

Salt Partners

High purity salt for membrane chloralkali electrolysis: What exactly does it mean?

Vladimir M. Sedivy MSc (Hons) Chem Eng, IMD

President

Salt Partners Ltd, Zurich, Switzerland

The presentation is broadcasting on YouTube under the following link:

<https://youtu.be/o9tfvxxczu0>

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Salt production world-wide

Salt type	World production
Solar salt	100'000'000 t/y
Rock salt	100'000'000 t/y
Brines	100'000'000 t/y
Total	300'000'000 t/y

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Salt consumption world-wide

Salt user	Salt consumption
Chemical industry	180'000'000 t/y
Food	60'000'000 t/y
Other	60'000'000 t/y

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Salt Purities

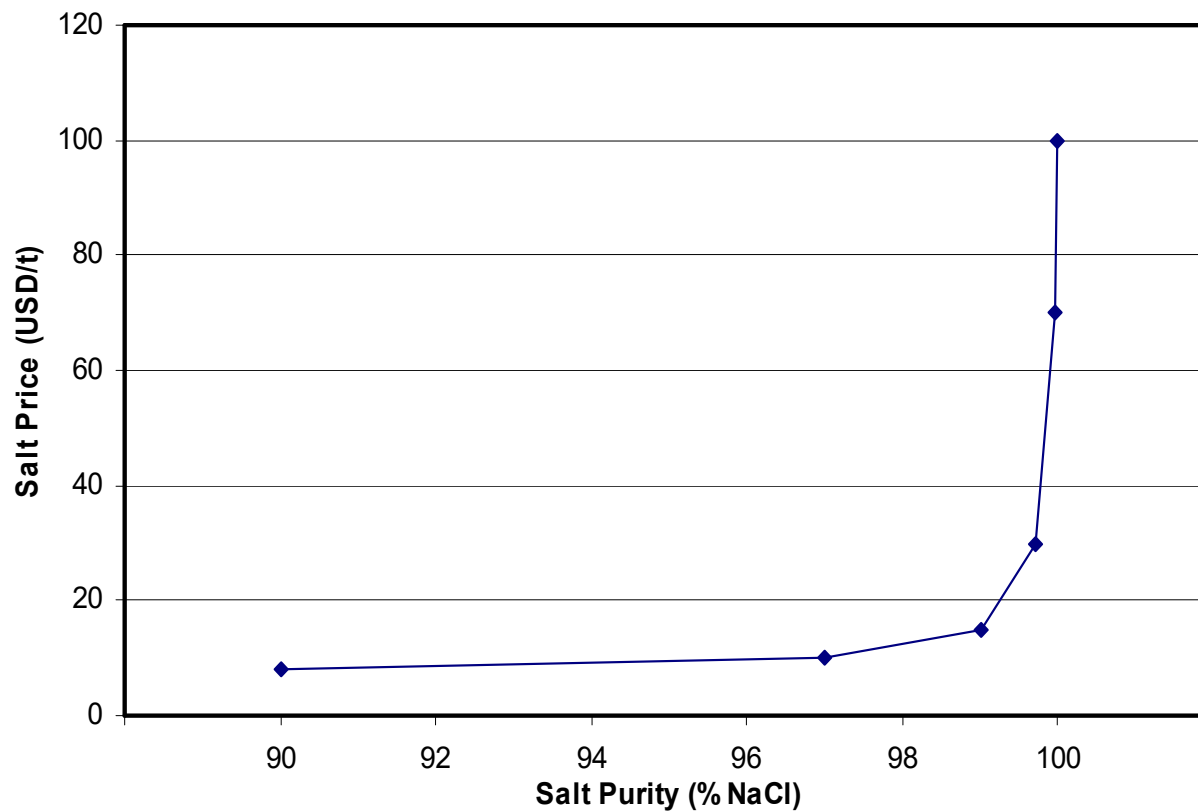
NaCl Purity (%)

