Salt Partners

Economy of Ultrapure Salt Feedstock in Membrane Cell Chloralkali Plants

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Second International Flemion Seminar, Zurich, Switzerland, 13. - 14. June 2012

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Salt production world-wide

Salt type	World production
Solar salt	90’000’000 t/y
Rock salt	80’000’000 t/y
Brines	80’000’000 t/y
Total	250’000’000 t/y

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Salt consumption world-wide

Salt user	Salt consumption
Chemical industry	150’000’000 t/y
Food	60’000’000 t/y
Other	40’000’000 t/y

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Salt Purities

	NaCl Purity (%)
Rock salt	90 - 97
Crude sea salt	97 - 99
Washed sea salt	99 – 99.6
Purified sea salt	99.6 – 99.8
Refined salt	99.8 – 99.9
Vacuum refined salt	99.9 – 99.97
Ultrapure salt	99.97 – 99.997

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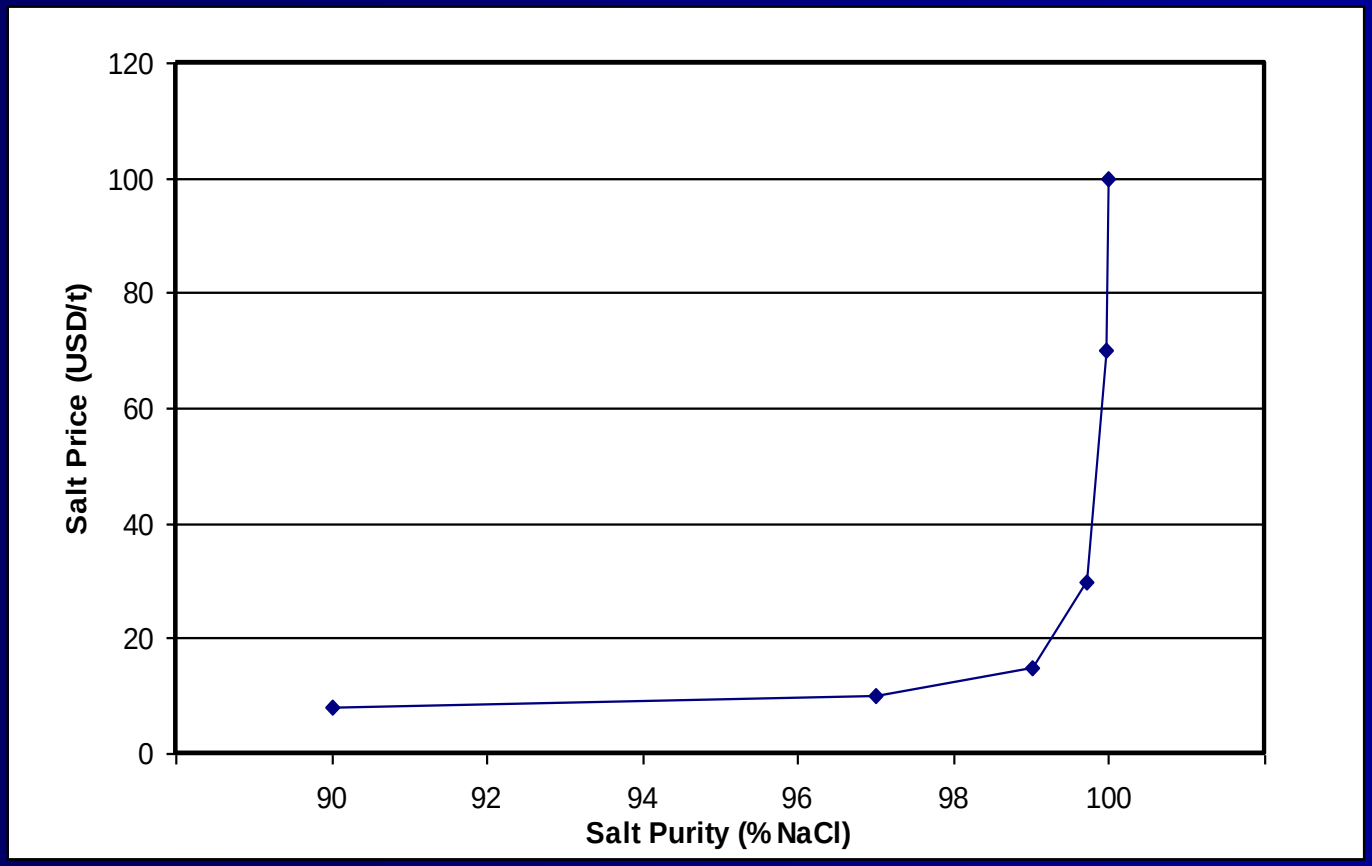
Salt Prices Depend on Salt Purity



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

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Important Impurities in Salt in 1996

	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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Important Impurities in Salt in 2012

Ag, Al, As, Ba, Br, Ca, Cd, Cr, Cu, F, Fe, Hg, I, K, Li, Mg, Mn, Mo, N (as NH3 and as NO2), Ni, P, Pb, S (as SO4), Si (soluble), Si (total), Sr, Ti, V, Zn, TOC (Total Organic Carbon), Moisture, NORM (Naturally Occurring Radioactive Substances), Insolubles in 10% neutral brine, Insolubles in 2% neutral brine, Insolubles in alkaline brine, etc.

