Glass Performance Days 2025

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GLASS PERFORMANCE DAYS 2025

Chemical strengthening of Silicate Glasses by Ion Exchange: the role of Alkali Nitrate Salts.

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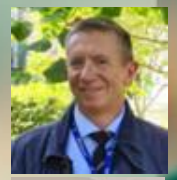

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OUTLINE:

- ✓ Relevance of Chemically Strengthened Glass by Ion Exchange (IX): Products & Applications.
- ✓ Ion Exchange (IX) for chemical strengthening of silicate glass: Theory & Mathematical Model.
- ✓ The Alkali Nitrate Salt (namely KNO_3): industrial production and chemical characterization for IX.
- ✓ Experimental methods.
- ✓ Results of comparison with different types of industrial KNO_3 salts.
- ✓ Conclusion.

Why Chemical Strengthening of Glass by Ion Exchange ?

Ion Exchange (IX) is a silicate glass processing approach with the capability to modify: Mechanical, Optical and Electrical properties of a formed silicate glass article.

IX consists in the interdiffusion controlled removal of ions located within the glassy matrix with their replacement with other ions coming from an external ions source (usually an alkali molten salts).

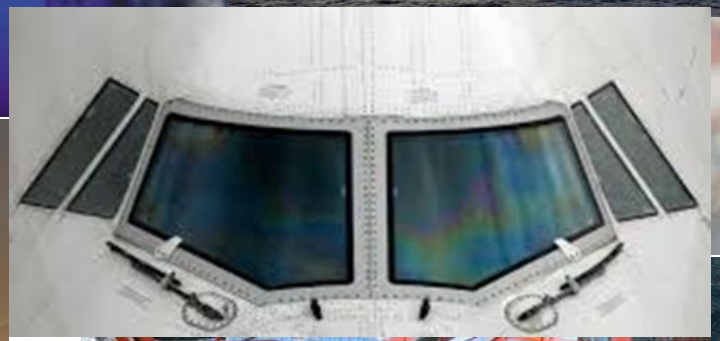
When the incoming ion has a larger molar volume in respect to the removed one, and the process is performed below the transition temperatures range, uncompensated strain generates stress effects resulting in an equibiaxial residual stress characterized by a near surface compression balanced by an inner tensile satus.

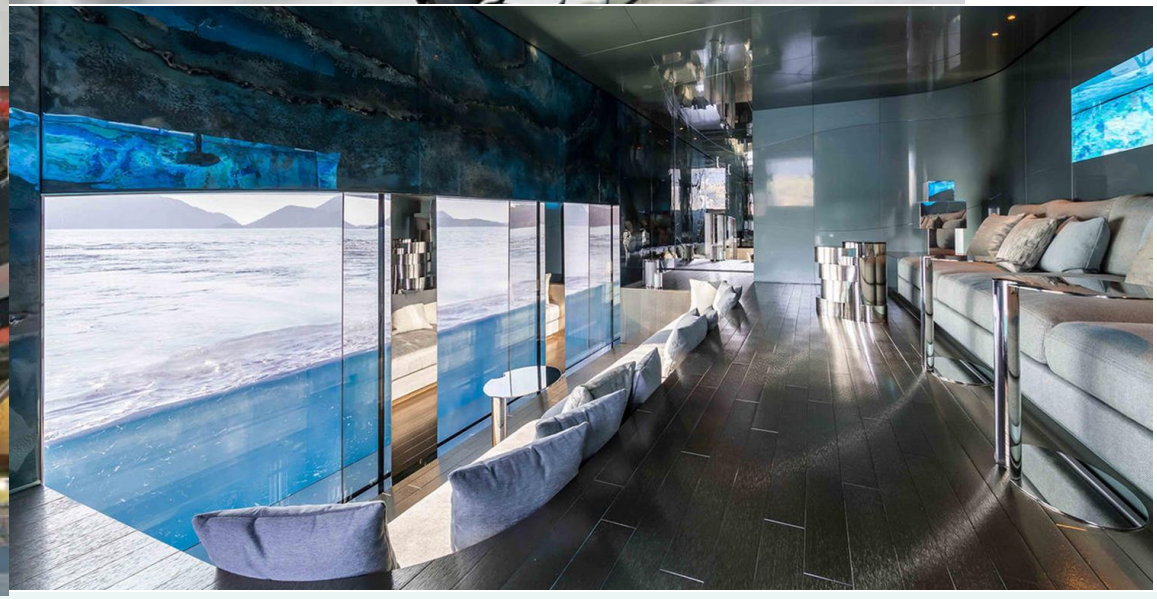
The near surface compression layer works against the growth, propagation and generation of surface flaws resulting in an effective increase of glass strength under bending.