Rock salt	90 - 97
Crude sea salt	97 - 99
Washed sea salt	99 – 99.5
Purified sea salt	99.5 – 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

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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 2018

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), THC (Total Hydro Carbons), 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

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	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 (Chlorine) Caustic and Chlorine from Salt

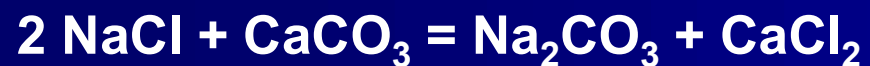


119	36	82	71	2
1.45		1		
1.68			1	

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The Basic Chloralkali Equation (Soda)

Soda Ash from Salt and Lime



119

110

111

120

1.1

0.93

1

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Why must brine for chloralkali manufacture be pure?

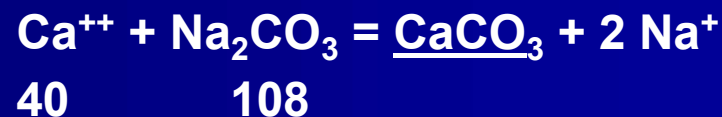
- Membrane damage in membrane cells
- Hydrogen evolution in Hg-cells
- Incrustations in soda ash production
- Contaminated effluents
- Bromine in chlorine for organic synthesis
- etc.

Brine for chloralkali manufacture must be purified.

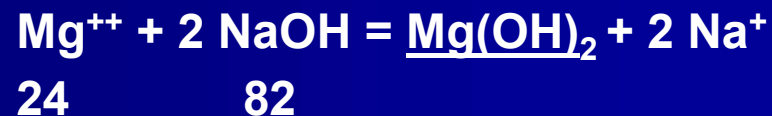
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Brine Purification: Ca and Mg Precipitation

Calcium precipitation



Magnesium precipitation



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Brine Purification: Overdosing of Reagents

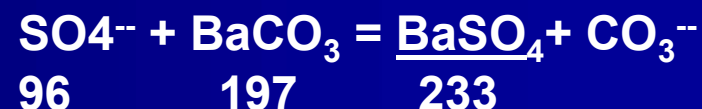
For calcium precipitation 0.4 kg Na_2CO_3 per m3 of brine

For magnesium precipitation 0.15 kg NaOH per m3 of brine

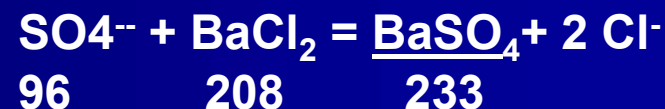
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Brine Purification: Sulphate Removal