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Important Impurities in Brine for Membrane Cells

	Max.	Membrane Licensor A	Membrane Licensor B
Ca + Mg	ppb	20	20
SO4	g/l	5	4 - 8
I	ppm	0.1	0.2
Ba	ppm	0.1	0.5
Sr	ppm	0.4	0.1
Al	ppm	0.1	0.1
SiO2	ppm	5	5
Fe	ppm	0.05	0.1
Hg	ppm	0.1	0.1
Ni	ppm	0.01	0.01
Mn	ppm	-	0.01
F	ppm	-	0.5
TOC	ppm	10	10

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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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Why must brine for chloralkali manufacture be pure?

- **Membrane damage in membrane cells**
- **Hydrogen evolution in Hg-cells**
- **Incrustations in soda ash production**
- **Contaminated effluents**
- **Bromine in chlorine for organic synthesis**
- **etc.**

Brine for chloralkali manufacture must be purified.

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Brine Purification: Ca and Mg Precipitation

Calcium precipitation	$Ca^{++} + Na_2CO_3 = \underline{CaCO_3} + 2\ Na^+$
	40 108
Magnesium precipitation	$Mg^{++} + 2\ NaOH = \underline{Mg(OH)_2} + 2\ Na^+$
	24 82

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Brine Purification: Overdosing of 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**

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Brine Purification: Sulphate Removal

With $BaCO_3$	$SO4^{--} + BaCO_3 = \underline{BaSO_4} + CO_3^{--}$ 96 197 233
With $BaCl_2$	$SO4^{--} + BaCl_2 = \underline{BaSO_4} + 2\ Cl^-$ 96 208 233
With $CaCl_2$	$SO4^{--} + CaCl_2 = \underline{CaSO_4} + 2\ Cl^-$ 96 111 136
With Nanofiltration	From 4 – 8 g/l to 80 g/l in purge as Na2SO4

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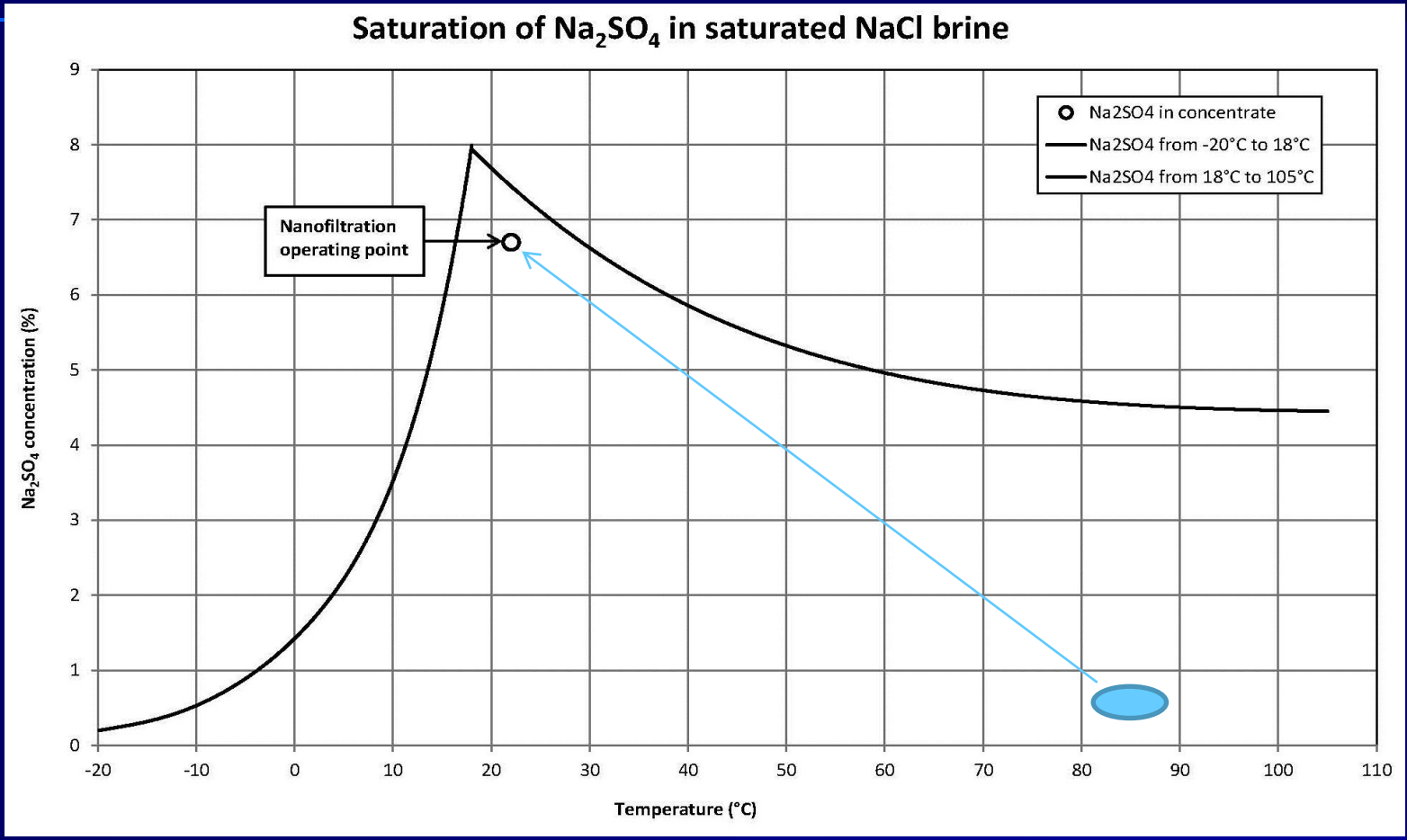
Nanofiltration Operating Point