Chemical strengthening has the advantages to have practically no limitations in respect to thickness and shape of glass articles and results in a superior optical quality.

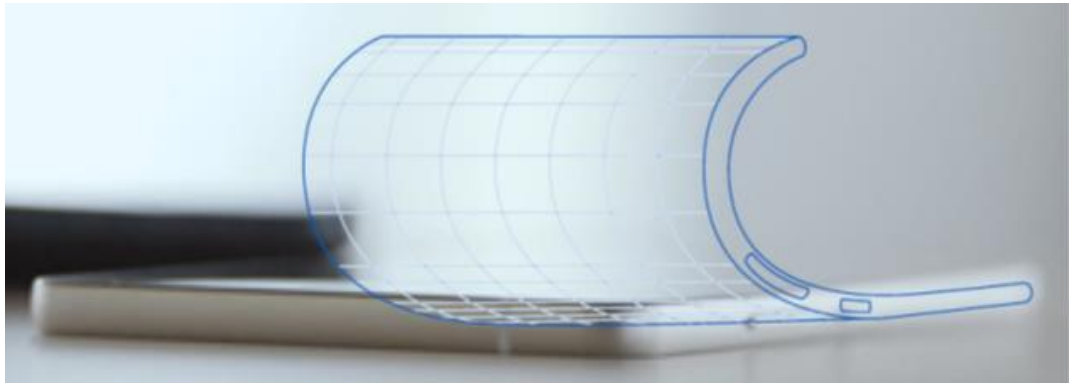
Industrial applications of IX for glass chemical strengthening can be dated back to the sixties of last century and it is presently widely used in a number of glass and glazing applications.

Applications: Transportation and Architectural



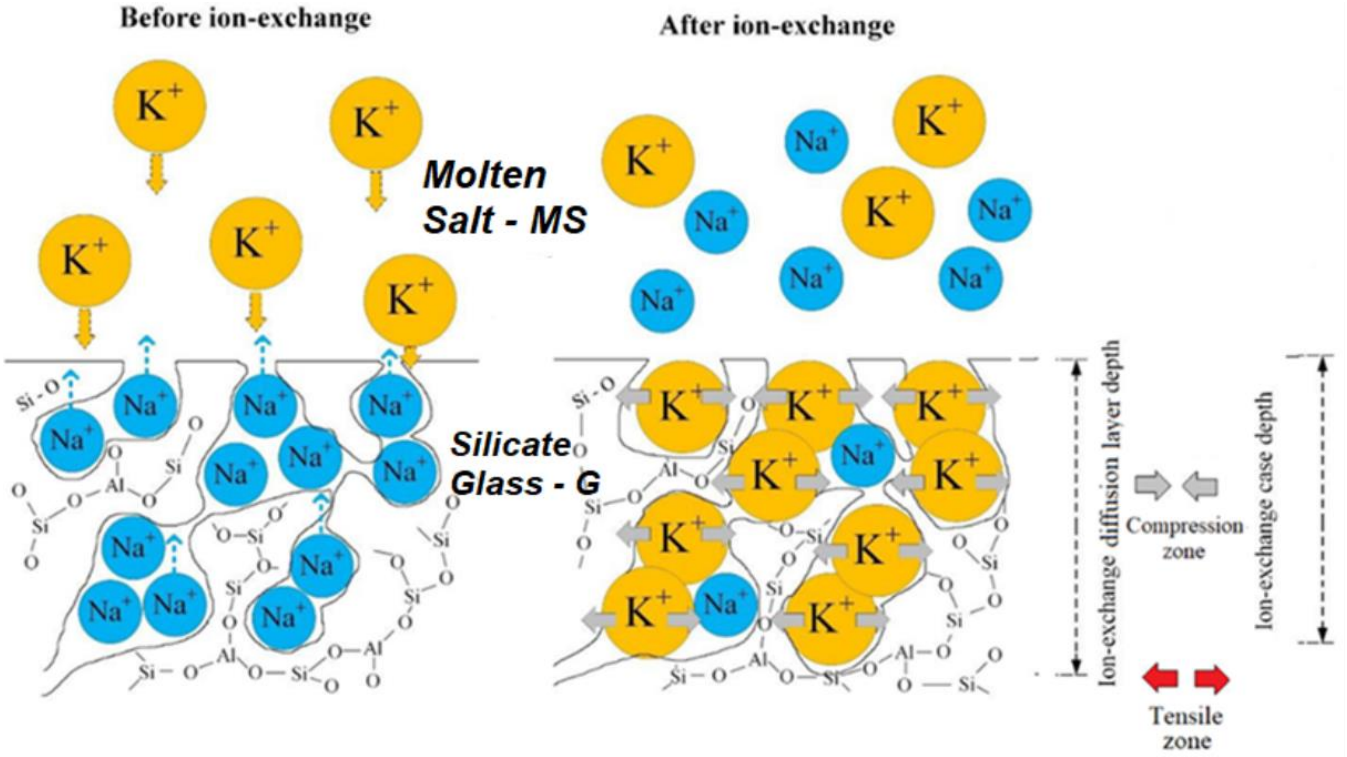


Applications: Thin and Ultra Thin Glass for Consumer Electronics, Pharma vials.



