Salt Partners

Economy of Salt in Chloralkali Manufacture

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Salt production world-wide

Salt type	World production
Solar salt	90,000,000 t/y
Rock salt	60,000,000 t/y
Brines	80,000,000 t/y
Total	230,000,000 t/y

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Salt consumption world-wide

Salt user	Salt consumption
Chemical industry	140,000,000 t/y
Food	50,000,000 t/y
Other	40,000,000 t/y

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The Basic Chloralkali Equation

Caustic and Chlorine from Salt

$$2\ NaCl + 2\ H_2O + \text{Electrical Energy} = 2\ NaOH + Cl_2 + H_2$$

119	36	82	71	2
1.45		1		
1.68			1	

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The Basic Chloralkali Equation

Soda Ash from Salt and Lime

$$2\,NaCl + CaCO_3 = Na_2CO_3 + CaCl_2$$

119	110	111	120
1.1	0.93	1	

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Impurities in salt

	Rock salt	Sea salt	Lake salt	Brines
CaSO4	0.5 – 2%	0.5 – 1%	0.5 – 2%	Saturated
MgSO4	Traces	0.2 – 0.6%	Traces	Traces
MgCl2		0.3 – 1%	Traces	
CaCl2			Traces	
Na2SO4			Traces	
KCl			Traces	
NaBr			Traces	
Insolubles	1 – 30%	0.1 – 1%	1 – 10%	

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Why must salt for chloralkali manufacture be pure?

- **Hydrogen evolution**
- **Membrane damage**
- **Incrustations**
- **Contaminated effluents**

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Brine Purification Process

Ca and Mg Precipitation

Calcium precipitation

$$Ca^{++} + Na_2CO_3 = \underline{CaCO_3} + 2\ Na^{+}$$
$$40 \qquad 108$$

Magnesium precipitation

$$Mg^{++} + 2\ NaOH = \underline{Mg(OH)_2} + 2\ Na^{+}$$
$$24 \qquad 82$$

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Brine Purification Process

Sulphate Precipitation

With $BaCO_3$

$$SO4^{--} + BaCO_3 = \underline{BaSO_4} + CO_3^{--}$$
$$96 \qquad 197 \qquad 233$$

With $BaCl_2$

$$SO4^{--} + BaCl_2 = \underline{BaSO_4} + 2\ Cl^-$$
$$96 \qquad 208 \qquad 233$$

With $CaCl_2$

$$SO4^{--} + CaCl_2 = \underline{CaSO_4} + 2\ Cl^-$$
$$96 \qquad 111 \qquad 136$$

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Brine Purification Process

Overdosing of Chemical Reagents

For calcium precipitation	**0.4 kg Na_2CO_3 per m3 of brine**
For magnesium precipitation	**0.15 kg NaOH per m3 of brine**
For barium precipitation	**5 - 6 kg sulphate per m3 of brine with DuPont membranes** **8 - 10 kg sulphate per m3 of brine with Asahi Glass Flemion membranes**

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Solar Salt of Variable Quality

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One of the largest solar saltworks in India producing salt of variable quality

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Cost Components of Salt by Uses

- **Chloralkali and Soda Ash**
  - **Production Cost**
  - **Transport Cost**
  - **Brine Purification Cost**

