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Economy of Salt in Chloralkali Production

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MESSO AG, Krebs Swiss Salt Technologies

Figure 2

The Basic Chloralkali Equation

Caustic and Chlorine from Salt

$$2\ NaCl + 2\ H_2O + Energy = 2\ NaOH + Cl_2 + H_2$$

119	36		82	71	2
1.45			1		
1.68				1	

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

119	100	108	111
1.1	0.93	1	

Figure 3

Sources of Salt

Salt Production World-wide

❋ Solar Salt	70,000,000 t/y
❋ Rock Salt	60,000,000 t/y
❋ Brines and Vacuum Salt	70,000,000 t/y

Figure 4

Main Salt Uses World-wide

Caustic / Chlorine	36
Soda Ash	17
Other Chemicals	3
Human Consumption	22
Road De-icing	12
Other Uses	10
Total	100

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Figure 5

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 +

Figure 6

Salt Cost versus Purity

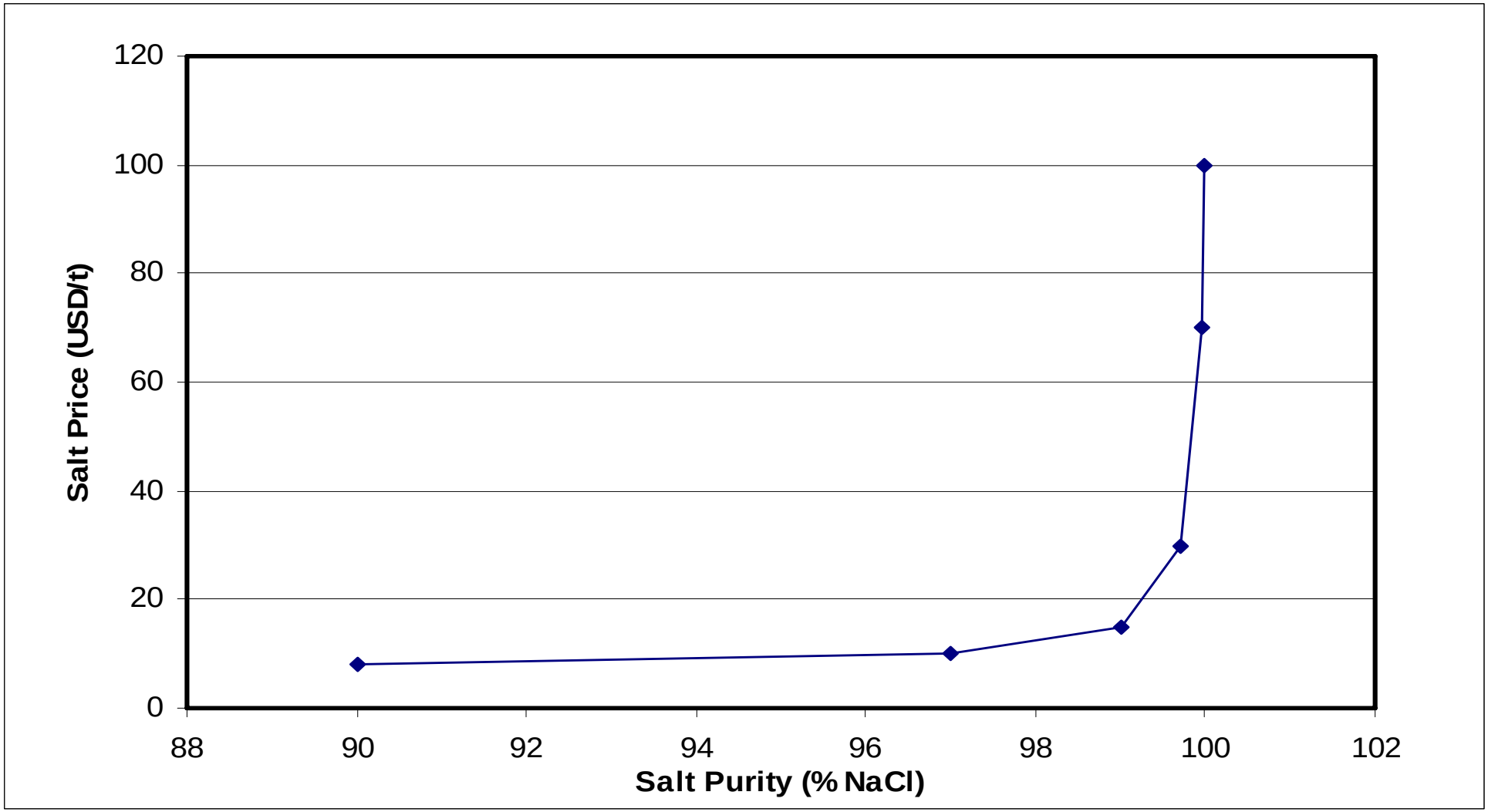

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Figure 7

Cost Components of Salt by Uses

- Chloralkali and Soda Ash
  - Production Cost
  - Transport Cost
  - Brine Purification Cost
- Other Uses
  - Production Cost
  - Transport Cost