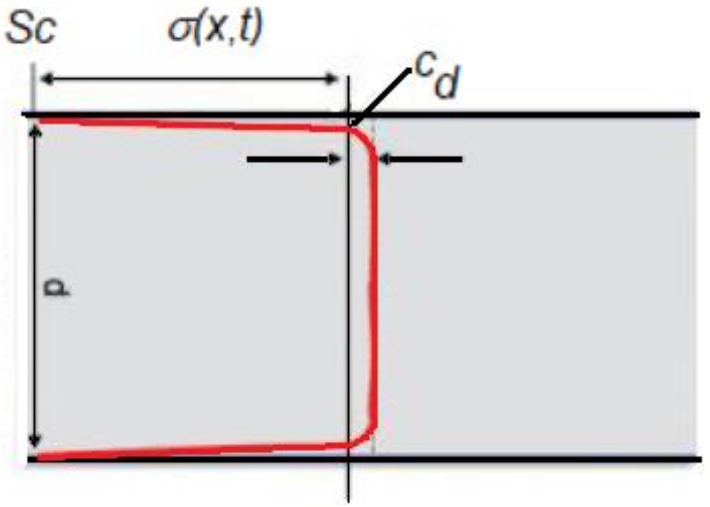
Ion Exchange for Glass Strengthening

Equimolar chemical reaction – N - Number of exchanged moles



$$Na_G^+ + K_{MS}^+ \leftrightarrow Na_{MS}^+ + K_G^+$$

$$\Delta W = N \cdot [M_{WK} - M_{WNa}]$$



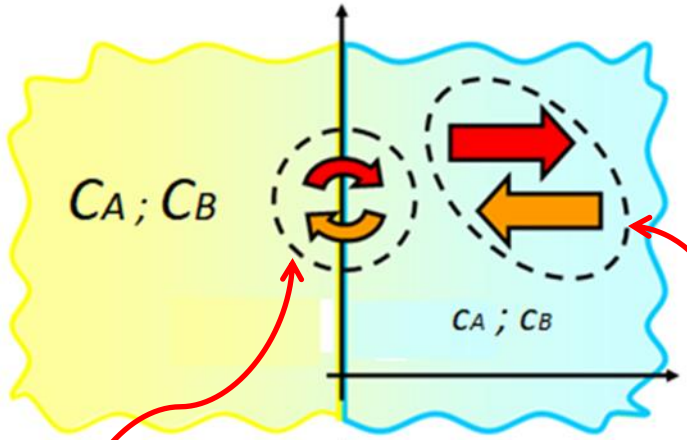
Thermodynamics & Kinetics of Ion Exchange

The Ions Flux

$$J(x,t) = -D\frac{\partial C(x,t)}{\partial x}$$

$$F_{KNa} = \int_0^{t_t} J(0,t)dt = 2 \cdot C_s\sqrt{D \cdot t_t/\pi}$$

A-Na^+
B – K^+



Thermodynamic Equilibrium Process at Surface
τ << t_t
IX Immersion/Process time – t_t
Time to reach equilibrium at surface - τ

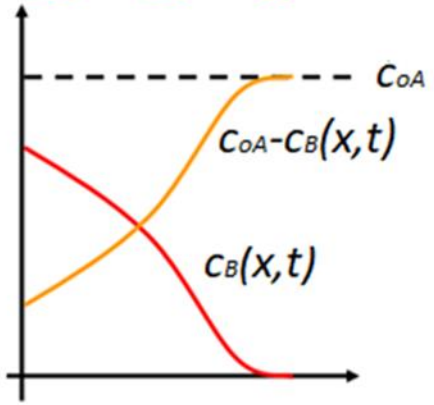
C_s

The Interdiffusion Coefficient

$$D = \pi/t_t\left(F_{KNa}/(2 \cdot C_s)\right)^2$$

Kinetic Transport Process in Glass Matrix

D



The Ions Concentration

$$C(x,t) = C_s \cdot erfc\left(x/(2 \cdot \sqrt{D \cdot t})\right)$$

$$C_{ave}(t_t) = 1/d\int_0^d C(x,t_t)dx = 4 \cdot C_s/d \cdot \sqrt{D \cdot t_t/\pi}$$