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

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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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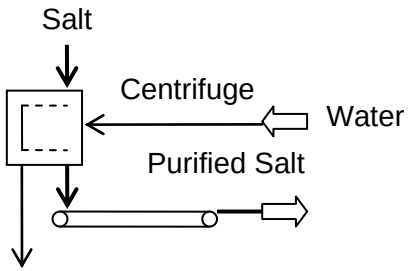
HYDROSAL Process



Centrifuge separates salt and brine

Conventional washing with water in the centrifuge

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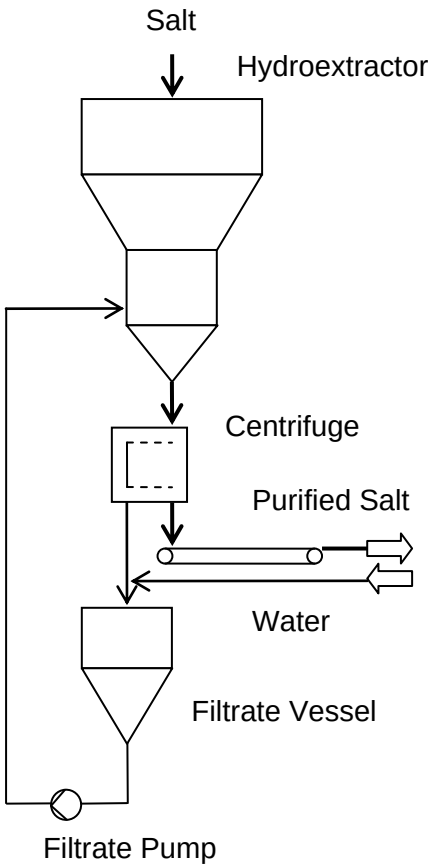
HYDROSAL Process



Dissolve salt fines in water and use this pure brine to remove impurities from salt in the hydroextractor

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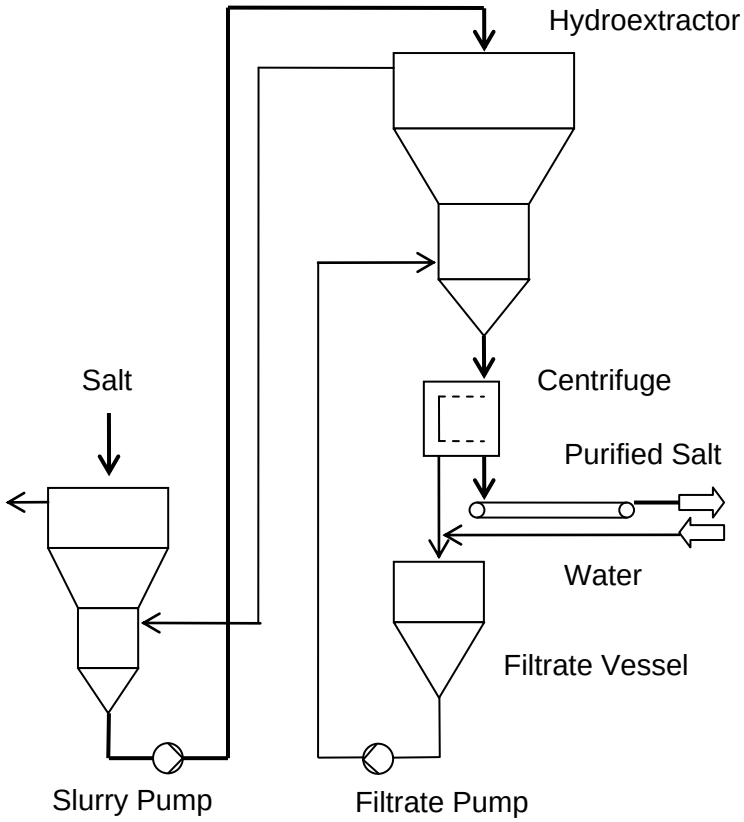
HYDROSAL Process



