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The manufacture of soda ash in the Arabian Gulf

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Abstract

This paper is concerned with the technical and economic aspects of the soda ash production in the Arabian Gulf. Five different manufacturing methods are outlined. The two main manufacturing methods (the Solvay and Dual processes) are examined in detail. The technical aspects regarding the raw material quantitative and qualitative requirements, the battery limits plant production units and utility requirements are specified in each case. A preliminary economic evaluation of each of these two processing routs concludes that soda ash production by either route is competitive with imported soda ash assuming full marketability of soda ash and its by-products in the Arabian Gulf and neighbouring regions. The Solvay and Dual processes are estimated to produce soda ash at a cost of 132 and 144 $/ton respectively. These production costs compare favourably against delivered costs of imported soda ash of 177 $/ton.

1. Introduction

Soda ash is the commercial name of the technical grade sodium carbonate (Na_2CO_3) which is a white crystalline hygroscopic powder. It is the third largest chemical manufactured in modern times next only to sulfuric acid and ammonia [1]. It is produced as light or dense soda ash and contains 99.3% Na_2CO_3 and is graded according to its bulk density and its content of sodium oxide. Dense soda ash is obtained from light soda ash by hydrating it to produce sodium carbonate monohydrate which is calcined to produce sodium carbonate (dense soda ash):

$$Na_2CO_3(\text{light}) + H_2O \rightarrow Na_2CO_3 \cdot H_2O$$

$$Na_2CO_3 \cdot H_2O \xrightarrow{\text{Calc.}} Na_2CO_3(\text{dense}) + H_2O$$

About 50% of soda ash (dense grade) produced in the USA in 1981 was used as a raw material in the glass industries and 18% in the manufacturing of chemicals. Industrial applications of soda ash include paper and paper board, sodium silicate, sodium bicarbonate, caustic soda, sodium nitrite/nitrate, synthetic detergents, sodium sulphite, sodium thiosulphate, and sodium hydrosulphite. Large quantities of soda ash are also used by laundries [1]. Manufacturing of sodium bicarbonate and caustic soda are carried out according to the following two reactions:

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3$$

$$Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3$$

2. Manufacturing methods

There are five basic methods for producing soda ash on a world basis:

(i) By the standard solvay process (also known as the ammonia soda process) which uses salt (NaCl) and limestone as basic raw materials and produces $CaCl_2$ as a byproduct.

(ii) By the dual process (or the modified solvay process) which uses mainly salt, CO_2 and ammonia as raw materials and produces in addition to soda ash the valuable fertilizer compound ammonium chloride.

(iii) By carbonating sodium hydroxide to produce sodium carbonate monohydrate which is calcined to produce sodium carbonate (dense soda ash):

$$2NaOH + CO_2 \rightarrow Na_2CO_3 \cdot H_2O$$

The economics of this process depend on the availability of surplus quantities of NaOH produced as a byproduct of chlorine manufacture from brine.

It is interesting to note that the soda ash market is dependent on the demand for chlorine because during the production of chlorine, caustic soda is also produced which competes in most applications with soda ash. Therefore, if the chlorine market grows at a high rate, the resulting byproduct caustic soda, may take over much of the soda ash market and depress prices. Thus the market and feasibility studies for soda ash should take into account the present and projected caustic/chlorine markets.

(iv) From natural Trona deposits. Such deposits consist largely of $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ compounds. It is worth noting that in the USA natural soda still continues to be the major source of soda ash in the USA and in the recent past a few solvay plants have been shut down because of the heavy competitive edge from natural soda [2,3].

(v) Recovery from naturally occurring alkaline brines.

Of these five methods the most relevant processes for the Saudi case are the standard and dual processes and these will be described in some detail and then compared on a technical and economic basis.

