desalination plants employing the dual-salt process will be in a good position for three reasons:

1. NH_4Cl is required as a starting material and is a product in the dual-salt process.
2. NaCl is precipitated in the AB synthesis and can be recycled back to the dual-salt process eliminating the need to purchase NaCl for the dual-salt process.
3. Boron is an element found in sea water at (~ 4.5 mg/L) as either boric acid or as borate ions that can be removed (and is sometimes done so to maintain WHO recommended levels of less than 0.5 mg/L). Two-passes of an RO membrane are usually required to remove boron to adequate levels as well as maintaining $\text{pH}=8$. Boron may be recovered using ion selective membranes, but this will require NaOH & HCl (Na_2CO_3 is sometimes substituted for NaOH also known as caustic soda and if so, then this would benefit the dual-salt process).

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

There are certainly economic, environmental abatement and social incentives to employ the DS process at desalination plants in Latin America and the Caribbean. The economic incentive will have to be shown to be very strong before financial investment is taken even with overwhelming environmental abatement and social incentives being clearly realized. Desalination plants present an opportunity to employ the DS process because the desalination process shares mutual functions such as water intake pre-treatment and concentrate discharge with 7% NaCl that is currently considered a waste product with environmentally damaging consequences yet is desired for the DS process. The Point Lisas, Trinidad SWRO desalination plant in conjunction with the ammonia production facility located nearby, offer a near ideal proving ground to trial the DS process.

The economic incentives offer the potential to help offset operational costs of the desalination plant by increasing revenue. Rough estimation based on international soda ash manufactures shows the DS process to be profitable after materials, energy, labor and maintenance are factored in. True net profit will be determined by estimating the capital costs of the construction of a DS facility and the financing required.

The environmental incentives offer a solution to the desalination industry that has seen opposition to new desalination plants because of concentrate discharge as took place in Australia, where sensitive coral reefs and national parks would have been affected. If the concentrate is not discharged (as in the case of zero liquid discharge, ZLD) or significantly reduced, the environmental impact would lessen and if that same concentrate can be converted into profitable chemicals that economically reduce acid rain from coal flue stacks, then the solution is a win-win solution that could be described as elegant. Even if desalination plants are currently injecting their concentrate into deep wells, they could still produce added-value revenue.

Research indicates that only a small percentage of concentrate discharge will be utilized in the DS process (less than 10%) which is not as great as anticipated. Furthermore, the product sodium carbonate synthesized is in competition with the natural sodium carbonate (mined trona from Wyoming, US). The market is limited to just Latin America and the Caribbean due to this competition. Subsidies may have to be enacted to

offset the price differential. Tariffs, currency fluctuations and other trade barriers may make locally produced sodium carbonate more attractive to Latin America and Caribbean coal burning energy plants to reduce sulfur levels. Glass production will always require sodium carbonate and will be a larger consumer most likely than for environmental reasons.

Socially, the DS process offers additional jobs; temporary construction workers and permanent operations and management jobs. Other jobs would be indirect and affect shipping and handling of the soda ash and ammonium chloride. These jobs would include longshoremen, merchant marine personnel to ship new routes, and jobs created by economical soda ash availability. For example, new glass manufacturing could employ hundreds based upon the newly available soda ash. If ammonium chloride can be successfully used as a rice and palm fertilizer in Latin America and the Caribbean as it is in Asia such as in Japan, China and India, then rice production may be more economical and rice prices could lower as a result.

Latin America currently produces next to 2% of world soda ash; and regionally producing soda ash, Latin American countries have more control and independence from tariffs, trade agreements, and currency fluctuations. Ammonium chloride may offer rice growers a cheaper alternative to current rice fertilizers and allow countries to be more self-reliant and independent.

Additionally, desalination will certainly be part of the water portfolio for future planners of Latin America to protect against droughts, global warming, subsidence, over withdrawals of surface and subsurface waters and to reduce salt-water intrusion into freshwater aquifers along coastal regions. Therefore, the concentrate that is currently being discharged that increases salinity levels in coastal discharge areas needs to be addressed.

5.2 Recommendations

At the moment, the only potential candidates in Latin America & the Caribbean for DS deployment at desalination plants are Trinidad and Tobago, Venezuela and Colombia with the possibility of Mexico, Brazil and Argentina depending on their natural gas production facilities in the future.

Therefore, the Point Lisas, Trinidad and Tobago SWRO operated by DesalcoTT and the ammonia facility (operated by the Caribbean Nitrogen Company, CNC) located in the Point Lisas industrial park offer the best possibility to explore the DS process as a mutual and

synergistic collaboration. A more detailed assessment of the capital costs of constructing a DS facility in Trinidad and Tobago will be needed performed by a chemical engineering firm familiar with the DS process and construction.

