

Corrosion Behavior of High-Chromia Refractories in Waste Glasses

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PRAGUE**

Motivation

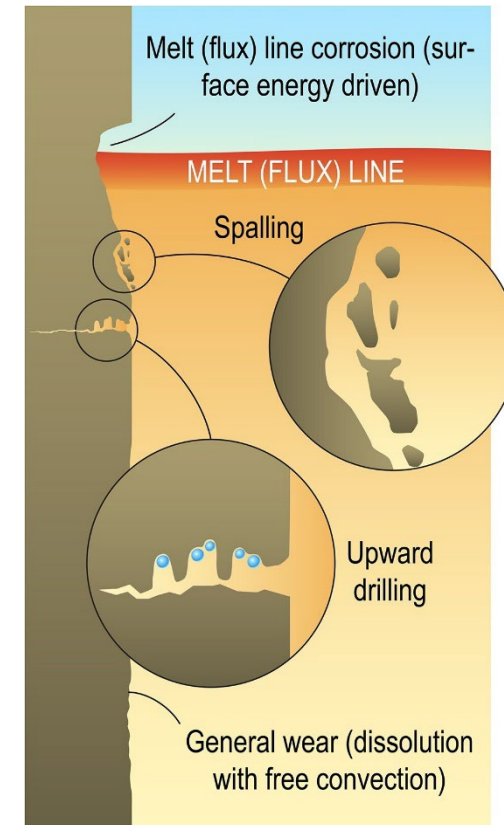


UCT PRAGUE

- ▶ Corrosion of refractory material is critical for the reliability and lifetime of all-electric melters during both glass melting and nuclear waste vitrification.
- ▶ This work evaluates both subsurface (submerged) and melt-line (neck) corrosion behavior of Monofrax K-3 refractory in contact with LAW glass melts subjected to forced convection.
- ▶ Our goal is to develop corrosion model simulating effect of melt flow rate, temperature and glass composition, which will be implemented to CFD melter model.
- ▶ Corrosion behavior of AZS and sintered high chromia refractories.



Corrosion damage of Monofrax® K-3 refractory lining of production melters: DWPF Melter 2 (left) [1], and SRS M-Area DM5000A (right) [2]



Representation of typical refractory wear processes [1].

[1] Iverson DC, Imrich KJ, Bickford DF, et al. Examination of DWPF melter materials after 8 years of service. Ceram Trans. 2004;155:217-226.

[2] Jantzen CM., WSRC-TR-97-0061, Rev. 1. Westinghouse Savannah River Company, Savannah River Site, Aiken, SC, USA, 1999.

High-Alkali Boro-Aluminosilicate Glasses

- ❑ Vitrification of LAW or HLW (Al-19)
- ❑ Total content of alkali oxides Na_2O , K_2O , Li_2O : 19.0-24.3 wt.%.
 - ❑ HLW Al-19 glass: 13.29 wt.%
 - ❑ η at 1150°C: 1.09 – 5.86 Pas
 - ❑ ρ at 1150°C: 2.46 – 2.63 g/cm³
 - ❑ T_i : 464 - 483°C

Component	LORPM14R1	ORLEC9	ORLEC33	ORLEC52	IDMSref*	ORPLA14	Al-19
Al ₂ O ₃	5.57	7.8	9.23	9.92	5.39	10.7	23.97
B ₂ O ₃	7.546	10	11	11	7.2	7.2	19.19
BaO	0.00025	--	--	--	0.12	--	0.05
Bi ₂ O ₃	--	--	--	--	--	--	1.14
CaO	9.792	9.17	2.5	1.95	0.93	2.05	5.58
CdO	0.00025	--	--	--	--	--	0.02
Cl	0.020005	0.2	0.2	0.2	0.23	0.66	--
Cr ₂ O ₃	0.008035	0.08	0.08	0.2	0.19	0.5	0.52
Cs ₂ O	--	--	--	--	--	0.17	--
CuO	--	--	--	--	0.21	--	--
F	0.007485	0.08	0.08	0.08	0.04	--	0.67
Fe ₂ O ₃	2.395	1	0.2	0.2	10.27	0.94	5.9
K ₂ O	4.726	0.5	0.5	0.5	2.14	0.53	0.14
Li ₂ O	3.611	2.48	--	--	4.49	--	3.57
MgO	3.5	1	1	1	1.38	0.94	0.12
MnO	--	--	--	--	2.21	--	--
Na ₂ O	13.273	16	23	23.8	9.01	23.5	9.58
Nd ₂ O ₃	--	--	--	--	0.39	--	--
NiO	0.00075	0.01	0.01	0.01	0.92	--	0.4
P ₂ O ₅	0.012475	0.12	0.12	0.12	0.03	--	1.05
PbO	0.00075	0.01	0.01	0.01	--	--	0.41
SiO ₂	38.4	40.71	40.94	38.61	54.15	41.38	27
SnO ₂	3.622	--	--	0.8	--	2.78	--
SO ₃	0.24	1.47	1	0.9	0.23	0.18	0.2
SrO					0.02	--	--
TiO ₂	0.6	1	--	--	0.13	--	0.01
V ₂ O ₅	2.875	1.87	2.1	1.88	--	--	--
ZnO	1.8	3	3	3	0.21	2.47	0.08
ZrO ₂	2	3.5	5.03	5.83	0.13	6	0.39
Total	100	100	100	100.01	100.02	100	99.99