Figure 8

Impurities in Salt

Components of Sea Water

	Rock Salt	Sea Salt	Lake Salts	Brines
CaSO4	0.5 - 2 %	0.5 - 1 %	0.5 - 2 %	Saturated
MgSO4	Traces	0.2 - 0.5 %	Traces	Traces
MgCl2		0.4 - 1 %	Traces	
CaCl2			Traces	
Na2SO4			Traces	
KCl			Traces	
NaBr			Traces	
Insolubles	1 - 10 %	0.1 - 1 %	1 - 10 %	

Figure 9

Importance of Impurities to Salt Users

Impurity	All Users	Mercury	Membranes	Organic synthesis
Ca	!	!	!	
Mg	!	!	!	
SO4	!	!	!	
Insolubles	!	!	!	
Sr			!	
K				
Br				!
Fe		!		
Cr		!		
Ni		!		
Heavy metals		!		
Si			!	
Al			!	
I			!	
Ferrocyanide			!	

Figure 10

What Impurities in Salt Mean to Chloralkali Industry

In Mercury and Membrane Cells

- Hydrogen Evolution
- Mercury Butter
- Membrane Damage
- Incrustations
- Sludge Deposits

Figure 11

How the Chloralkali Industry Purifies Brine

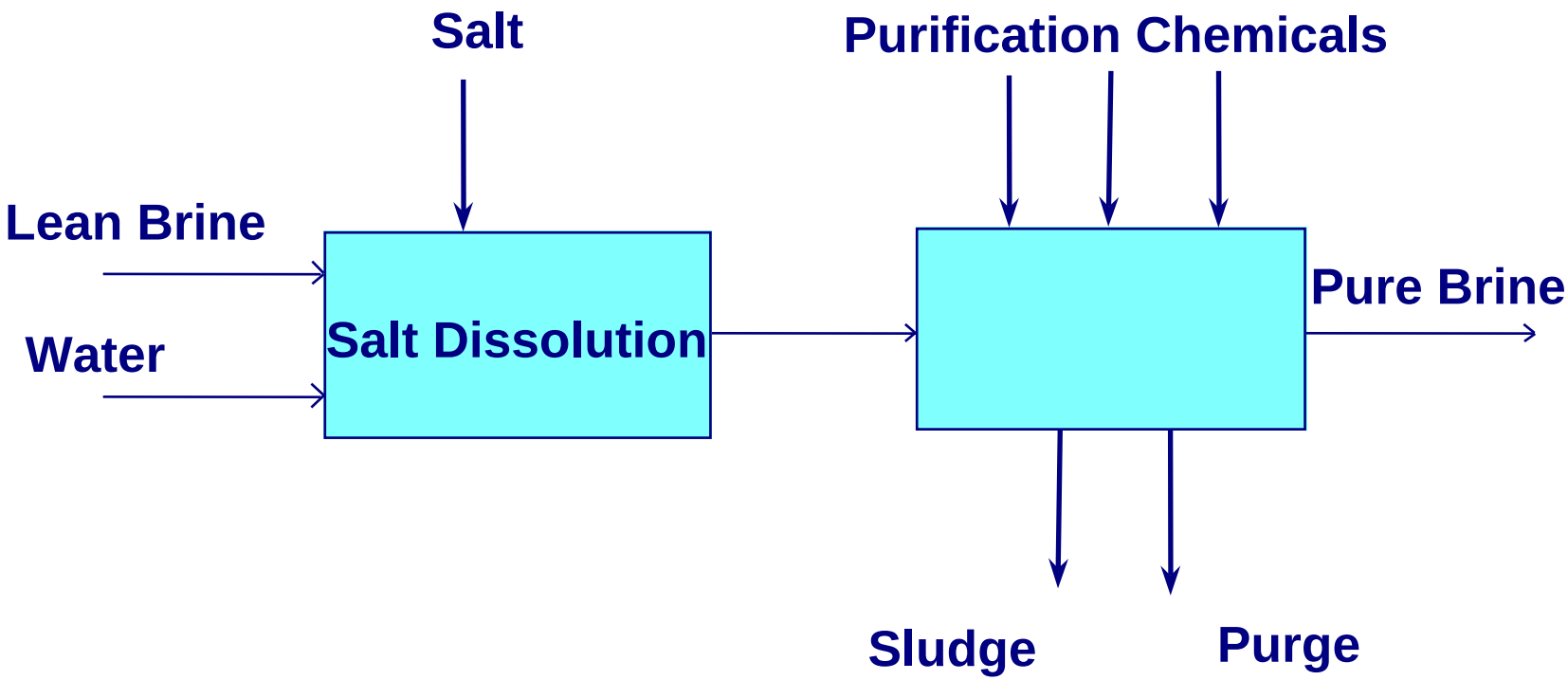

Figure 12

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

Figure 13

Brine Purification Processes

Ca and Mg Precipitation

Calcium precipitation

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

Magnesium precipitation

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

Figure 14

Brine Purification Processes

Sulphate Precipitation

With $BaCO_3$

$$SO4^{--} + BaCO_3 = \underline{BaSO_4} + 2\,Cl^-$$
$$96 \qquad 208$$

With $BaCl_2$

$$SO4^{--} + BaCl_2 = \underline{BaSO_4} + 2\,Cl^-$$
$$96 \qquad 197$$

With $CaCl_2$

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

Figure 15

Cost of Brine Purification

Stochiometrie

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

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

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

or BaCO3 or CaCl2 or purge

Figure 16

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 0.15 g/l NaOH x $Price_{NaOH}$ = $Cost_{MgOverdose}$

SO_4: does not require overdosing

Figure 17

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

Figure 18

Calcium Sulphate Solubility

in Electrolytic Brine at 60°C

(Solubility product (C_{Ca}) x (C_{SO4}) = 3.6 $(g/l)^2$)