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7. ANNEX

7.1 Sea water composition

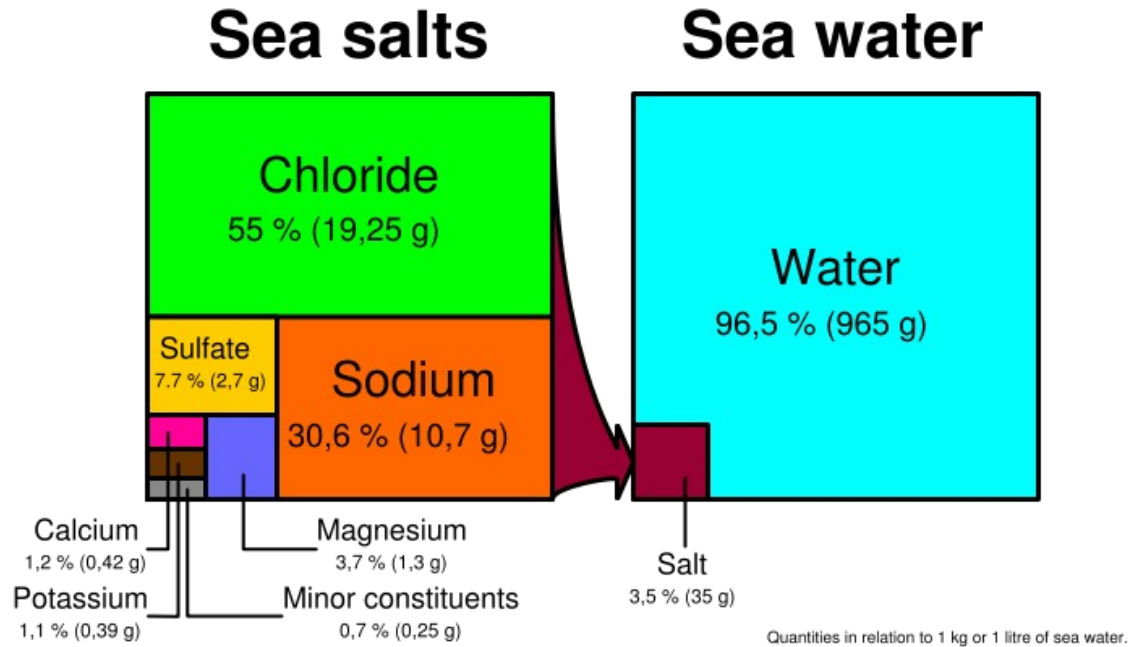


Figure 7.1 Sea water composition (source: Hannes Grobe, Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany; SVG version by Stefan Majewsky)

7.2 Periodic Table

The periodic table was utilized to determine the molar masses of the reactants and products utilized and produced in the DS process.

Table 7.1 IUPAC Periodic Table (source: CA DOE 2008)

Periodic Table of the Elements Chemistry Reference Sheet California Standards Test

1 1A		2 2A												13 3A	14 4A	15 5A	16 6A	17 7A	18 8A	
1	H Hydrogen 1.01																			He Helium 4.00
2	Li Lithium 6.94	Be Beryllium 9.01											B Boron 10.81	C Carbon 12.01	N Nitrogen 14.01	O Oxygen 16.00	F Fluorine 19.00	Ne Neon 20.18		
3	Na Sodium 22.99	Mg Magnesium 24.31											Al Aluminum 26.98	Si Silicon 28.09	P Phosphorus 30.97	S Sulfur 32.07	Cl Chlorine 35.45	Ar Argon 39.95		
4	K Potassium 39.10	Ca Calcium 40.08	Sc Scandium 44.96	Ti Titanium 47.87	V Vanadium 50.94	Cr Chromium 52.00	Mn Manganese 54.94	Fe Iron 55.85	Co Cobalt 58.93	Ni Nickel 58.69	Cu Copper 63.55	Zn Zinc 65.39	Ga Gallium 69.72	Ge Germanium 72.61	As Arsenic 74.92	Se Selenium 78.96	Br Bromine 79.90	Kr Krypton 83.80		
5	Rb Rubidium 85.47	Sr Strontium 87.62	Y Yttrium 88.91	Zr Zirconium 91.22	Nb Niobium 92.91	Mo Molybdenum 95.94	Tc Technetium (98)	Ru Ruthenium 101.07	Rh Rhodium 102.91	Pd Palladium 106.42	Ag Silver 107.87	Cd Cadmium 112.41	In Indium 114.82	Sn Tin 118.71	Sb Antimony 121.76	Te Tellurium 127.60	I Iodine 126.90	Xe Xenon 131.29		
6	Cs Cesium 132.91	Ba Barium 137.33	La Lanthanum 138.91	Hf Hafnium 178.49	Ta Tantalum 180.95	W Tungsten 183.84	Re Rhenium 186.21	Os Osmium 190.23	Ir Iridium 192.22	Pt Platinum 195.08	Au Gold 196.97	Hg Mercury 200.59	Tl Thallium 204.38	Pb Lead 207.2	Bi Bismuth 208.98	Po Polonium (209)	At Astatine (210)	Rn Radon (222)		
7	Fr Francium (223)	Ra Radium (226)	Ac Actinium (227)	Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (266)	Bh Bohrium (264)	Hs Hassium (269)	Mt Meitnerium (268)											
			Ce Cerium 140.12	Pr Praseodymium 140.91	Nd Neodymium 144.24	Pm Promethium (145)	Sm Samarium 150.36	Eu Europium 151.96	Gd Gadolinium 157.25	Tb Terbium 158.93	Dy Dysprosium 162.50	Ho Holmium 164.93	Er Erbium 167.26	Tm Thulium 168.93	Yb Ytterbium 173.04	Lu Lutetium 174.97				
			Th Thorium 232.04	Pa Protactinium 231.04	U Uranium 238.03	Np Neptunium (237)	Pu Plutonium (244)	Am Americium (243)	Cm Curium (247)	Bk Berkelium (247)	Cf Californium (251)	Es Einsteinium (252)	Fm Fermium (257)	Md Mendelevium (258)	No Nobelium (259)	Lr Lawrencium (262)				