2.1. Solvay process description

In 1861 Ernest Solvay developed the ammonia-soda process and hence the name "Solvay" process. It uses salt, limestone and coke or natural gas as raw materials and ammonia as a cyclic reagent. It is based on the fact that ammonia reacts with carbon dioxide and water to form ammonium bicarbonate, according to the following reactions:

$$NH_3+CO_2+H_2O \rightarrow NH_4HCO_3$$

$$NaCl+NH_4HCO_3 \rightarrow NaHCO_3+NH_4Cl$$

$$2NaHCO_3 \rightarrow Na_2CO_3+CO_2+H_2$$

In these reactions, the preformed ammonium bicarbonate reacts with salt to form sodium bicarbonate. This sodium bicarbonate is then calcined to low density soda ash. Chloride is also formed as a byproduct. It is neutralized with lime to form calcium chloride, as follows:

$$2NH_4Cl+Ca(OH)_2 \rightarrow CaCl_2+2NH_3+2H_2O$$

Almost all the ammonia formed by this reaction is recovered and recycled.

So the raw materials for Solvay process are salt, limestone, and carbon. Ammonia may be considered as a catalyst.

The process normally follows the following steps.

Process description [4]. The ammonia-soda process can be summarized according to the following equation:

$$2NaCl+CaCO_3 \rightarrow Na_2CO_3+CaCl_2$$

However, this chemical reaction is not directly applicable. The Solvay process utilizes an intermediary stage $(NH_4)HCO_3$ in obtaining Na_2CO_3 from NaCl and $CaCO_3$. The required ammonia (NH_3) is recycled.

This process is summarized in the following way:

(a) Brine purification, in order to obtain a pure sodium chloride solution:

$$Ca^{++}+CO_3 \rightarrow CaCO_3$$

$$Mg^{++}+2OH \rightarrow Mg(OH)_2$$

(b) Ammonia absorption:

$$2NH_4OH+CO_2 \rightarrow (NH_4)_2CO_3+H_2O$$

(c) Carbonation of this ammonia brine after CO_2 compression from reactions (e) and (f):

$$NH_3+H_2O+CO_2 \rightarrow NH_4HCO_3$$

and

$$NH_4HCO_3+NaCl \rightarrow NH_4Cl+NaHCO_3$$

(d) Filtration of sodium bicarbonate, obtained under (c).

(e) Decomposition of this bicarbonate into carbonate, and recovery of CO_2:

$$2NaHCO_3 \rightarrow Na_2CO_3+H_2O+CO_2$$

(f) Burning of limestone in lime kilns, and CO_2 recovery:

$CaCO_3 \rightarrow CaO + CO_2$

(g) Lime slaking:

$CaO + H_2O \rightarrow Ca(OH)_2$

(h) Ammonia regeneration (distillation):

$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + H_2O$

To summarize, the main raw materials are:

- brine, which is an aqueous concentrated solution of sodium chloride (NaCl).
- limestone, which is a calcium carbonate, impure $CaCO_3$.
- ammonia NH_3, to compensate the losses during the process.

Then add:

- sodium sulfide Na_2S, which is a corrosion inhibitor used in carbonation.
- fuel oil giving the necessary heat for limestone decomposition.

There is also an important by-product of this process: "the distillation sludges", which contains calcium chloride $CaCl_2$ and also excess lime and calcium carbonate. These sludges can be settled and the purified liquid used for milk of lime to supplement step (g) above.

Sludges from brine purification and various effluents are added to these thickened sludges which are usually stored in a pond.

In the salt preparation and purification step, impurities such as calcium sulfate, magnesium, and iron salts are removed. At this step, special pretreatments of brine with lime and soda are required as well as precipitation with ammonia and ordinary settling. The purified brine then goes to the second step, the ammoniation step. Brine absorbes the necessary ammonia and is then settled and cooled to 25 °C and pumped to the carbonation towers. The carbonation towers act as the heart of the Solvay process. Sodium bicarbonate is formed by absorption of carbon dioxide in those towers. The crude sodium bicarbonate is washed and filtered on a rotary open-drum filter, then it is drawn to the drying or calcination step. A steam-heated calciner is widely used. The produced soda ash from the calciner is then cooled and screened.