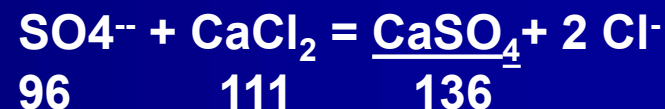
With BaCO_3



With BaCl_2



With CaCl_2

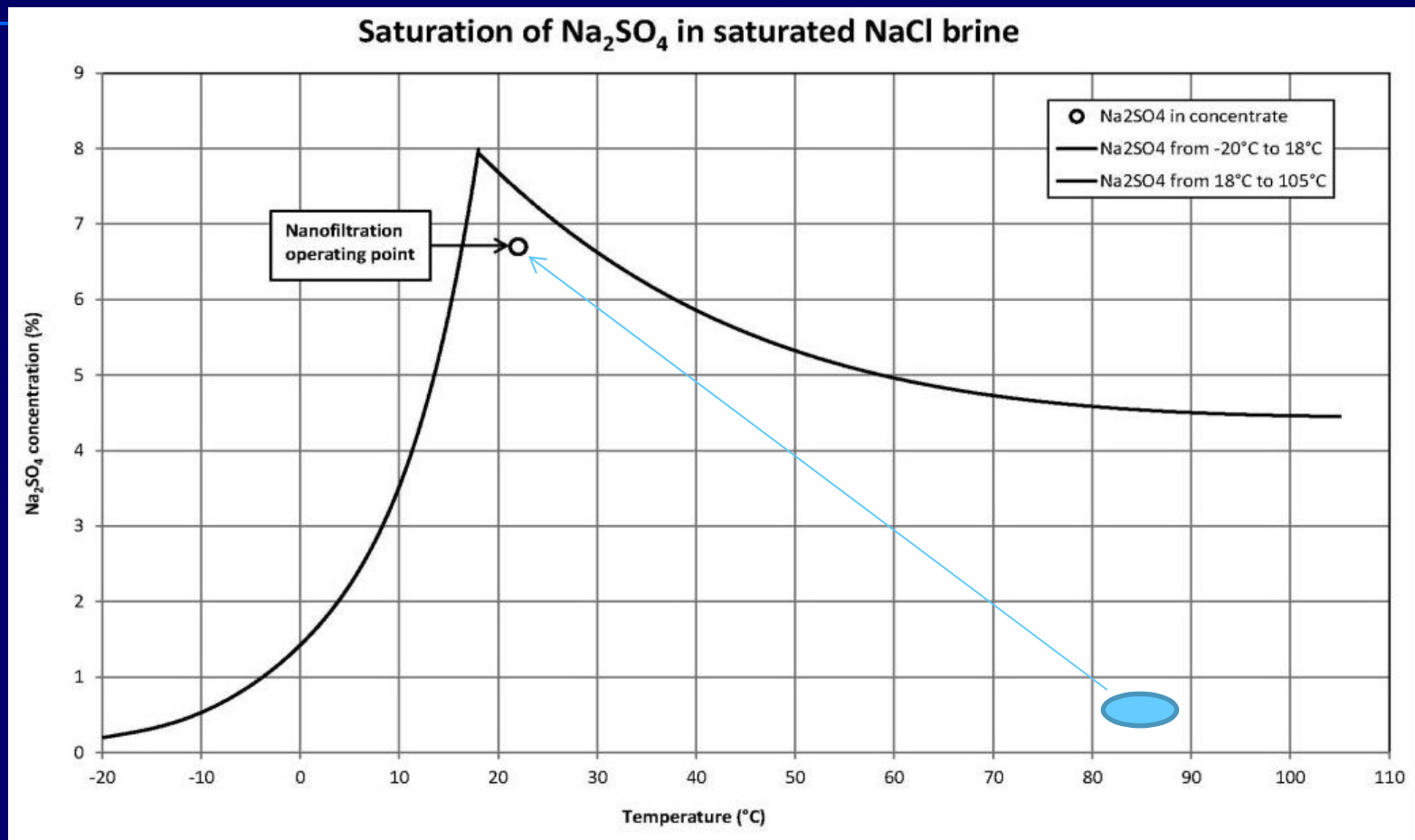


With Nanofiltration

From 4 – 8 g/l to 80 g/l in purge
as Na_2SO_4

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Nanofiltration Operating Point



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Salt Partners Cost Survey Contributors

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SNEP, Morocco	Proinsal, Argentina	Solvay, Spain	Modi, India
Enichem, Italy	GACL, India	Grasim, India	Saukem, India
Standard Alkali, India	Bandar Imam, Iran	Chemfab, India	Century, India
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	60

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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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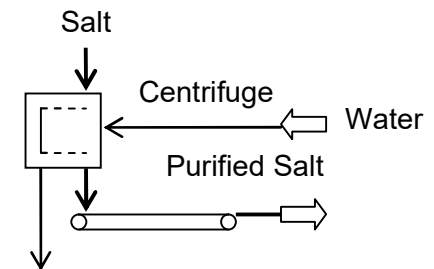
Principles of HYDROSAL Process

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**Centrifuge separates
salt and brine**