- **Other Uses**
  - **Production Cost**
  - **Transport Cost**

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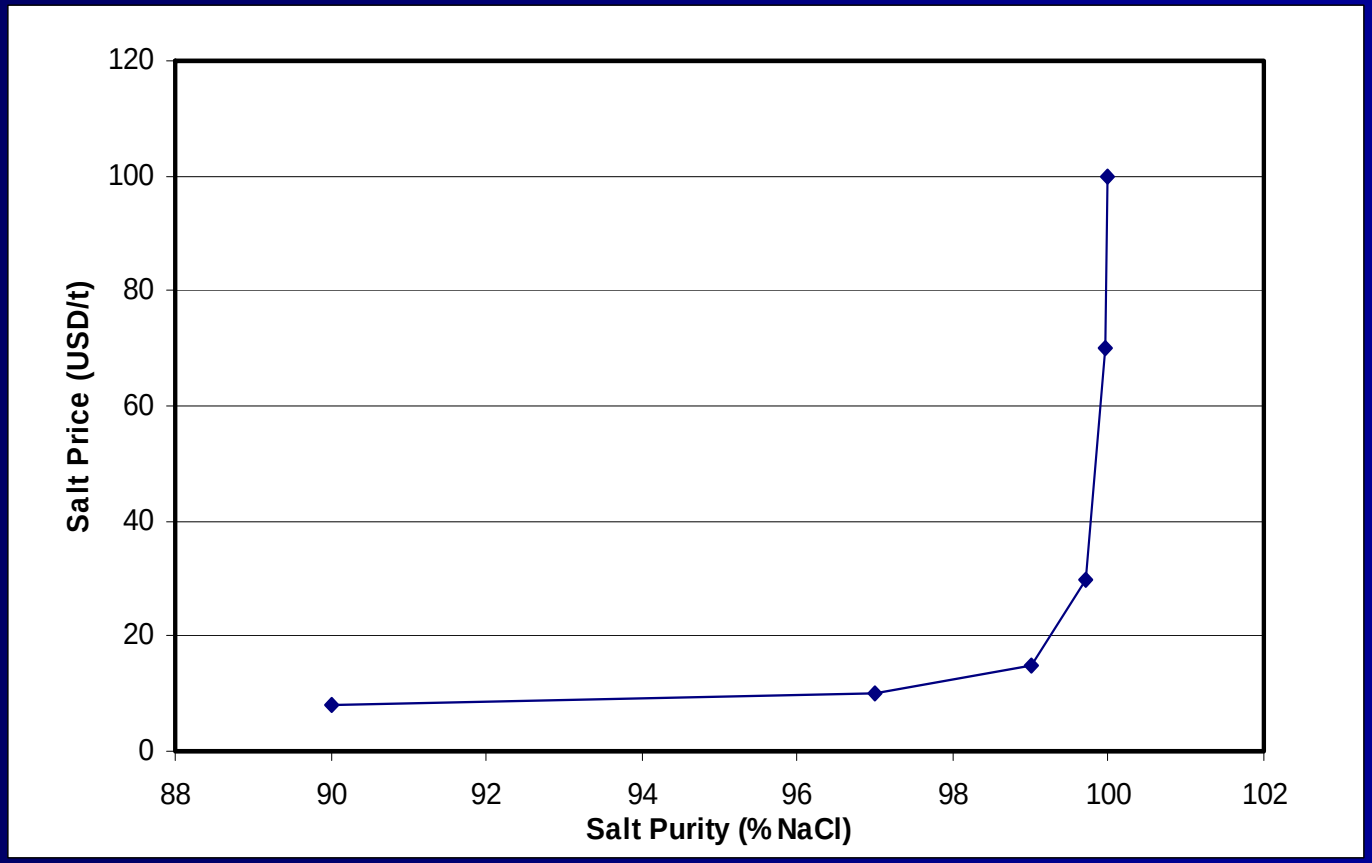
Salt Prices are Dependent on Salt Purity



Industrial salt prices vary between USD 10.-/t and USD 100.-/t depending on salt purity

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Salt Purities

	NaCl Purity (%)
Rock salt	90 - 97
Crude sea salt	97 - 99
Upgraded sea salt	99 – 99.7
Refined salt	99.7 – 99.95
Super refined salt	99.95 +

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Cost Components of Brine Purification

- Brine Purification Chemicals
- Salt and Brine Handling
- Contaminated Sludge Disposal
- Purge Decontamination and Disposal
- Loss of Salt in Purge
- Investment and Operating Cost

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Cost of Brine Purification Stoichiometrie

$\%Ca \times 108 / 40 = \%Na2CO3 \times Price_{Na2CO3} = Cost_{CaStoch}$

$\%Mg \times 82 / 24 = \%NaOH \times Price_{NaOH} = Cost_{MgStoch}$

$\%SO4 \times 208 / 96 = \%BaCl2 \times Price_{BaCl2} = Cost_{SO4Stoch}$

or $BaCO3$ or $CaCl2$ or purge

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Cost of Brine Purification Overdosing

Ca: m3 Brine / t salt x 0.4 g/l Na_2CO_3 x $Price_{Na2CO3}$ = $Cost_{CaOverdose}$

Mg: m3 Brine / t salt x 0.2 g/l NaOH x $Price_{NaOH}$ = $Cost_{MgOverdose}$

SO_4: does not require overdosing but must be maintained within limits to reduce barium solubility

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Typical Salt Analyses

	Ca %	Mg %	SO4 %	Insolubles %
Rock salt	1	0.05	2.5	2
Crude sea salt	0.2	0.1	0.6	1
Upgraded sea salt	0.04	0.02	0.12	0.03
Vacuum salt	0.001	0.0002	0.03	0.01

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Cost of Brine Saturation and Salt Dissolution in Mercury and Membrane Electrolytic Brine

	Lean brine (g NaCl/l)	Saturated brine (g NaCl/l)	Salt dissolution (kg NaCl/m^3)	Ca in rock salt (kg Ca/m^3)	Ca in crude sea salt (kg Ca/m^3)
Mercury brine	270	300	30	0.3	0.06
Membrane brine	150	300	150	1.5	0.3