The Strengthening Parameters:

a first approximation Mathematical Model (Relaxation effects are excluded)

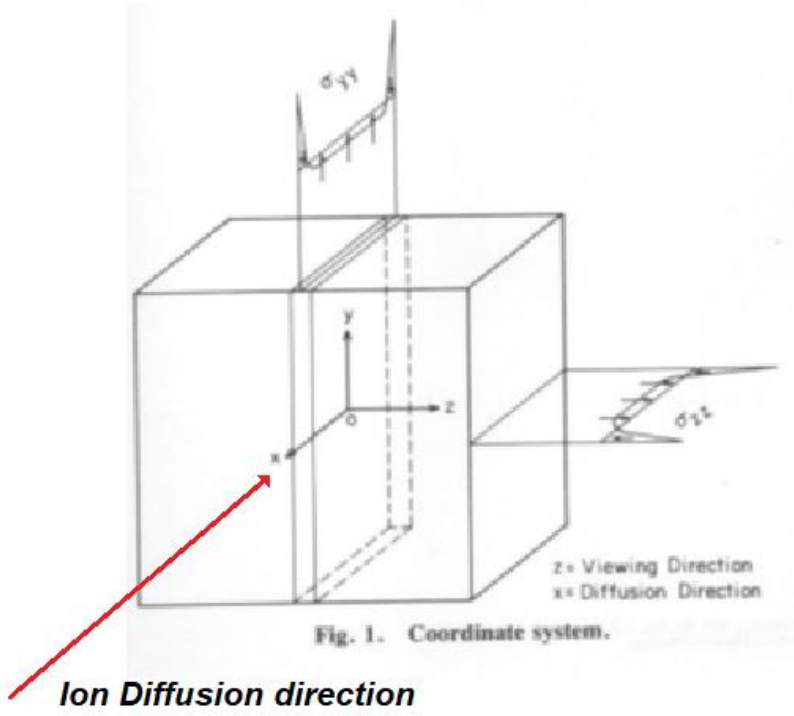
Residual equi-biaxial stress – σ(x,t)
Surface Compression – Sc (MPa)
Central Tension – Ct (MPa)
Depth of Compression – C_d (μm)

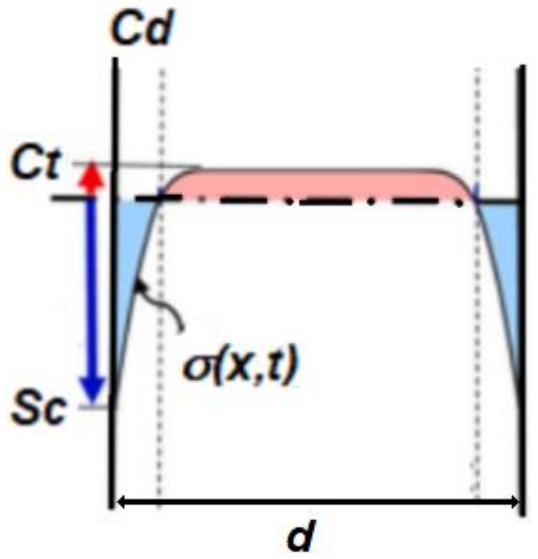
$$\sigma(x,t) = -{}^{B \cdot E}/_{(1-v)} \cdot \left(C(x,t) - C_{avg}\right)$$

$$Sc = \sigma(0,t) = -{}^{B \cdot E}/_{(1-v)} \cdot \left(Cs - C_{avg}\right)$$

$$\sigma(Cd,t) = 0 \quad \Rightarrow \quad C(C_d,t) = C_{avg}$$

$$erfc\left({}^{C_d}/_{\left(2 \cdot \sqrt{D \cdot t}\right)}\right) = {}^{C_{avg}}/_{C_s}$$