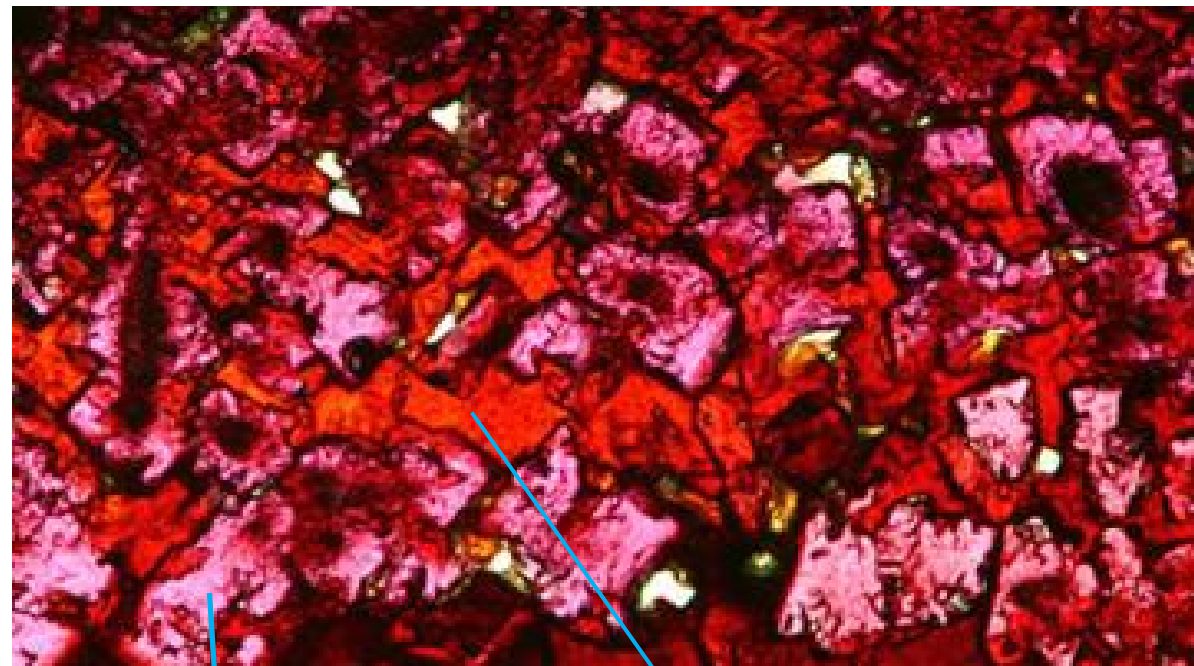
Monofrax K-3 refractory



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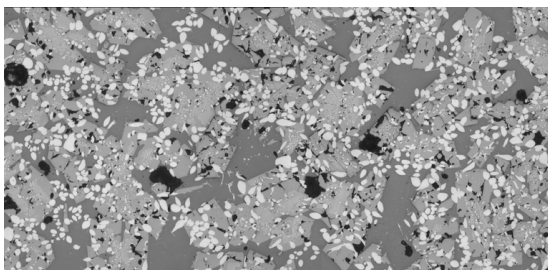
▶ Chemical composition (wt.%)