TABLE 1

	Light soda	Heavy soda
Na_2CO_3	99.1% min.	99.1% min.
NaCl	0.5% max.	0.5% min.
Na_2SO_4	0.04%	0.04%
Fe_2O_3	0.004%	0.004%
H_2O/insoluble	0.02%	0.02%
Bulk density	0.52 t/m^3	1.0 t/m^3
Screen analysis (Tyler)		+N° 16 negligible −N° 100 10% max.

The economic advantages of the Solvay process depend on the efficiency of ammonia recovery. A good economic process requires the addition of a low amount of ammonia. It utilizes the ammonia fed initially in a cyclic path with few losses. The ammonia recovery process usually takes place in distillation columns.

The clarified liquor is further concentrated until the molten mass solidifies on cooling giving what is known as 75% calcium chloride, corresponding to the formula $CaCl_2 \cdot 2H_2O$. Anhydrous calcium chloride can be made by heating this 75% $CaCl_2$ when some $CaCl_2$ is decomposed giving Ca and HCl. The scape of this HCl gas leaves a porous mass of fused $CaCl_2$ which is known as 95% $CaCl_2$. $CaCl_2$ solution is used as brine in the manufacture of ice and as an antifreeze solution, and 75% solid is used as a dust layer to minimize dust on public highways.

Product specifications. The product specifications achieved by the Solvay and Dual processes are essentially the same, see Table 1. This is known as 58% ash containing about 58% Na_2O. Excess of insoluble matter will cause cloudiness in soda solution. Excessive iron content will discolour the ash rendering it reddish.

Typical salt analysis. See Table 2.

See Fig. 1 for a complete flow diagram of the Solvay process [5].

2.2. Dual process

This is a modified Solvay process. It came in commercial use in 1980. Two important products, soda ash and ammonium chloride are produced. This process provides a substantial save in the amount of salt used. It also does not re-

TABLE 2

Temperature 25°C

	Brine (optimum)	Salt (maximum)
NaCl	310 kg/m^3	99% (dry basis)
Ca^{++}	1.6%	0.5%
Mg^{++}	0.31%	0.1%
SO_4^{--}	3.70%	1.2%
K^-	1.85%	0.6%
Nonsoluble/water	0.3%	0.1%
Humidity		3.0%
Liquid ammonia (standard quality)		
NH_3		99.5% wt. min.
Oil		10.0 ppm
Water		0.5% wt. max.
Fe		5.0 ppm
Sodium sulphide (standard quality)		
Na_2S		32.5% crystal $Na_2S\cdot 9H_2O$
$Na_2S_2O_3$		0.3%
Na_2CO_3		0.6%
Nonsoluble/water		0.06%
Fe		0.01%
Other products, chemicals, operating supplies		
H_2SO_4		98.5% wt. min.
HCl		32.0% wt. min.
NaOH		50.0% wt.
Chemicals for water treatment		
Chemicals for feed water and boiler water		
Reagents and chemicals for laboratory		
Consumable products		
Bags for soda ash bagging		

quire limestone, an important raw material used in the classical Solvay process.

The principal operation change offered by the dual process is mainly the treatment of the ammonium chloride formed according to the following reaction:

$$NaCl+NH_4+CO_2+H_2O\rightarrow NaHCO_3+NH_4Cl$$

In the Solvay process ammonia is recovered (and recycled) as suggested by the following reaction:

$$2NH_4Cl+Ca(OH)_2\rightarrow CaCl_2+2H_2O+2NH_3$$

In the dual process, ammonium chloride is retained and crystallized out and separated by the addition of sodium chloride.