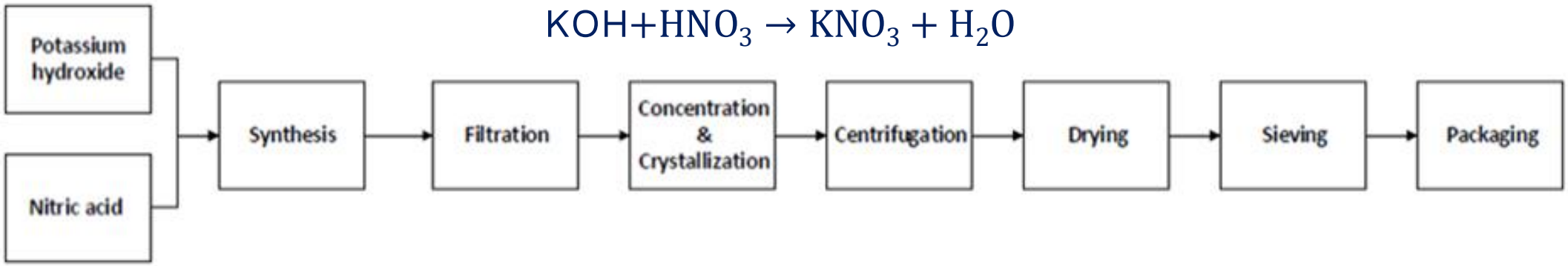




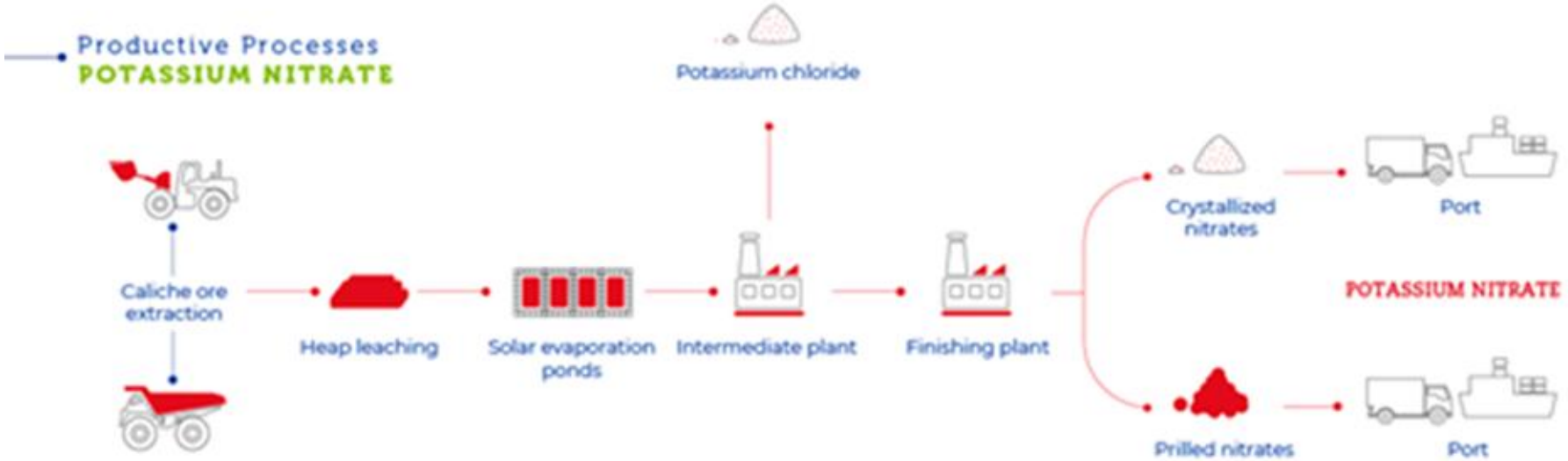
Industrial Production of Potassium Nitrate

Chemical Synthesis:

$$KOH + HNO_3 \rightarrow KNO_3 + H_2O$$



Mines Extraction:



Typical analysis of KNO_3 – Qemical ID:145804 (KNO_3-Synt).

Determination	Results	[units]
Assay (Acidim,dried basis)	100.0	(%)
Chlorides (Cl)	<0.002	(%)
Sulphates (SO4)	<0.010	(%)
Arsenic (As)	<0.0002	(%)
Iron (Fe)	<0.0005	(%)
Heavy Metals (as Pb)	<0.0005	(%)
Sodium (Na)	<0.1	(%)
Calcium (Ca)	<0.005	(%)
Magnesium (Mg)	< 0.002	(%)

Alkali Nitrate Salts Evaluation

Chemical analysis is not sufficient –˝You find what you are looking for !˝
Direct functional IX test on small IX lab equipment
Test schedule – at least three temperatures [T_1,T_2,T_3] for a fixed immersion time (16 or 24 hours)

Determination of: D(cm^2/s) [T], Sc(MPa) & Cd (µm)