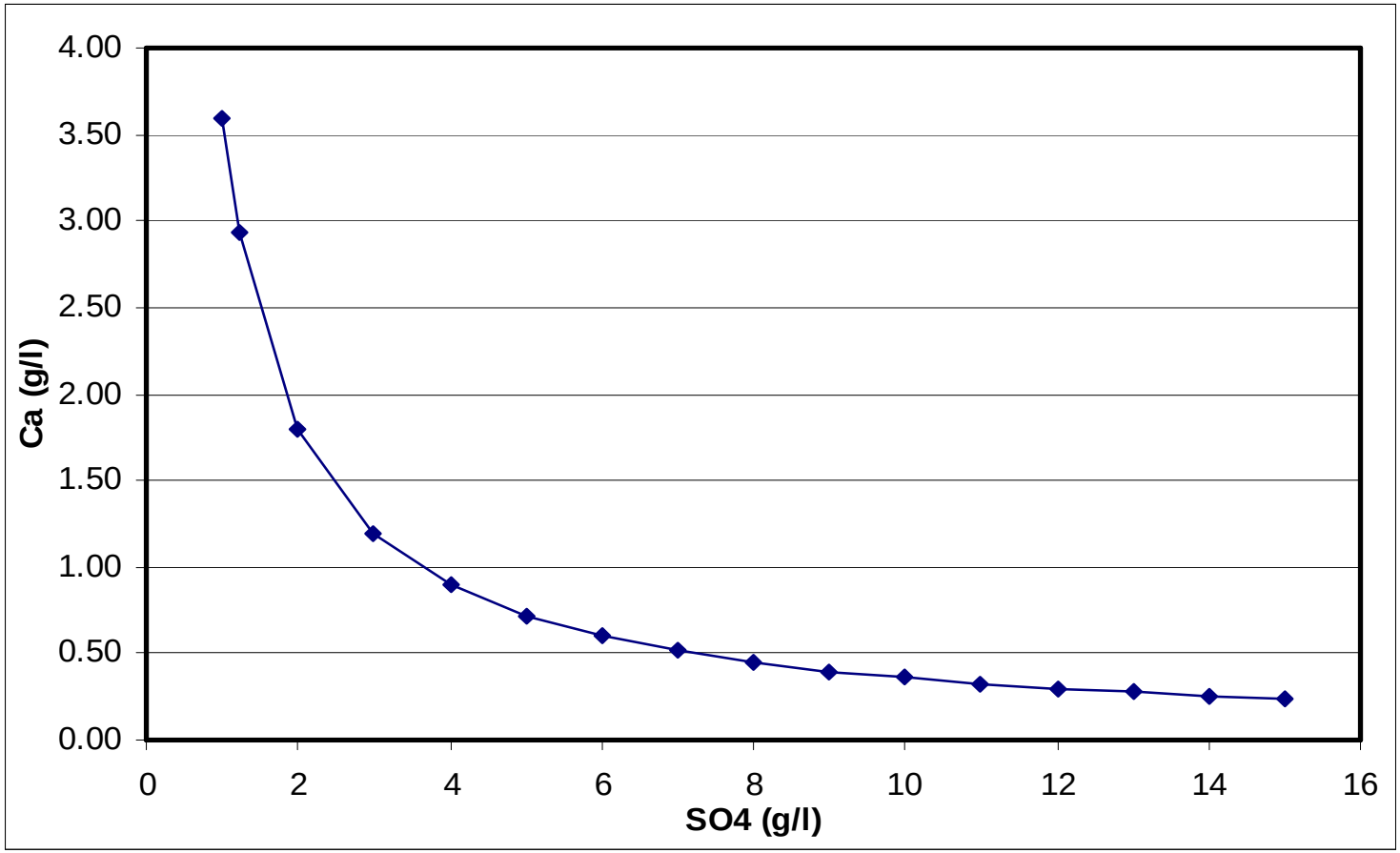

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Figure 19