Hydraulically transport salt to the hydroextractor and return the transport brine to the elutriator

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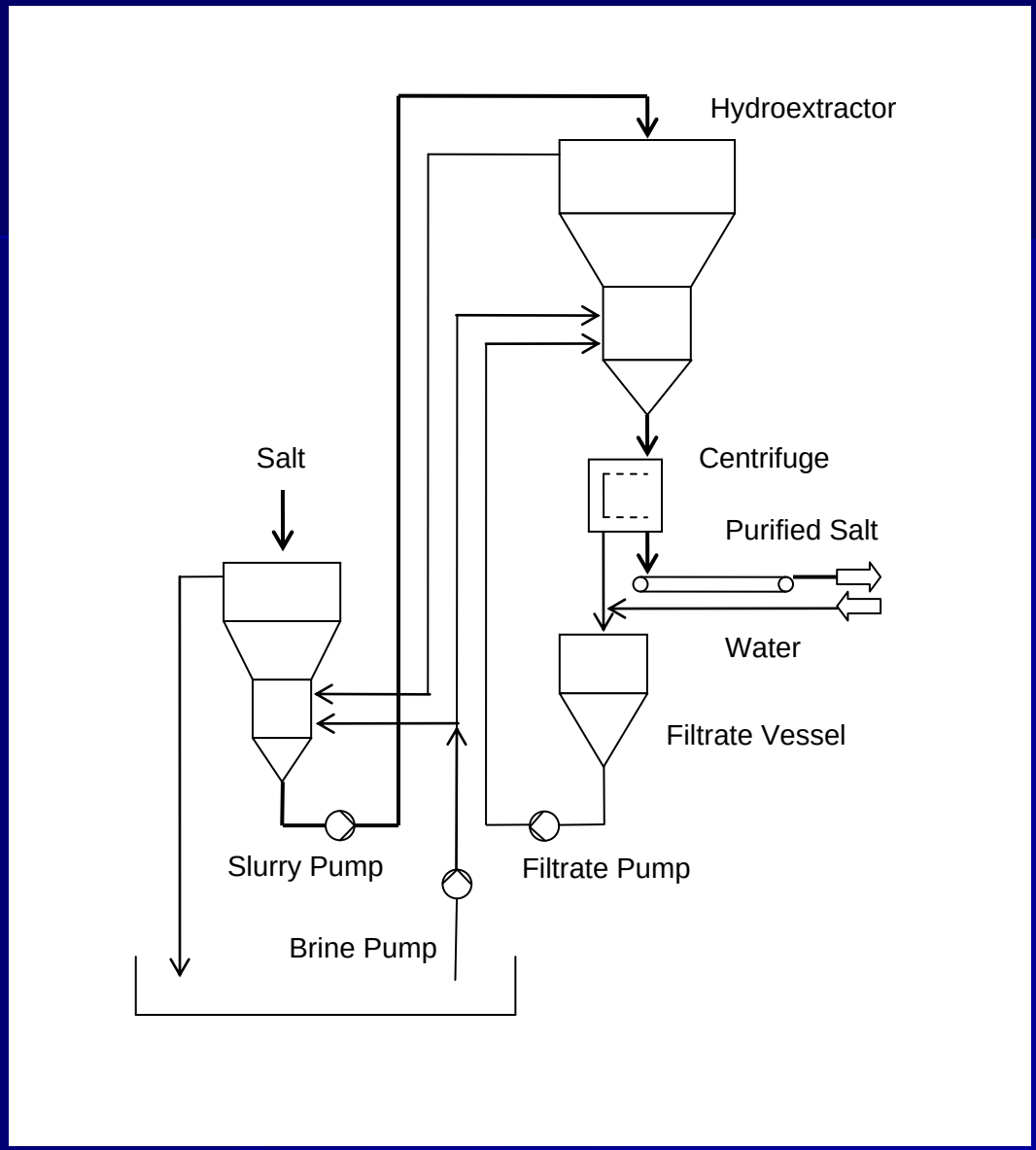
HYDROSAL Process