$\Delta W(g);\ F_{KNa}(mol/cm^2)$

$$F_{KNa} = {}^{N}/_{S} = {}^{\Delta W}/_{[S \cdot (M_{wK} - M_{wNa})]}$$

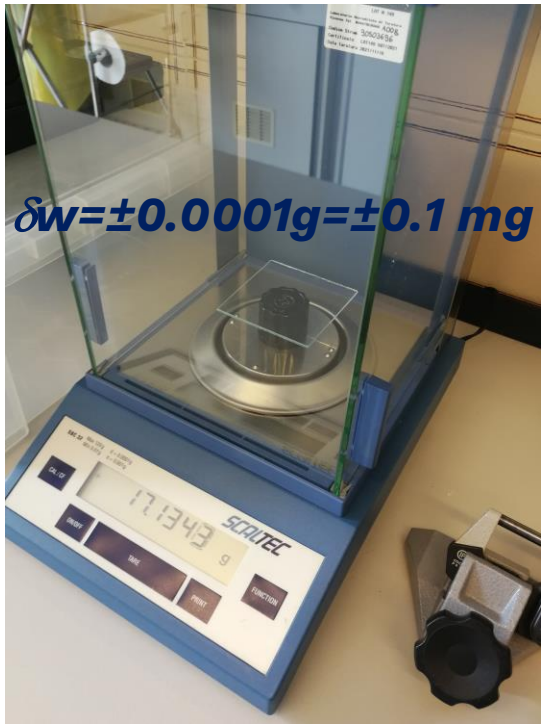
Samples - Different soda-lime glasses:

CF – 3mm - Clear Float,

EX – 3mm - Low Iron Float;

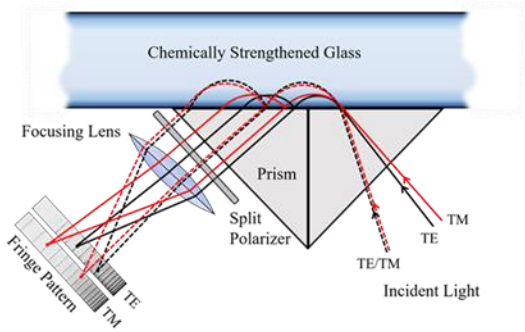
GE – 3mm - Body tinted Grey Float;

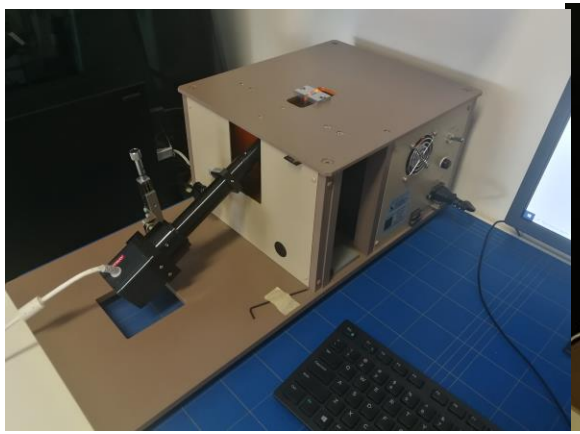
CFP – 1.6mm Clear Float for Process control)

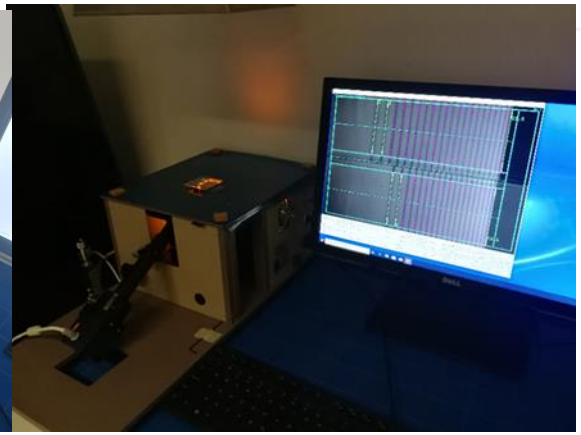


Characterization methods: Differential Surface Refractometry (DSR) and Weight Gain (WG)