**Conventional
washing with water in
the centrifuge**

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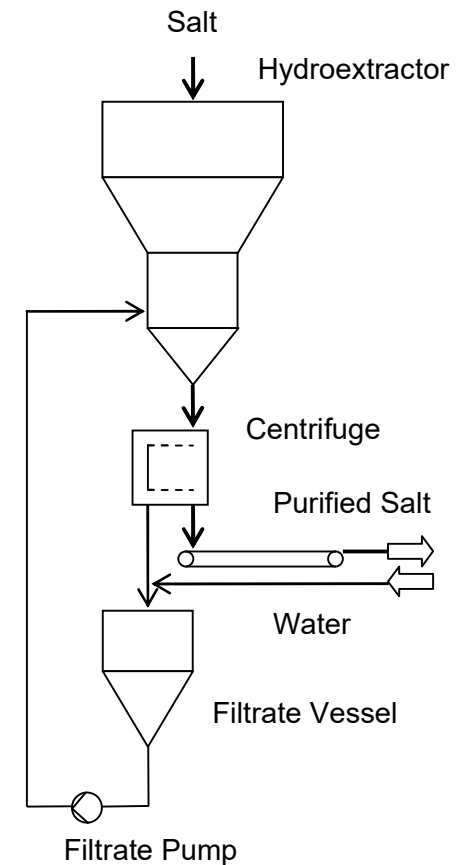
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HYDROSAL Process

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

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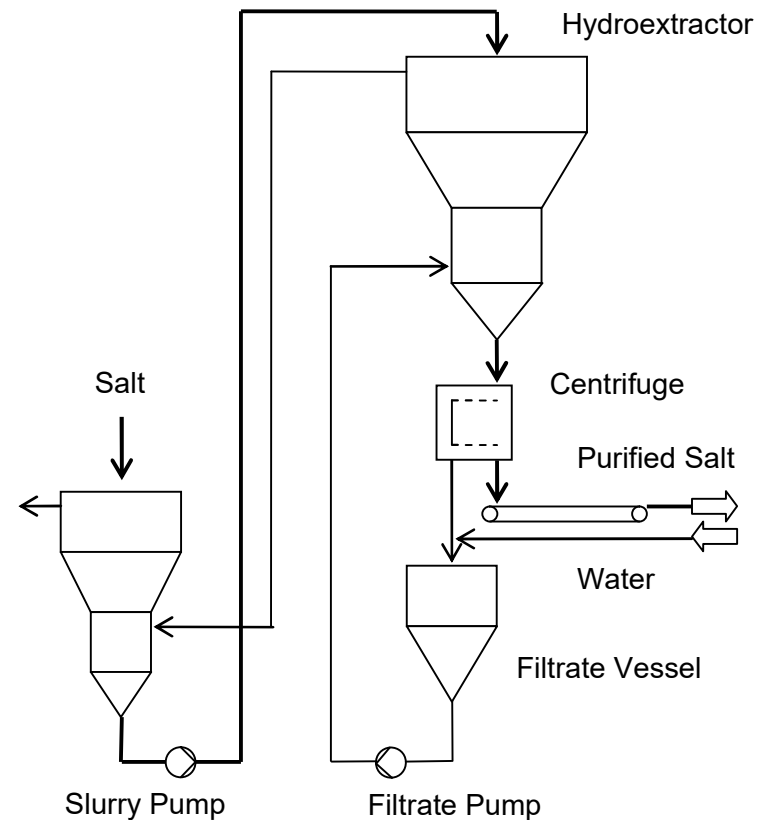
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HYDROSAL Process