Circulate impure brine to control hydroclassification and elutriation efficiency

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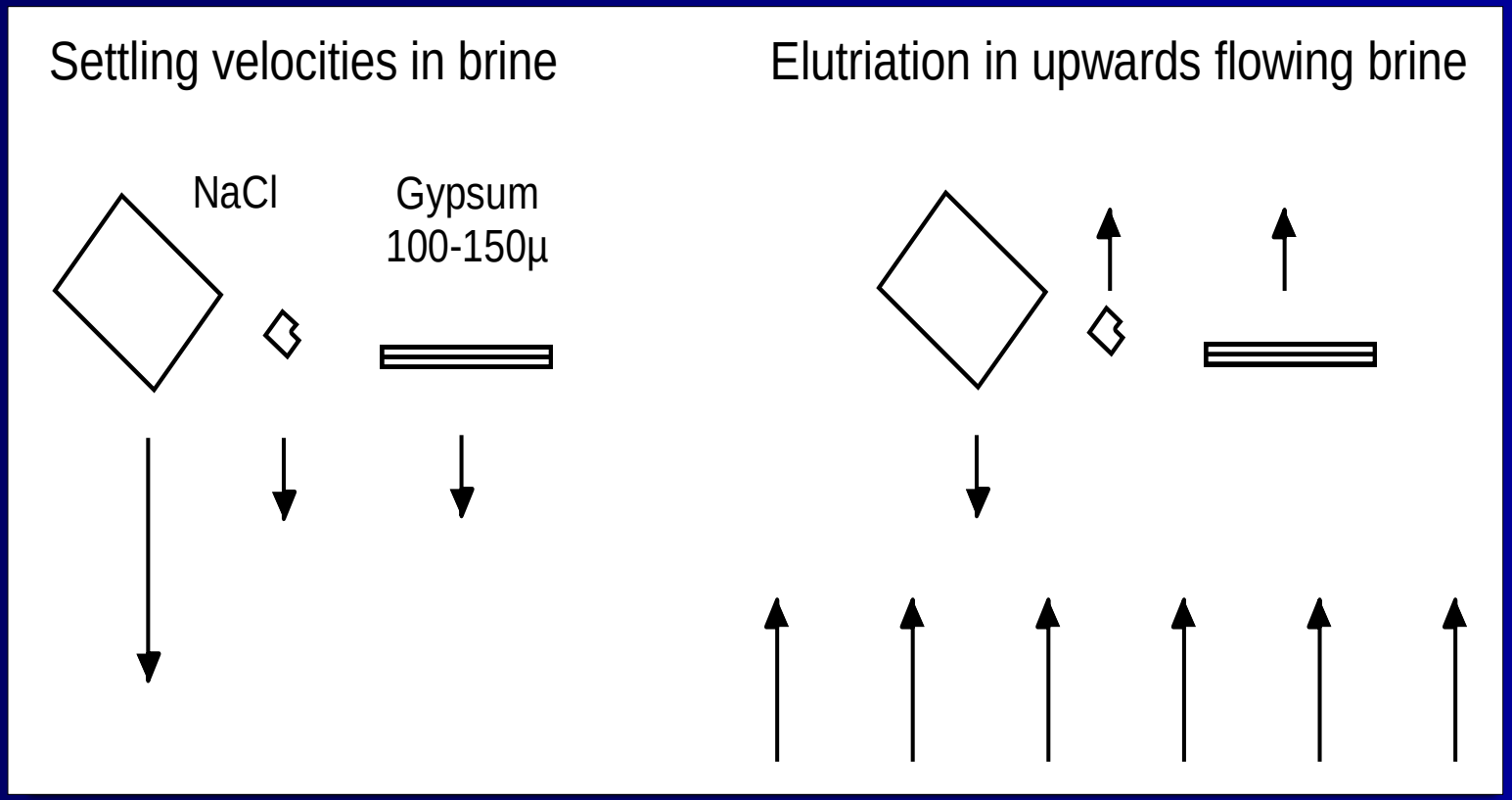
Elutriation



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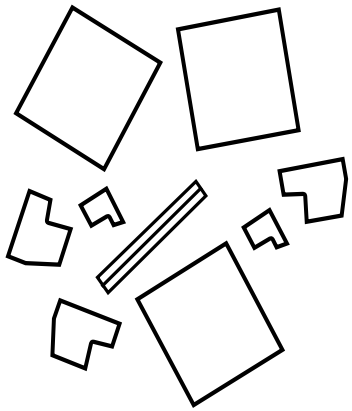
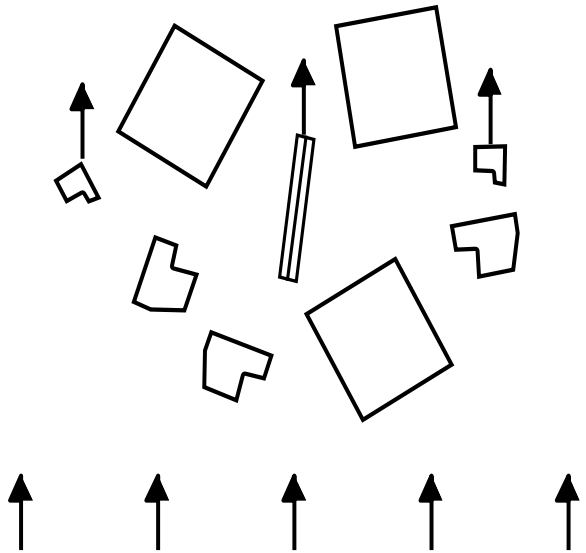
Hydroclassification