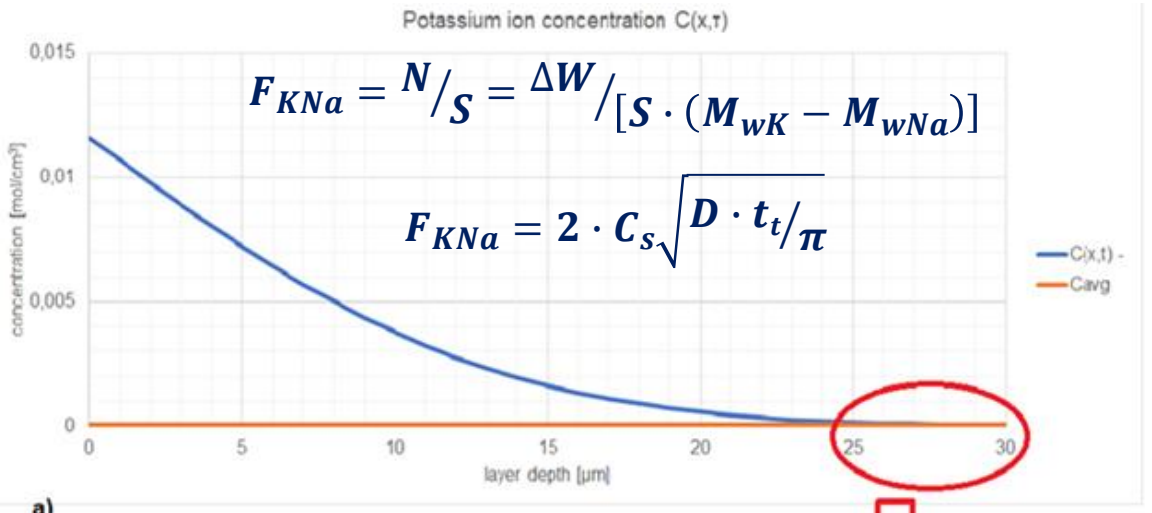
DSR:
FSM 6000
Sc(MPa) & Cd(μm) Determination

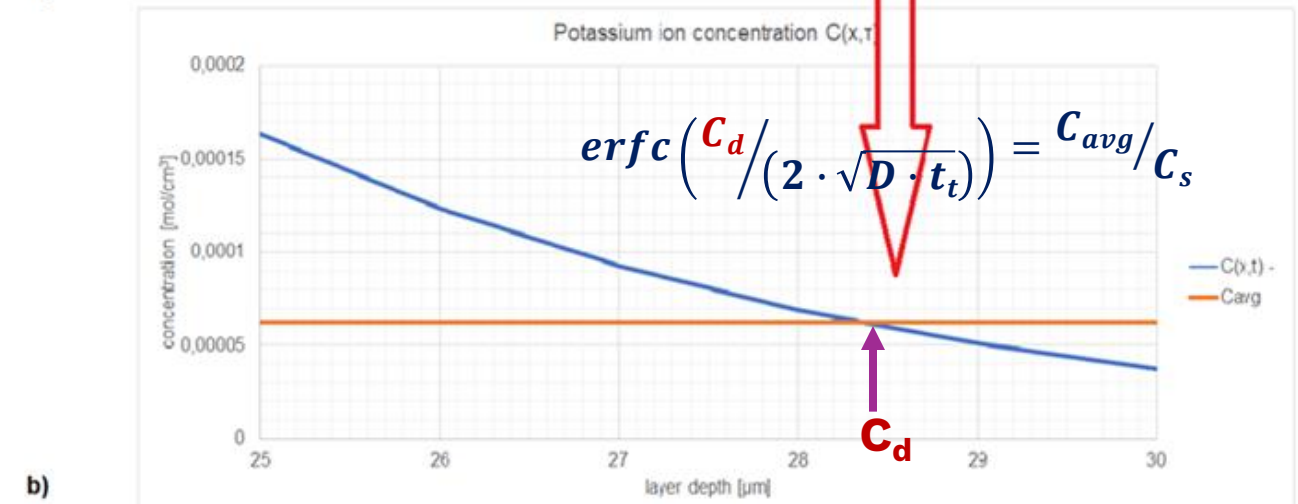






WG:
D (cm^2/s) & Cd (μm) Determination





RESULTS: Potassium Nitrate Salts Comparison

Strengthening characteristics [Sc(MPa and Cd(μm)] and chemical attack (Corr) on different soda-lime glasses (CF – Clear Float, EX – Low Iron Float; GE – Body tinted Grey Float; CFP – Clear Float for Process control) for two different salts: KNO_3 from Synthesis (KNO3-Synt.) and KNO_3 from mine extraction and prilled (KNO3-Prilled).