In both processes, the sodium bicarbonate is calcined, soda ash is then formed as follows:

$$2NaHCO_3\rightarrow Na_2CO_3+CO_2+H_2O$$

The dual process can be summarized by the following steps:

(1) Salt washing with purified brine and removal of calcium and magnesium ions, as follows

$$C^{++}+Na_2CO_3\rightarrow CaCO_3+2Na^+$$

$$Mg^{++}+2NaOH\rightarrow Mg(OH)_2+2Na^+$$

(2) Ammonia absorption

$$NH_3+H_2O\rightarrow NH_4OH$$

$$2NH_4OH+CO_2\rightarrow (NH_4)_2CO_3+H_2O$$

(3) Carbonation of the ammonia brine and production of sodium bicarbonate and ammonium chloride

$$(NH_4)_2CO_3+CO_2+H_2O$$

$$\rightarrow 2NH_4HCO_3(NH_4)HCO_3+NaCl$$

$$\rightarrow NaHCO_3+NH_4Cl$$

(4) Filtration of sodium bicarbonate

(5) Crystallization and separation of ammonium chloride.

(6) Decomposition of bicarbonate into soda ash and recovery of carbon dioxide

$$2NaHCO_3\rightarrow Na_2CO_3+H_2O+CO_2$$

See Fig. 2 for full drawing of the process [4].

2.3. *Raw materials*

The main raw materials are

- Rock salt, sodium chloride
- Ammonia
- CO_2
- Sea water

An examination of the dual process reveals the following features of the process in comparison with the standard Solvay process [1,2]:

(1) High quality fertilizer (NH_4Cl) is produced as a coproduct with low salt content while the standard Solvay process produces as byproduct the relatively less valuable byproduct $CaCl_2$.

(2) The soda ash produced has a higher density compared with the product from the Solvay

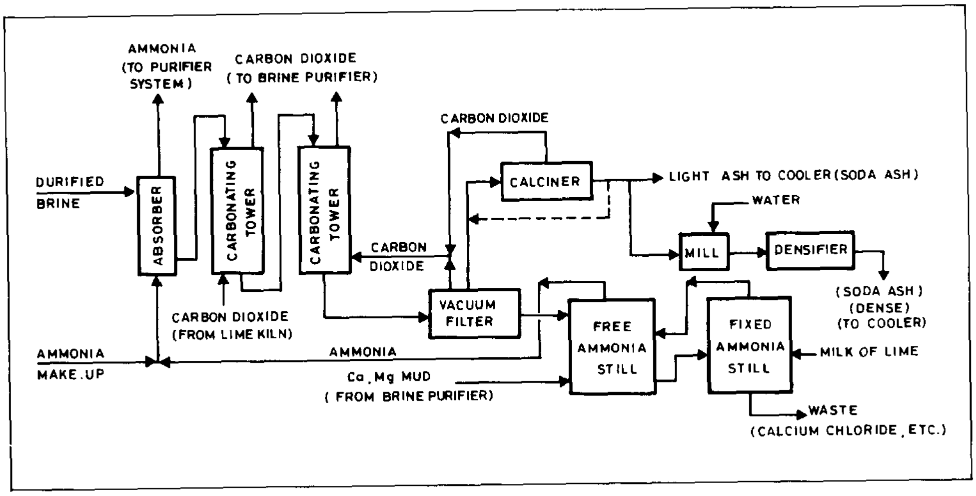

Fig. 1. The Solvay process.

process, thus requiring less bagging cost.

(3) The process does not require purified salt or a separate brine purification plant as it purifies the brine "in process".

(4) Total elimination of cooling surfaces in contact with process liquor in the process crystallization. Thus avoiding shut down of the plants for cleaning of heat transfer surfaces.

(5) Use of steam ejectors for cooling. Steam ejectors are cheap, can utilize low pressure steam, have no moving parts and are easy to operate.

(6) Reaction with CO_2 takes place in low cost carbonator units instead of the expensive Solvay carbonating towers.