Salt bed with buried impurities



Hydroclassification of impurities in partially fluidised salt bed



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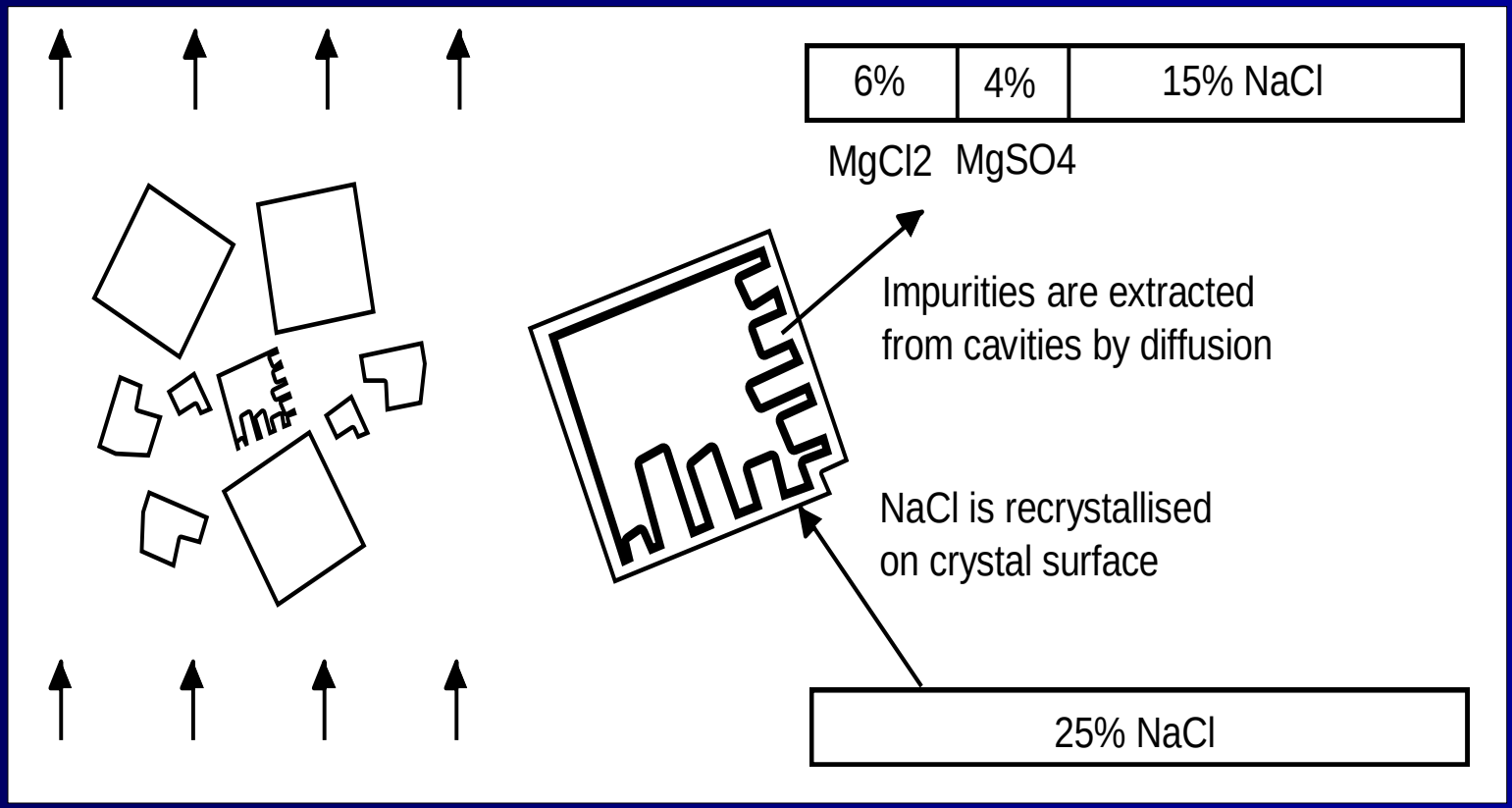
Hydroextraction