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Contaminated Effluent Disposal from Mercury and Membrane Electrolytic Brine

	Brine Effluent	Solids
Mercury brine	Demercurisation	Special depository (salt mines)
Membrane brine	Neutralisation	Desalination and land fill

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Cost of Salt and Brine Treatment

Cost of salt / %NaCl content / 100 + Salt handling losses + Ca_{Sochio} + $Ca_{Overdose}$ + Mg_{Sochio} + $Mg_{Overdose}$ + $SO4_{Stochio}$ (or loss of salt with purge) + Alkalisation + Acidification + Regeneration + Effluent decontamination + Effluent disposal

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Disposal Cost of Brine and Solids

	Brine disposal cost (USD / t of salt)	Solids disposal cost (USD / t of salt)
Minimum	**0.05**	**0.20**
Average	**0.30**	**1.50**
Maximum	**0.60**	**4**

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Cost of Salt and Brine Treatment

	Cost of brine treatment and disposal (USD / t salt)	Cost of salt, brine treatment and disposal (USD / t salt)
Minimum	1.50	10
Average	10	25
Maximum	30	50

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Relative Brine Treatment Cost

	Cost of brine treatment as percentage of salt cost	Percentage of chloralkali production cost
	%	%
Minimum	100	3
Average	170	15
Maximum	300	40

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Three saltworks areas that are critical to production of high quality solar sea salt

- **Sea water pre-concentration area**
- **Solar salt crystallisation area**
- **Salt purification plant**

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What to do and what to avoid in the sea water pre-concentration area

- Increase concentration gradually, avoid back-mixing
- Prevent seepage
- Cultivate dark pre-concentration pond bottom
- Maintain clear brine
- Avoid calcium sulphate over-saturation
- Allow nutrients in brine to get consumed

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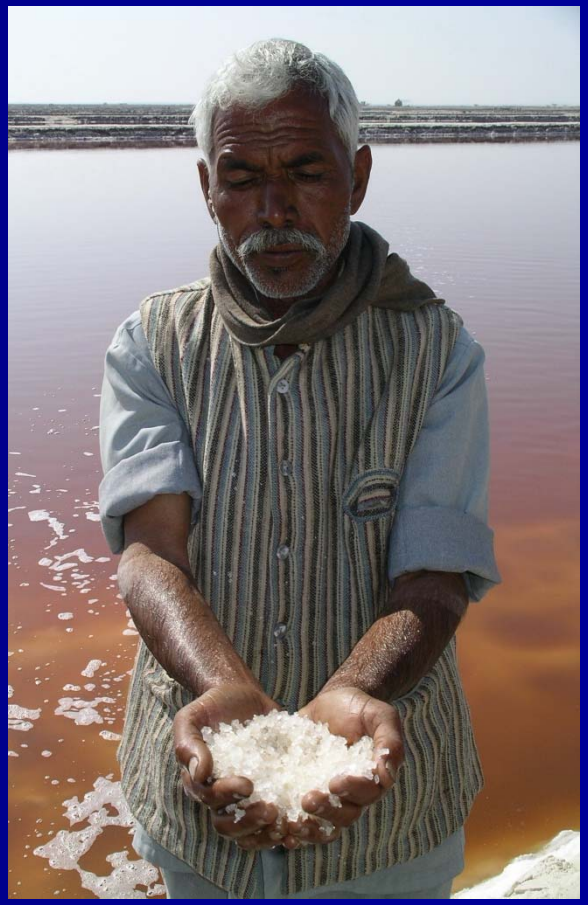
Solar salt crystallisation area

- Employ crystallisers in series
- Drain 28.5°Bè brine
- Support growth of *Halobacterium* that colours the brine red
- Allow thick brine layer to avoid reflection of solar radiation
- Avoid organic matter that causes formation of small crystal agglomerates
- Harvest under level control to avoid salt contamination with insolubles



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Solar salt from poorly managed saltworks

Salt that looks like a crystal, but it is an agglomerate.

The agglomerate can be broken by hand.

Impurities are imbedded between the small crystal fragments.

The salt is not well upgradeable.

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Solar salt from well managed saltworks

Hard, clear crystal, impossible to break by hand.

Impurities are only on the crystal surface. The salt is very well upgradeable with low losses.