(7) Use of higher purity CO_2 results in smaller compressors and lower power consumption.

In fact the dual process for the manufacture of soda ash and ammonium chloride basically differs from the Solvay process in the treatment of the mother liquor after the precipitation of sodium bicarbonate. In the standard Solvay process mother liquor is treated with milk of lime and heated to recover ammonia whereas in the dual process the mother liquor is treated, under controlled conditions after addition of ammonia and salt to precipitate ammonium chloride. Thus in the standard Solvay process, there is regeneration of ammonia by destruction of ammonium chloride, in the dual process there is production of ammonium chloride [2]. It is worth noting that ammonium chloride is a commercial product in its own right and hence the name "dual process".

3. Project economic evaluation

In this section we will make a preliminary economic evaluation in order to compare the relative profitability of the two competing technological alternatives; the Solvay and dual processes. The third alternative, namely the carbonation of caustic soda, remains a viable alternative but unfortunately not enough economic data were available to us to facilitate the financial evaluation of the process. It is worth noting, however, that a recent preliminary study made by a local investment corporation estimates the product cost of soda ash by the NaOH carboration route in Jubail to be 171 $/ton (Assuming a unit price of 50% NaOH to be 170 $/ton.)

Project definition. The foreseen project will have the following basis:

- Production capacity: 200000 MT/year
- Product specification:
  120000 MT/year light soda ash
  80000 MT/year heavy soda ash
- Location: Al Jubail (Saudi Arabia)
- Time: First half of 1990

Utilities costs.

Cooling water (seawater)	1.90 ¢/m^3
Steam	4.60 $/MT

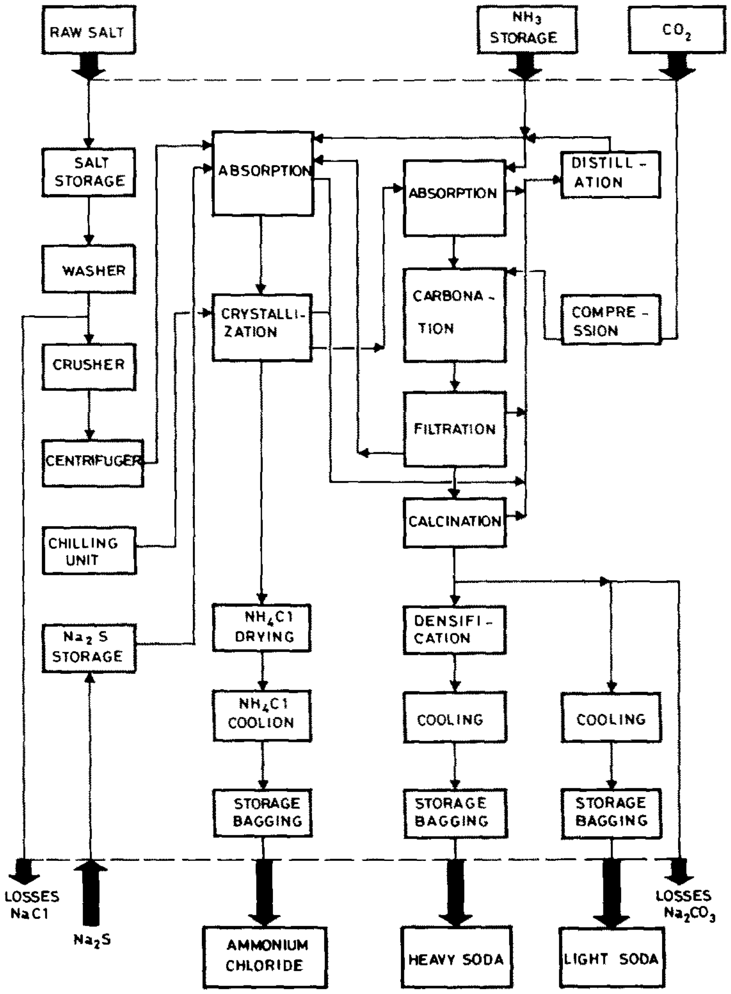

Fig. 2. The dual process.