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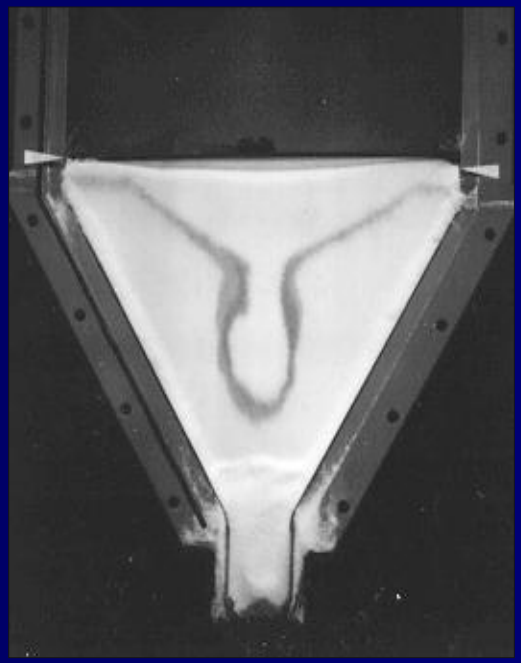
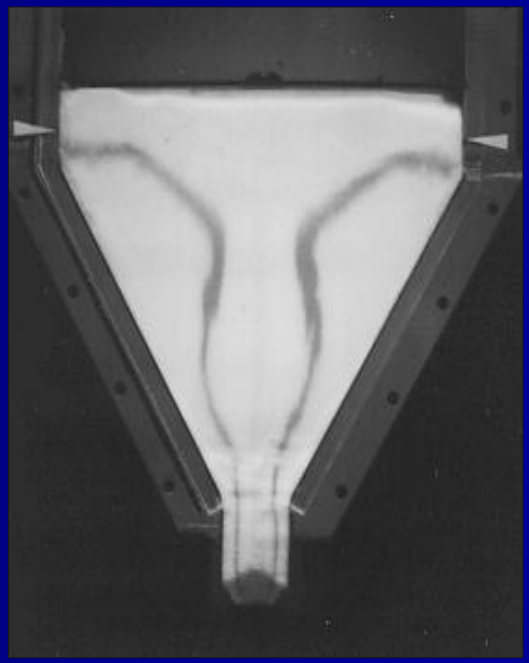
Hydroextraction does not work in all vessels



In this vessel salt flows out mainly through the centre



So called rat hole develops in the centre of the vessel

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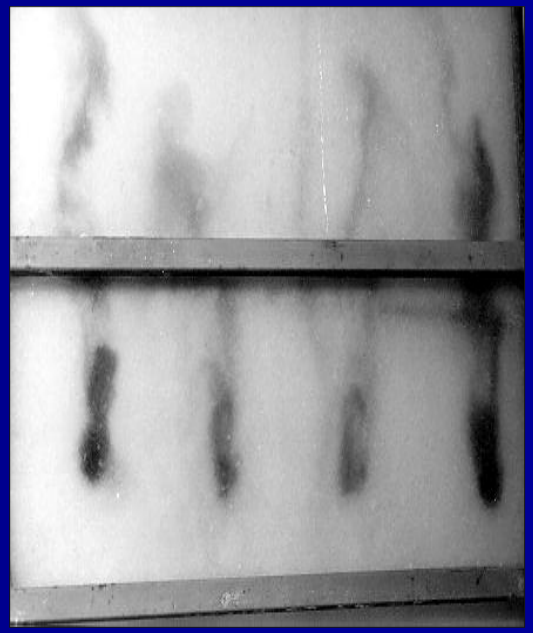
Hydroextraction works only with plug flow of salt

Picture 1: Injection of black ink into brine flowing upwards through salt flowing downwards in plug flow

Picture 2: Black ink flows upwards with brine in counter-current flow



Picture 3: Second black ink injection. There are no traces of black colour in the salt flowing downwards in plug flow

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Solution mining for natural gas storage, co-generation, brine purification, salt crystallisation and refining plant in Portugal

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

		Performance test
Ca	ppm	0.6
Mg	ppm	0.2
SO4	ppm	53

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High quality European vacuum salt “A” before and after HYDROSAL purification

		Commercial vacuum salt product	HYDROSAL purified
Ca	ppm	< 1	< 1
Mg	ppm	0.12	0.07
SO4	ppm	118	29
K	ppm	87	72
Br	ppm	35	34
I	ppm	< 0.1	< 0.1
Ba	ppm	< 0.02	< 0.02
Sr	ppm	< 0.1	< 0.1
Al	ppm	< 0.05	< 0.05
SiO2	ppm	0.58	0.23

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High quality European vacuum salt “E” before and after HYDROSAL purification