Key

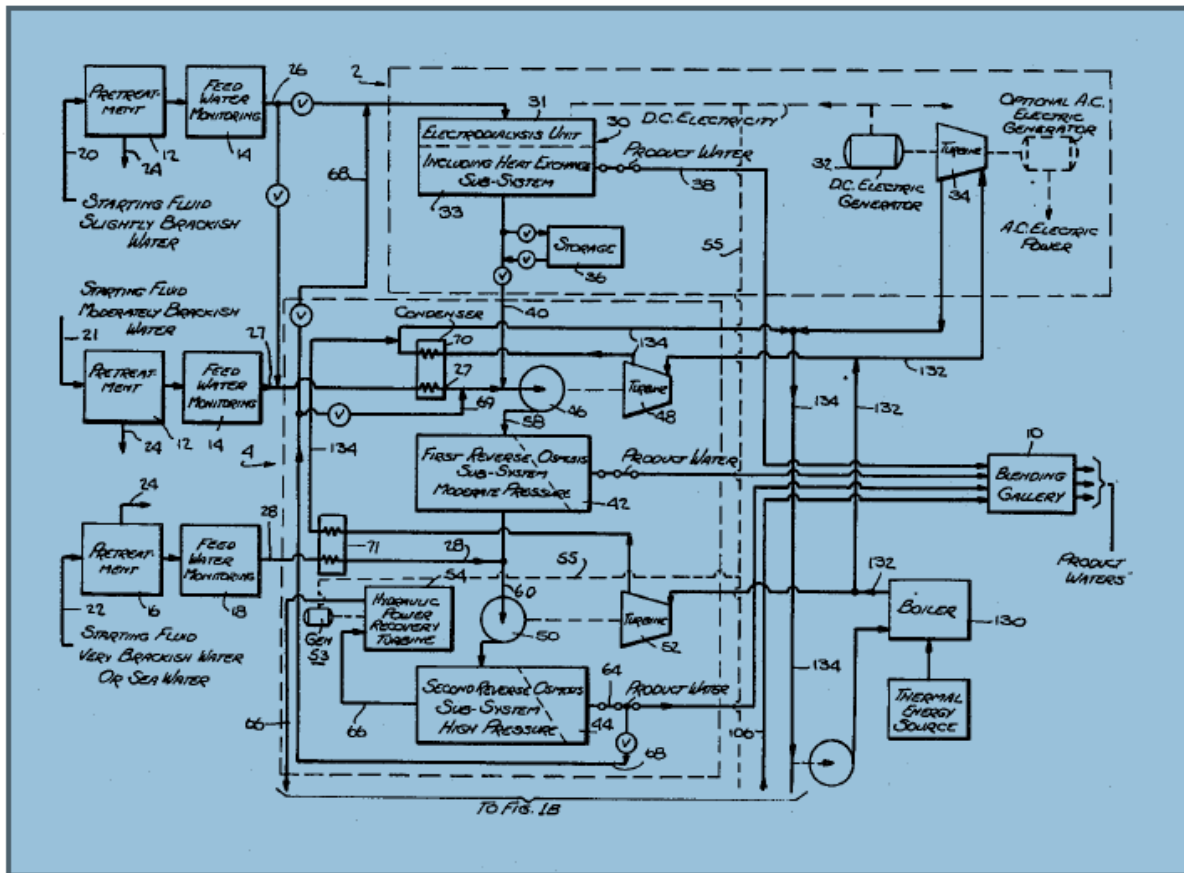
- 11 — Atomic number
- Na** — Element symbol
- Sodium — Element name
- 22.99 — Average atomic mass*

* If this number is in parentheses, then it refers to the atomic mass of the most stable isotope.