Brine Saturation and Salt Dissolution

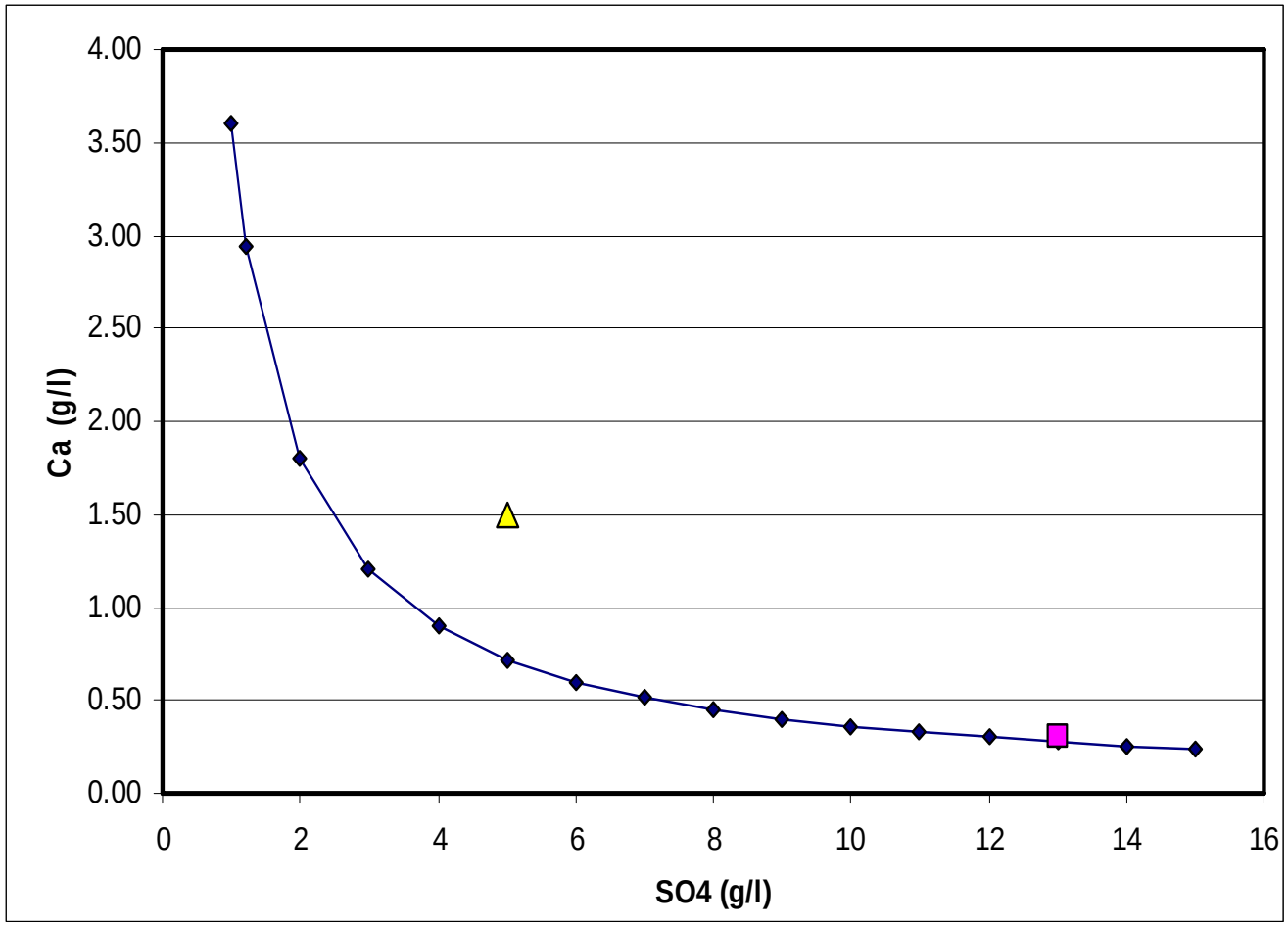
in Mercury and Membrane Electrolytic Brine