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

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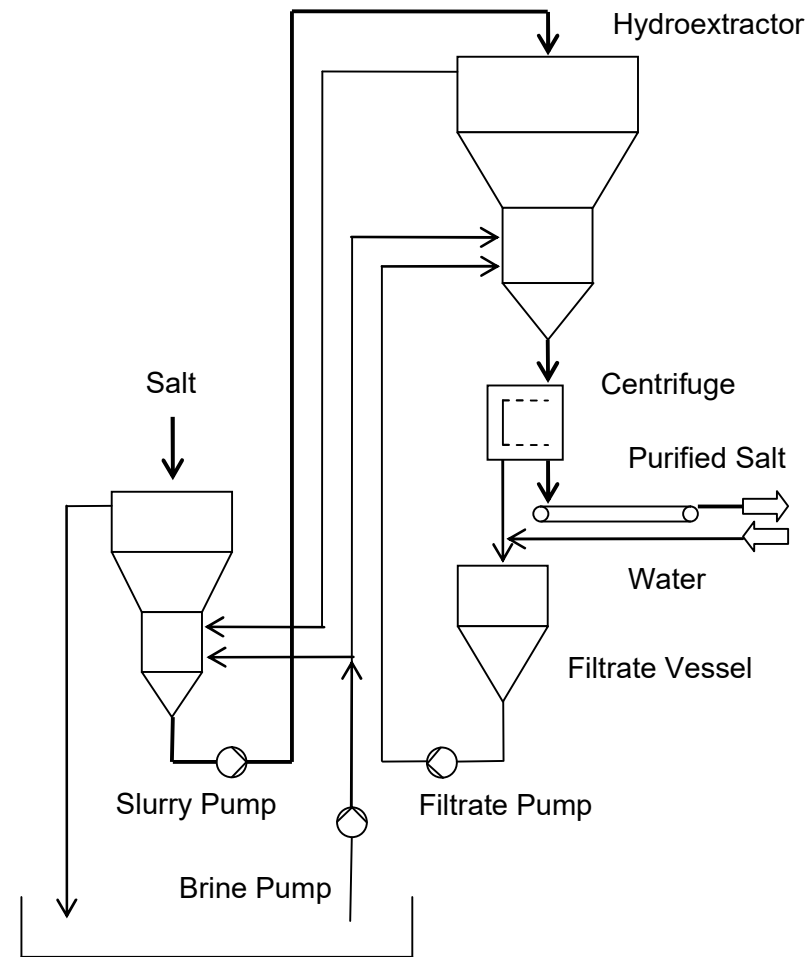
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HYDROSAL Process

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**Circulate impure
brine to control
hydroclassification
and elutriation
efficiency**

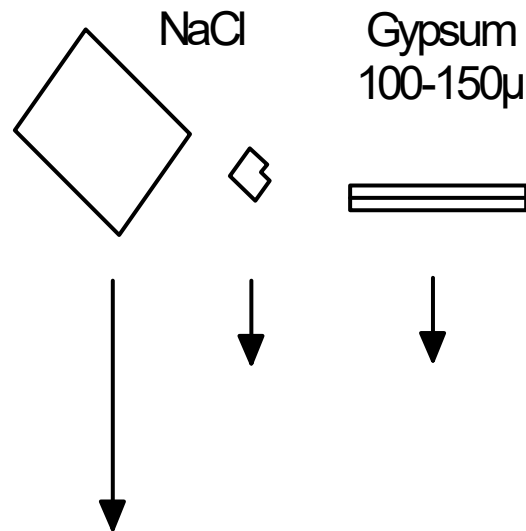
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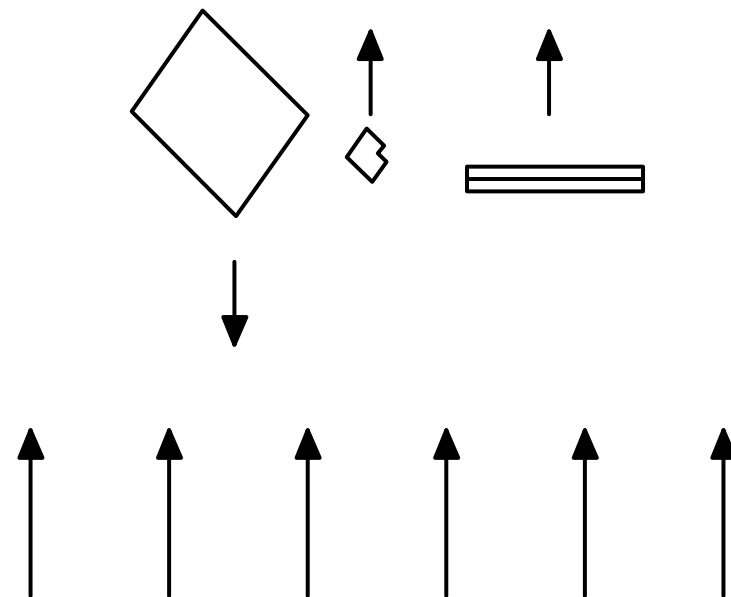
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Elutriation