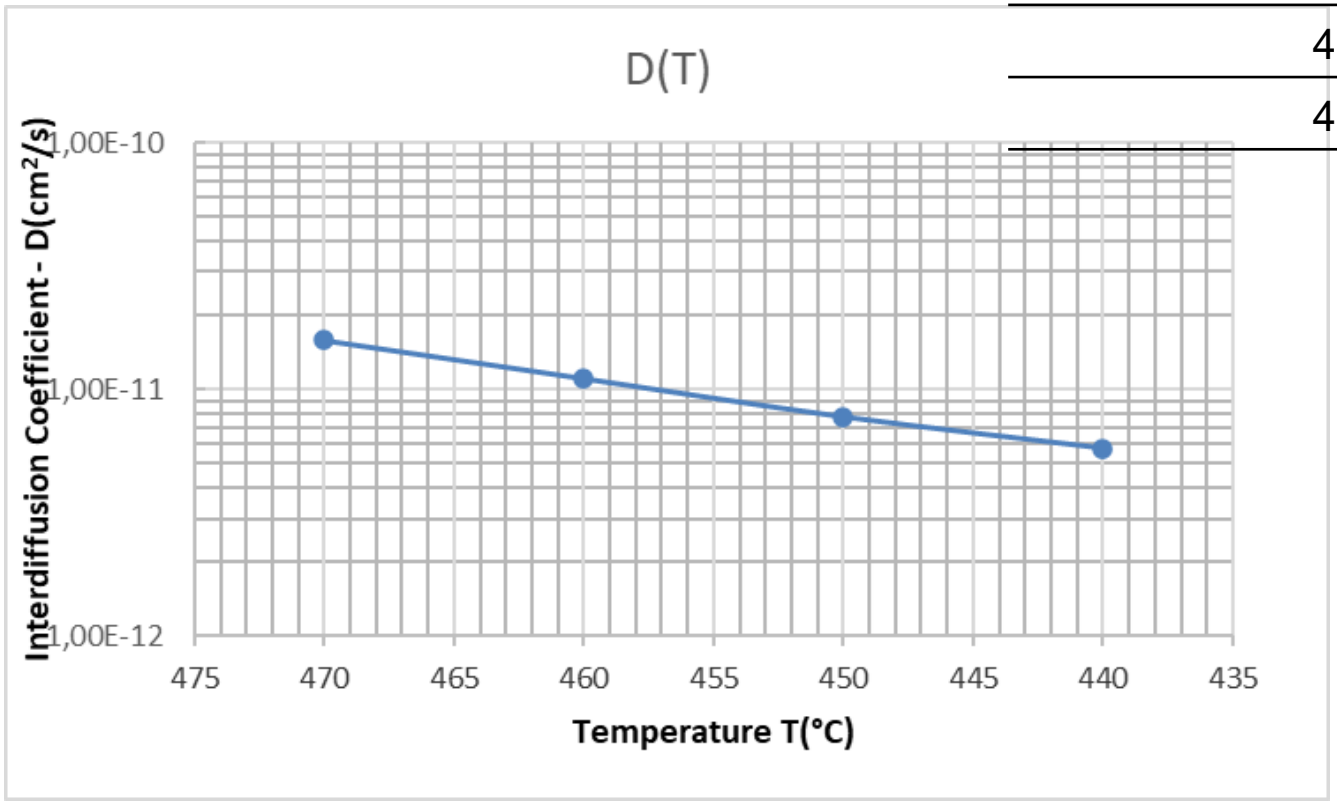
.Type of Glass→	CFP			CF			EX			GE		
Type of salt	**Sc**	**Cd**	**Corr**	**SC**	**Cd**	**Corr**	**Sc**	**Cd**	**Corr**	**Sc**	**Cd**	**Corr**
KNO 3- Synt	499	28.2	No	531	25.0	No	531	27.4	No	476	24,7	No
KNO3- Prilled	ND	ND	Yes	ND	ND	Yes	ND	ND	Yes	ND	ND	Yes

ND – Not Detectable

Interdiffusion Coefficient VS Temperature curve D[T]

$$D = D_0 \cdot exp\left(-{}^{Ea}/_{(R \cdot T)}\right)$$

Ion Exch.Temperature T (°C)	Interdiffusion coefficient D(cm^2/s)
440	$5.77 \cdot 10^{-12}$
450	$7.75 \cdot 10^{-12}$
460	$1.11 \cdot 10^{-11}$
470	$1.59 \cdot 10^{-11}$



$$D_0 = 0.568\ {}^{cm^2}/_{s}$$

$$E_a = 150.2\ {}^{kJ}/_{mol}$$

CONCLUSIONS:

- ✓ Chemically Strengthened Glass by Ion Exchange is a silicate glass processing of industrial relevance presently used mainly in: transportation and architectural glazing, consumer electronics and pharma (vials, ampoules) applications.
- ✓ Technological characteristics of IX Chemical strengthening (Surface compression Sc(MPa) and compression layer depth Cd(μm)) have been identified.
- ✓ The quality of Alkali Nitrate Salt (namely KNO_3) is of paramount relevance for the process efficiency.
- ✓ Methods to characterize and qualify KNO3 salts have been proposed
- ✓ Results have been presented where KNO_3 by chemical synthesis exhibits superior characteristics in comparison with mine sourced and prilled KNO_3.
- ✓ The characterization of the KNO_3 salt in terms of D(T) allows to build-up a mathematical model to predict chemical strengthening parameters at different temperatures and immersion times.