	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

Figure 20

Rock Salt Dissolution

in Electrolytic Brine



□ **Saturation of mercury cell brine (all CaSO4 dissolves in brine)**

△ **Saturation of membrane cell brine (only half of CaSO4 dissolves in brine)**

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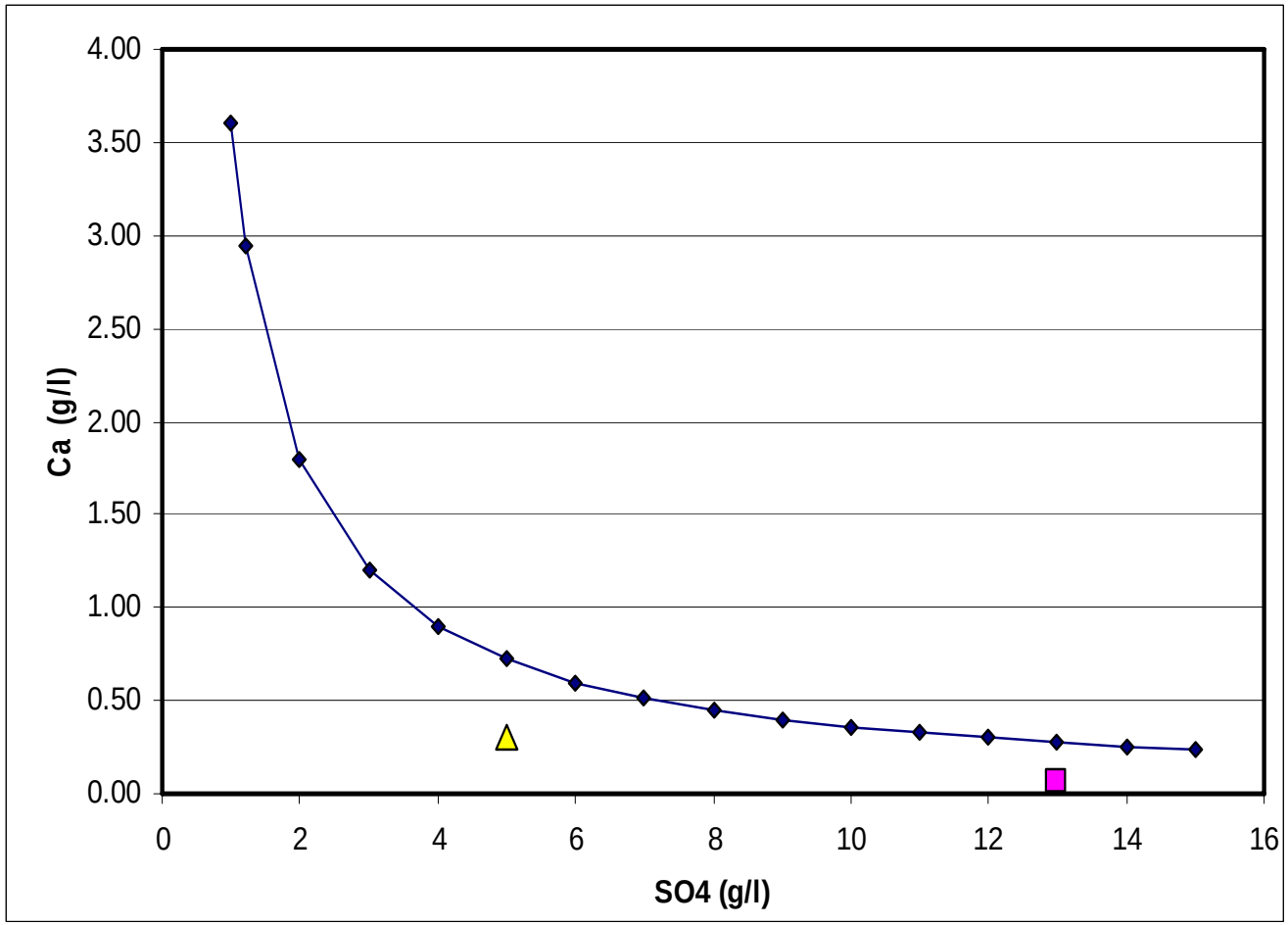
Figure 21