		Commercial vacuum salt product	HYDROSAL purified
Ca	ppm	6.5	5.8
Mg	ppm	3.1	2.9
SO4	ppm	191	33
K	ppm	36	29
Br	ppm	29	28
I	ppm	< 0.1	< 0.1
Ba	ppm	< 0.02	< 0.02
Sr	ppm	0.1	< 0.1
Al	ppm	< 0.05	0.05
SiO2	ppm	0.81	0.47

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High quality European vacuum salt "N" before and after HYDROSAL purification

		Commercial vacuum salt product	HYDROSAL purified
Ca	ppm	211	66
Mg	ppm	6.8	1.2
SO4	ppm	820	229
K	ppm	225	185
Br	ppm	43	36
I	ppm	0.4	< 0.1
Ba	ppm	0.04	< 0.02
Sr	ppm	6.3	2.2
Al	ppm	1.0	0.1
SiO2	ppm	< 0.1	< 0.1

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Costs Related to Salt Use in Membrane Chloralkali Manufacture

- Salt Storage and Handling
- Salt Dissolution and Brine Purification
- Contaminated Sludge Handling and Disposal
- Purge Decontamination, Disposal and Salt Loss
- Ferrocyanide, Silica, Bromine and Iodine Removal
- Power Consumption
- Hydrochloric Acid Consumption
- Membrane Life
- Production Loss or Extra Production Capacity

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Comparative Study on Differential Costs in a Membrane Cell Plant having Following Parameters:

- Plant Capacity: 300’000 t/y of Chlorine
- Conversion from Mercury to Membranes
- Sulphate Removal with Nanofiltration
- Washed Salt with Bromine, Iodine and Ferrocyanide
- Ultrapure Salt without Bromine, Iodine and Ferrocyanide
- Ultrapure Salt in Silos, no Contamination
- Primary Brine Purification Plant Redundant
- Membrane Cells with Acidification
- Production Loss or Extra Production Capacity

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Membrane Plant Operation with Salt A and B

		Washed Salt A	Ultrapure Salt B
Ca	(%)	0.1	0.00005
Mg	(%)	0.01	0.00001
SO4	(%)	0.4	0.003
Insolubles	(%)	0.5	0
Moisture	(%)	7	0.02
NaCl (dry basis)	(%)	98.9	99.996

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Membrane Plant Operation with Salt A and B

		Washed Salt A	Ultrapure Salt B
Salt cost	(EUR/y)	14’820’000	23’010’000
Salt handling labour	(EUR/y)	330’000	300’000
Fuel	(EUR/y)	40’000	0
Salt handling maintenance	(EUR/y)	80’000	120’000
Process water	(EUR/y)	20’000	330’000
Brine purification chemicals	(EUR/y)	1’170’000	50’000
Primary brine purification power	(EUR/y)	330’000	0
Primary brine purification labour	(EUR/y)	330’000	0
Primary brine purif. maintenance	(EUR/y)	300’000	0
Solids disposal	(EUR/y)	770’000	0

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Membrane Plant Operation with Salt A and B

		Washed Salt A	Ultrapure Salt B
Nanofiltration plant cost	(EUR/y)	800’000	0
Nanofiltration power	(EUR/y)	120’000	0
Nanofiltration refrigeration water	(EUR/y)	20’000	0
Nanofiltration treated water	(EUR/y)	40’000	0
Nanofiltration reactants	(EUR/y)	50’000	0
Nanofiltration membrane replacement	(EUR/y)	40’000	0
Nanofiltration plant maintenance	(EUR/y)	60’000	0
Bromine removal	(EUR/y)	1’500’000	0
Ferrocyanide removal	(EUR/y)	0	0
Iodine removal	(EUR/y)	0	0

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Membrane Plant Operation with Salt A and B

		Washed Salt A	Ultrapure Salt B
Power consumption differential	(EUR/y)	0	- 830'000
Hydrochloric acid differential	(EUR/y)	0	- 980'000
Membrane life differential	(EUR/y)	0	- 220'000
Plant depreciation differential	(EUR/y)	0	- 720'000
Total	(EUR/y)	21'060'000	21'060'000
Salt delivered cost	(EUR/t)	27.25	46.58
Salt price differential	(EUR/t)	-	+ 20.33
Salt price differential	(%)	-	+74.6%

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Conclusions:

- Ultrapure salt makes primary brine purification redundant
- With ultrapure salt ,anion removal systems are not required
- With ultrapure salt, membrane life of up to 8 years is possible
- With ultrapure salt, plant operating cost is reduced
- With ultrapure salt, plant extra capacity is not required
- With ultrapure salt, loss of production is avoided
- Ultrapure salt can be EUR 20.33 / t or 74.6% more expensive than washed salt for the same chlorine production economy calculated in the example
- Each case must be examined considering specific costs

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Mabuhay Vinyl, Philippines	Arabian Chlorine, Saudi Arabia	Abadan Petrochemical, Iran	DSW, Israel

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Why not turn your salt into gold?

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