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BIOSAL Process Results

	Raw salt 1996 harvest	Raw salt 2006 harvest	Impurity reduced to
Ca	0.183	0.175	96%
Mg	0.527	0.097	18%
SO4	1.29	0.595	46%
Insolubles	0.04	0.02	50%

Quality improvement achieved by application of BIOSAL biological management techniques in South West African solar saltfields

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BIOSAL Process Results

	HYDROSAL upgradeability 1996	HYDROSAL upgradeability 2006	Impurity reduced to
Ca	0.070	0.032	46%
Mg	0.020	0.008	40%
SO4	0.200	0.101	51%
Insolubles	0.01	0.01	100%

Quality improvement achieved by application of BIOSAL biological management techniques in South West African solar saltfields

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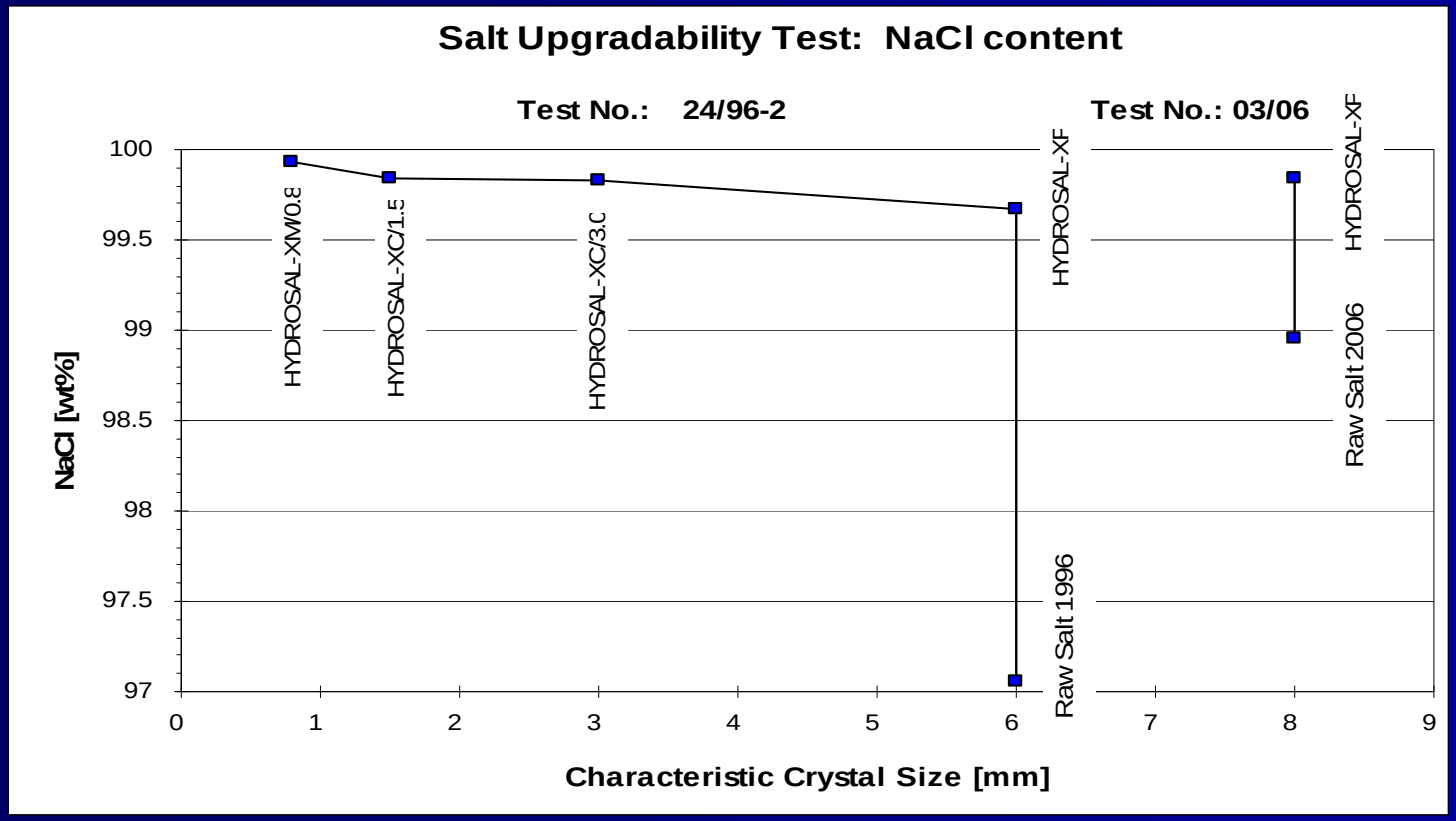
Salt upgradability test, NaCl content



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SALEXPOR 15 t/h solar salt refining plant in Portugal

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100 t/h industrial salt upgrading plant in Spain

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40 t/h salt upgrading plant in Portugal producing purest industrial salt in Europe

		Performance test
Ca	ppm	0.6
Mg	ppm	0.2
SO4	ppm	44

Efficiency	97.4%
NaCl losses	3.9%

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Why not turn your salt into gold?

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