Solar Salt Dissolution

in Electrolytic Brine



□ Saturation of mercury cell brine (all CaSO4 dissolves in brine)

△ Saturation of membrane cell brine (all CaSO4 dissolves in brine)

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Figure 22

Contaminated Effluent Disposal

Mercury and Membrane Electrolytic Brine

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

Figure 23

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

Figure 24

Prices of Brine Purification Chemicals

	NaOH (USD / t)	Na_2CO_3 (USD / t)	$BaCO_3$ (USD / t)	$BaCl_2$ (USD / t)	$CaCl_2$ (USD / t)
Minimum	41	124	265	444	79
Average	180	183	305	720	164
Maximum	247	245	347	990	269

Figure 25

Disposal Cost of Brine and Solids

	Brine disposal cost (USD / t of salt)	Solids disposal cost (USD / t of salt)
Minimum	0.06	0.20
Average	0.32	1.14
Maximum	0.58	3.09

Figure 26

Typical Brine Purification Cost

Calculated from typical salt composition and average prices of brine purification chemicals

	Brine Purification Process		
	$BaCO_3$ (USD / t salt)	$BaCl_2$ (USD / t salt)	$CaCl_2$ (USD / t salt)
Rock salt	30	71.6	45.8
Crude sea salt	9.6	19.5	14.7
Upgraded sea salt	4	5.9	5.7
Vacuum salt	2.9	3.4	3.4

Figure 27

Cost of Salt and Brine Treatment

Reported by Contributors to MESSO AG Cost Survey

	Cost of brine treatment and disposal (USD / t salt)	Cost of salt, brine treatment and disposal (USD / t salt)
Minimum	1.45	11.09
Average	9.20	25.09
Maximum	27.42	49.35

Figure 28

Relative Brine Treatment Cost

Reported by Contributors to MESSO AG Cost Survey

	Cost of brine treatment as percentage of salt cost %	Percentage of chloralkali production cost %
Minimum	120	3.6
Average	166	15
Maximum	256	37

Figure 29

Data Contributors

to MESSO AG Cost Survey

SNEP, Morocco
Enichem, Italy
Standard Alkali, India
NRC, India
Safi Salt, Jordan
Atul, India
Dwory, Poland
Hellenic, Greece
Nirou Clor, Iran
Aragonesas, Spain
Saboo, India
Atanor, Argentina
Andhra Sugars, India
Punta de Lobos, Chile
SPIC, India
Mabuhay Vinyl, Philippines
Proinsal, Argentina
GACL, India
Bhandar Imam, Iran
Borregaard, Norway
Arab Potash, Jordan
MISR, Egypt
Petkim, Turkey
Borsodchem, Hungary
Kothari, India
Ercros, Spain
Solvay, Argentina
Jayshree, India
Emisal, Egypt
DCW, India
Formosa Plastic
Arabian Chlorine, Saudi Arabia
Solvay, Spain
Grasim, India
Chemfab, India
GHCL, India
Da Qing He, China
Quimpac, Peru
TCC, India
Sind Alkalies, Pakistan
Uniteca, Portugal
Shriram, India
Ballarpur, India
Fine Salt, India
Sales Monzon, Spain
Tekel, Turkey
Rio Doce, Brazil
Abadan Petrochemical, Iran
Modi, India
Saukem, India
Century, India
Heilbronn, Germany
EPETCO, Egypt
Azraq, Jordan
Tata, India
Frutarom, Israel
Ittehad, Pakistan
Sitara, Pakistan
Salexpor, Portugal
Tokuyama, Japan
Reliance, India
Salgema, Brazil
El Nasr, Egypt
DSW, Israel