Settling velocities in brine



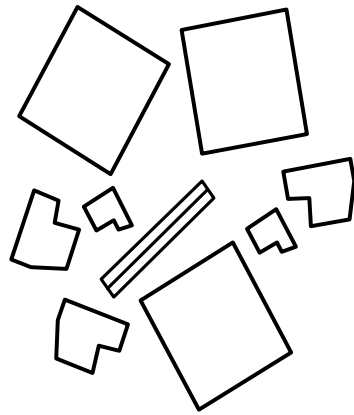
Elutriation in upwards flowing brine



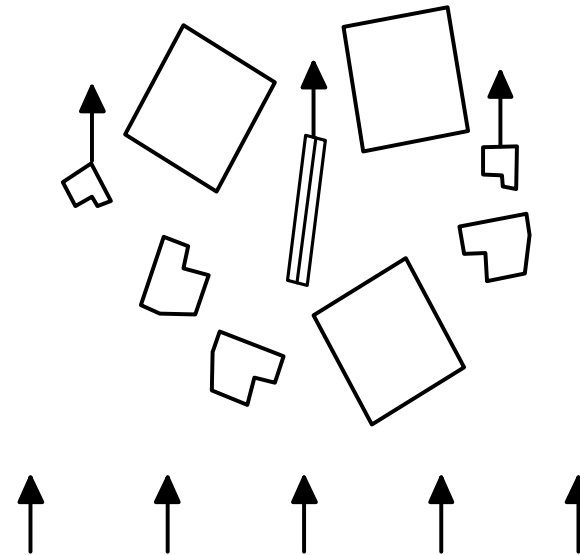
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Hydroclassification