TABLE 3

Breakdown of total capital investment of soda ash plant (Solvay process), Design capacity = 200,000 MT/year

Direct costs	$000	Indirect cost	$000
Purchased equipment (delivered)	55,100	Spare parts	3,640
Purchased equipment installation	14,892	Engineering & supervision	18,367
Instrumentation & controls	3,806	Training & technical assistance	1,820
Piping	8,273	Contractors fees (2% of direct costs)	2,073
Electrical equipment	1,655	Contingency (8% of direct & indirect cost)	11,378
Buildings (including services)	19,939		
Fixed capital investment 140,943			
Working capital 24,872			
Total capital investment 165,815			

TABLE 4

Raw material and utility requirements per ton of soda ash (Solvay process)

Raw materials and chemicals		Utilities	
Limestone (15 $/ton)	1.35 ton/T	Fuel oil (for boilers and kiln)	442.0 Kg/T
Salt (20 $/ton)	1.65 ton/T	Sea water	218.0 m^3/T
Ammonia (110 $/ton)	5.0 Kg/T	Process water	13.0 m^3/T
Na_2S	3.0 Kg/T		
Sodium carbonate	30.0 Kg/T		
Lime	7.5 Kg/T		

TABLE 5

Manufacturing cost estimate

Direct production costs	$/ton
Raw materials	38.8
Operating labour	18.0
Utilities	47.0
Maintenance and repairs	6.33
Operating supplies	0.63
Laboratory charges	1.9
Fixed charges	
Depreciation	46.98
Taxes and insurance	13.87
Plant overhead costs	20.0
General expenses	
Administrative costs	3.0
Byproduct credits* ($CaCl_2$)	(65.0)
Total product cost	131.51

*Estimated $CaCl_2$ price (plant gate) is 65 $/ton.

Process water	80.0 ¢/m^3
Electricity (from local grid)	1.5 ¢/kwh
Inert gas	1.1 ¢/Nm^3
Natural gas	47.0 ¢/Gigajoule
Fuel oil	80.0 $/Ton

Scope of cost estimates. The plant location is the industrial area in Al Jubail. For this reason the cost estimates exclude the costs of dock facilities, sea water (for cooling purposes) and process water sources, CO_2 and NH_3 plants. Start up, commissioning and infrastructure facilities costs are also excluded.

Production cost basis.

Operating labour [1] ($/hr actually worked including costs of fringe benefits and 10% shift overlap).	$ 36.4
Operating supplies (% of operating labour)	10%
Control laboratory (% of operating labour)	20%
Plant overhead (% of operating labour plus maintenance labour plus control laboratory labour)	100%
Taxes and insurance (%/year of total fixed investment).	2%

Alternative A: The Solvay process.

(i) The total capital investment. On the basis of a 1982 [1] cost estimate the purchased equipment cost for the main plant and quarry section was $ 38,786,000.

Using the appropriate cost indices, the 1990 cost of the purchased equipment (delivered plant site) = $ 38,786,000 × 895/630 = $ 55,100,000.

On this basis, Table 3 gives a preliminary estimate (scope estimate) of the total capital investment which has a probable accuracy estimate within ±20%.

(ii) The total product cost. The raw material and utility requirements per ton of soda ash (Solvay process) are as estimated in Table 4 [4].

Manufacturing cost estimate. Table 5 shows the manufacturing cost estimate (direct production cost + fixed charges + plant overhead costs) of the soda ash plant (Solvay process).

Alternative B: The dual process (also known as the modified Solvay process).