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7.3 US Patent #4,141,825 Desalination process system & by-product recovery

This comprehensive desalination process combines electro-dialysis, reverse osmosis and brine concentration with by-product recovery. This desalination plant includes an ammonia synthesis plant where the hydrogen is obtained from brine electrolysis (instead of steam methane reforming, SMR). In addition to H₂, the brine electrolysis also produces Cl & NaOH. A Solvay plant is included for by-product recovery of NaHCO₃, Na₂CO₃ & CaCl₂. The following 2 schematics (figures 7.2 & 7.3) demonstrate the integrated approach to desalination, but the second schematic is the most relevant, for it demonstrates the concentrate recovery with brine electrolysis and the Solvay process which requires an



ammonia producing plant.

Figure 7.2 US Patent & Trademark Office #4,141,825 Desalination process system & by-product recovery

Notice the brine concentrator (see figure 7.3) is incorporated to allow on-site production of crystallized salt even though this is very energy-intensive. The brine electrolysis allows for direct H_2 production instead of from the steam methane reforming process at methane plants. Chlorine is also a by-product which can be used for post-treatment chlorination of the product water.

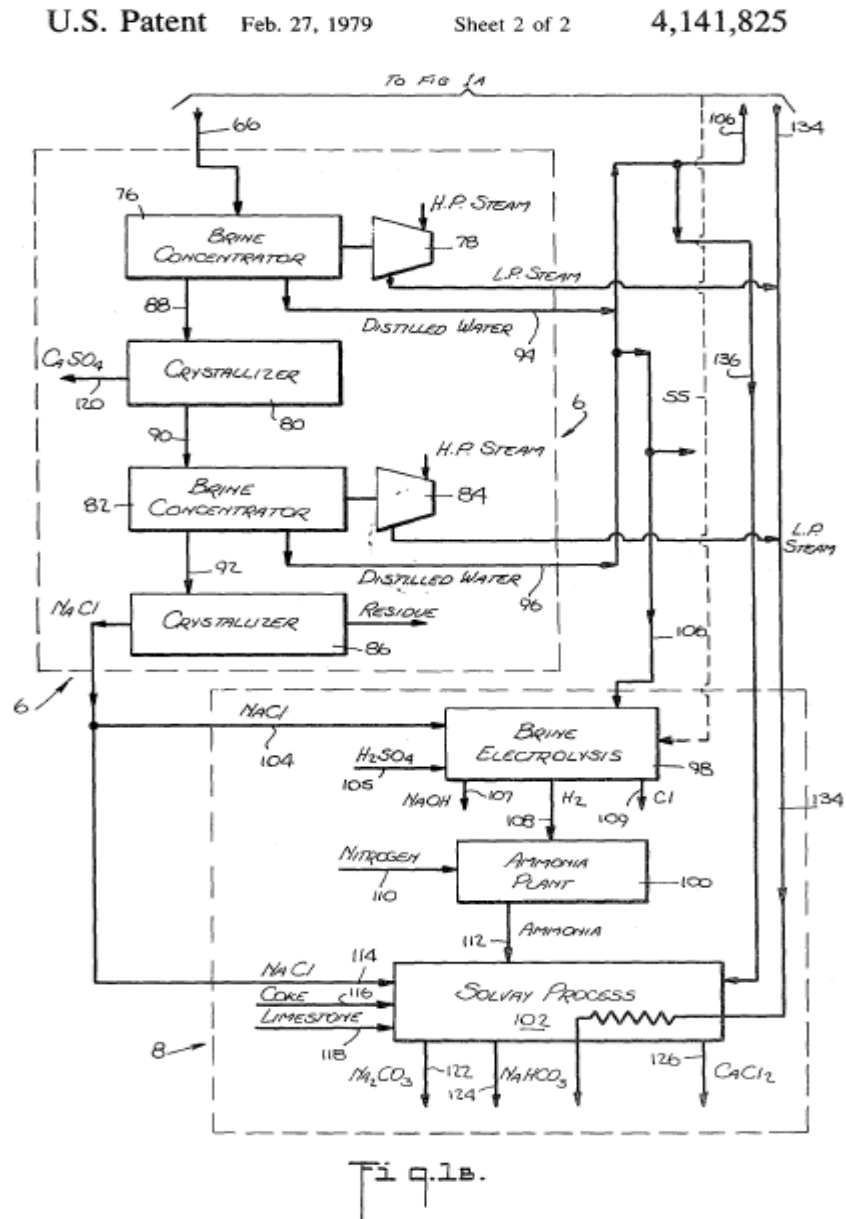


Figure 7.3 US Patent & Trademark Office #4,141,825 diagram