Salt bed with buried impurities

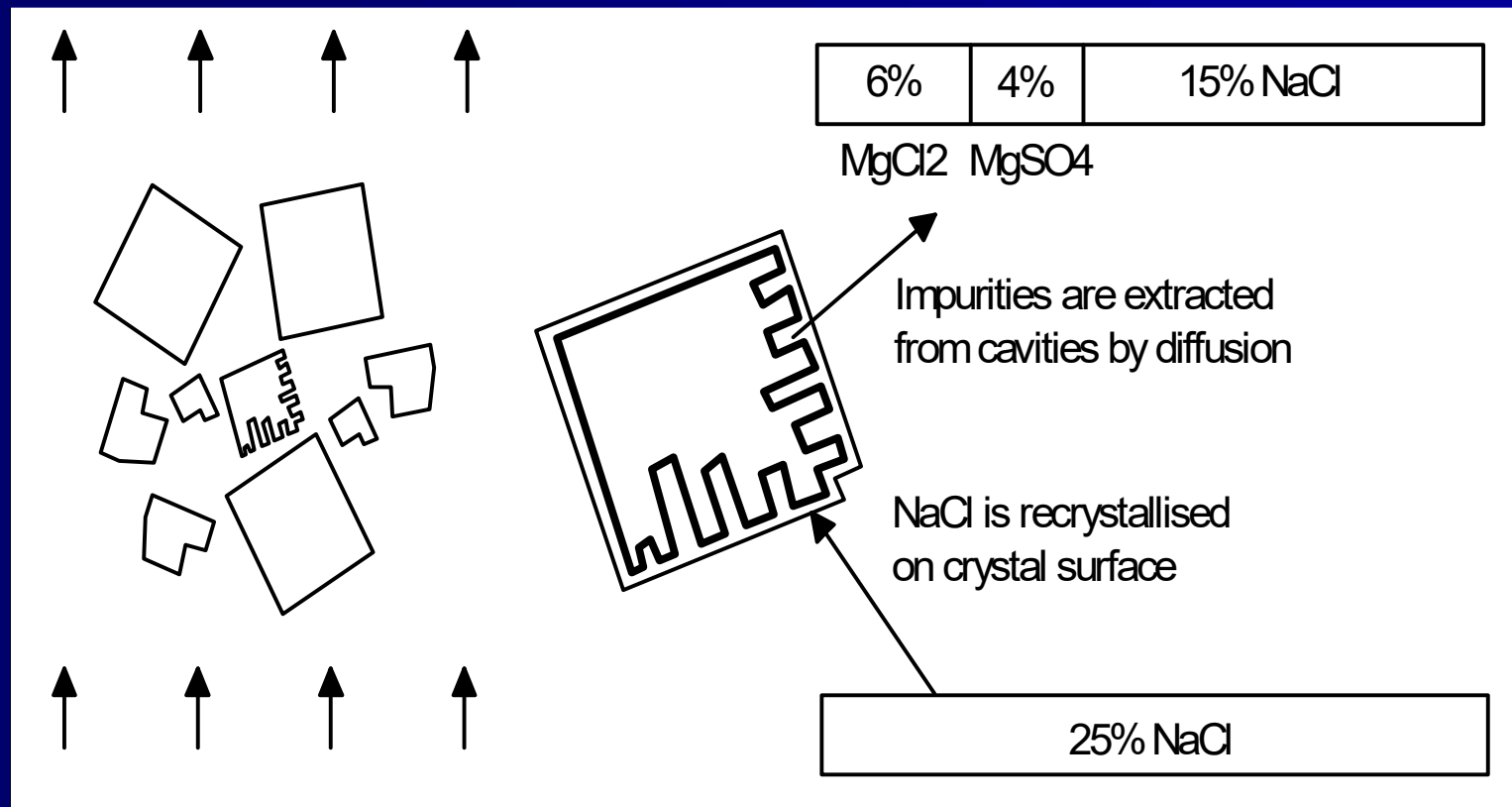


Hydroclassification of impurities in partially fluidised salt bed



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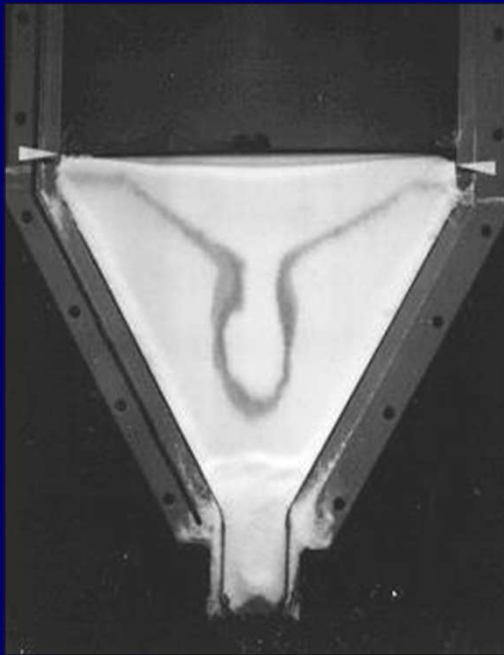
Hydroextraction