TABLE 6

Breakdown of total capital investment of soda ash plant (dual process), 200,000 MT/year

Direct costs	$000	Indirect costs	$000
Purchased equipment	54,594	Spare parts	3,836
Purchased equipment installation	21,715	Engineering & supervision	19,929
Instrumentation & controls	4,871	Training and technical assistance	1,765
Piping-valves-supports	10,960	Contractor's fee (5% of direct costs)	6,485
Electrical equipment	6,494	Contingency (8% of direct & indirect cost)	13,314
Buildings (including services)	31,051		
	Fixed capital investment	175,013	
	Working capital	30,885	
	Total capital investment	205,898	

TABLE 7

Raw material and utility requirements per ton of soda ash (dual process)

Raw materials and chemicals		Utilities	
Rock salt (20 $/ton)	1.2 ton/T	Electrical power	360.0 KWh/T
CO_2 (37 $/ton)	1.0274 ton/T	Fuel oil	0.252 Kg/T
Ammonia (110 $/ton)	0.325 ton/T	Cooling water	220.0 m^3/T
Na_2S	3.0 Kg/T	Process water	7.2 m^3/T
Sodium carbonate	50.0 Kg/T		
NaOH	9.5 Kg/T		

TABLE 8

Direct product costs	
Raw materials	97.76
Operating labour	17.2
Utilities	35.5
Maintenance and repairs	31.65
Operating supplies	3.17
Laboratory charges	1.81
Fixed charges	
Depreciation	58.34
Taxes and insurance	16.59
Plant overhead costs	19.21
General expenses	
Administration costs	3.0
Byproduct credits (NH_4Cl)*	(140.0)
Total product cost	144.23

*Estimated NH_4Cl price (plant gate) is 140 $/ton.

(i) The total capital investment. The production capacity is 200,000 MT/year of soda ash (60% dense soda ash and 40% light soda ash), in addition to 200,000 MT/year of ammonium chloride, see Table 6. The purchased equipment cost in 1990 (delivered) is estimated to be 38,429,000 × 895/630 = $ 54,594,000.

(ii) The total product cost. The raw materials and utilities requirements per ton of soda ash (dual process) are as estimated in Table 7.

Manufacturing cost estimate. Manufacturing cost = direct production cost + fixed charges + plant overheads, see Table 8.

4. Conclusion and discussion

The Solvay and dual processes resulted in soda ash product costs of 131.51 and 144.23 $/ton respectively. However, for a preliminary calculation of this nature which has a probable accuracy of ±20% these product costs are expected to range from 105–152 \$/ton for the Solvay process and 115–173 \$/ton for the dual process. The quoted prices of soda ash in January 1990 from USA were as follows (FOB),

	(\$/ton)
58% light	123
58% dense	98

Since the product mix of the proposed Jubail plant consists of 40% light and 60% dense soda ash, then for comparison purposes we estimate the price of a hypothetical composite ton of soda ash (0.4 ton light and 0.6 ton dense soda ash) delivered in the Arabian Gulf at 176.5 \$/ton[1]. This price is well beyond the range of estimated production costs by the two soda ash production routes and the outlook for this industry is therefore encouraging and should be investigated further.

However, it should be pointed out quite clearly that in making these cost estimates the following underlying assumptions were made:

(1) All the soda ash produced (200,000 T/Y) will be marketed either within the Arabian Gulf countries or in the adjacent Middle East countries.

(2) The byproducts (calcium chloride in the case of the Solvay process and ammonium chloride in the case of the dual process) were assumed to find market outlets and realize their estimate prices of 65 \$/ton and 140 \$/ton respectively.

In fact the final product costs as calculated in this study are highly sensitive to the realized prices of the byproducts. The following table shows the percentage of byproduct credits and depreciation charges (the weighted effect of fixed charges) to the total product cost by either processing scheme.

	Solvay	Dual
Byproduct credits	49%	97%
Depreciation charges	36%	40%

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[1] An allowance of 30 \$/ton was made for transportation costs from west USA to an average Arabian Gulf location.