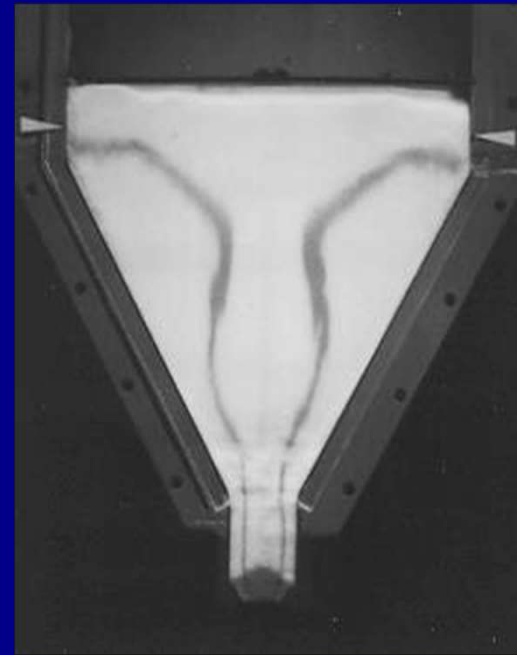
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Hydroextraction does not work in all vessels

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In this vessel salt flows out mainly through the centre

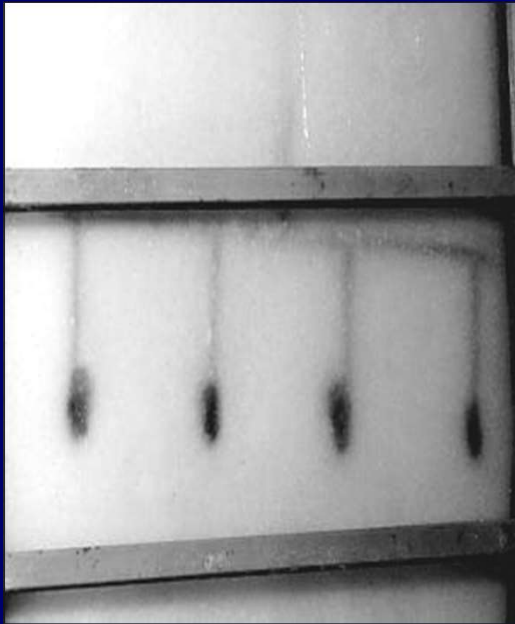


So called rat hole develops in the centre of the vessel

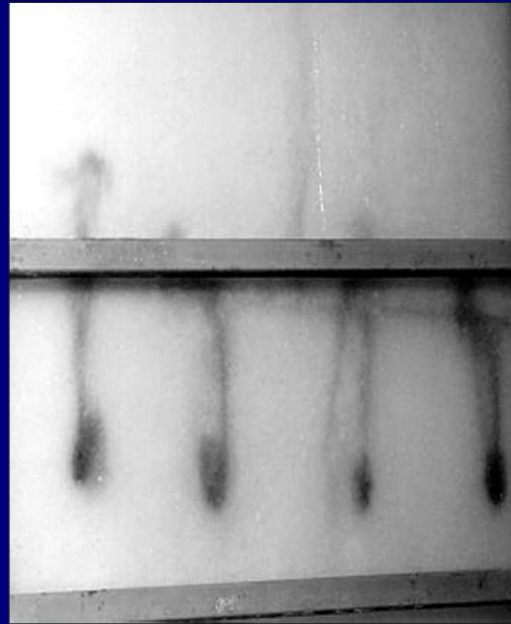
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Hydroextraction works only with plug flow of salt

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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, purification and refining plant

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**40 t/h salt purification
plant producing ultrapure
industrial salt**

		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**
- **High Purity Salt without Bromine, Iodine and Ferrocyanide**
- **High Purity 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	0.005
Insolubles	(%)	0.5	0
Moisture	(%)	7	0.02
NaCl (dry basis)	(%)	98.9	99.995

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Membrane Plant Operation with Salt A and B

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		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

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		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

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		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
Salt price differential	(%)	-	+75

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Conclusions:

- High purity salt makes primary brine purification redundant
- With pure salt ,anion removal systems are not required
- With pure salt, membrane life of up to 8 years is possible
- With pure salt, plant operating cost is reduced
- With pure salt, plant extra capacity is not required
- With pure salt, loss of production is avoided
- High purity 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

Why not turn your salt into gold?



Vladimir M. Sedivy
Salt Partners Ltd, Erlenbach ZH, Switzerland

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