- ▶ Al_2O_3 : 58
- ▶ Cr_2O_3 : 28
- ▶ MgO : 6
- ▶ Fe_2O_3 : 6 (90% Fe^{III})
- ▶ SiO_2 : 2

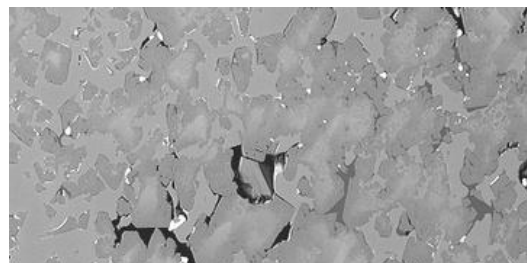


▶ Phase composition

- chromia-alumina solid solution (60-65 wt.%)
- Spinel ($\text{MgO} \cdot \text{FeO} \cdot (\text{Cr}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3)$) (35-40 wt.%)
- Glassy phase ~ 1 wt.%



AZS-32 microstructure



K-3 microstructure

Experimental – dynamic corrosion test



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- ▶ 100 x 25 x 5 mm refractory slabs (coupons) are eccentrically fixed in a rotating platinum crucible with a radius of 10 cm and a height of 10 cm, filled with ~2 kg of molten glass
- ▶ The leading edge of the slab was cut to form a wedge.
- The melt flow velocity along the sample is controlled by the rotation speed, which was set to 0 (static test), 2, 3, and 5 RPM, corresponding to a range from 0 to ~16 mm/s.
- ▶ Constant temperature (1150°C)
- ▶ The duration of the test is 24 hours

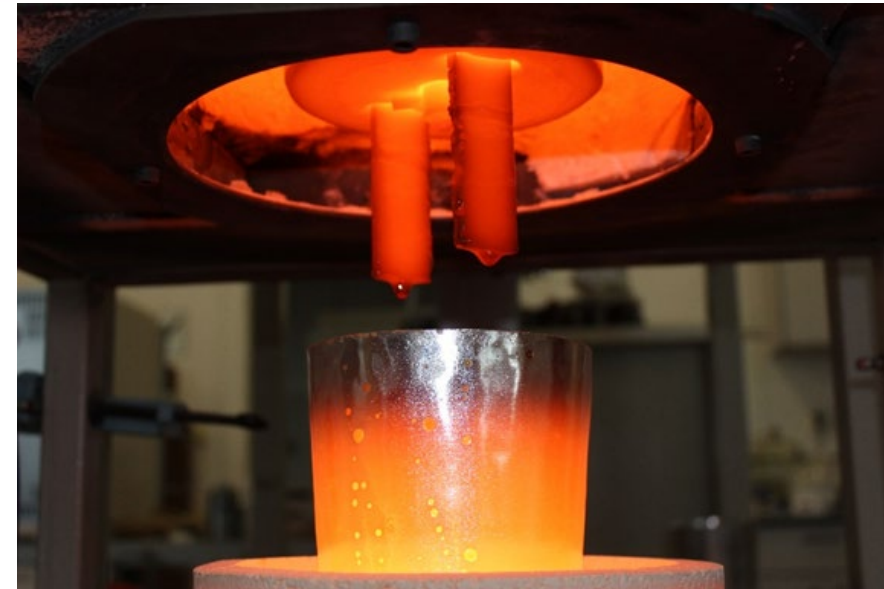
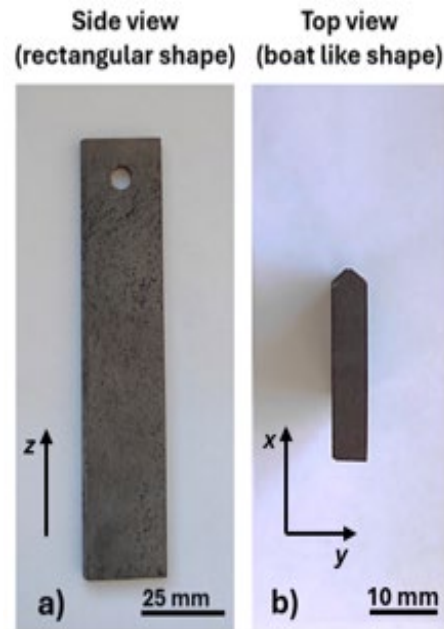
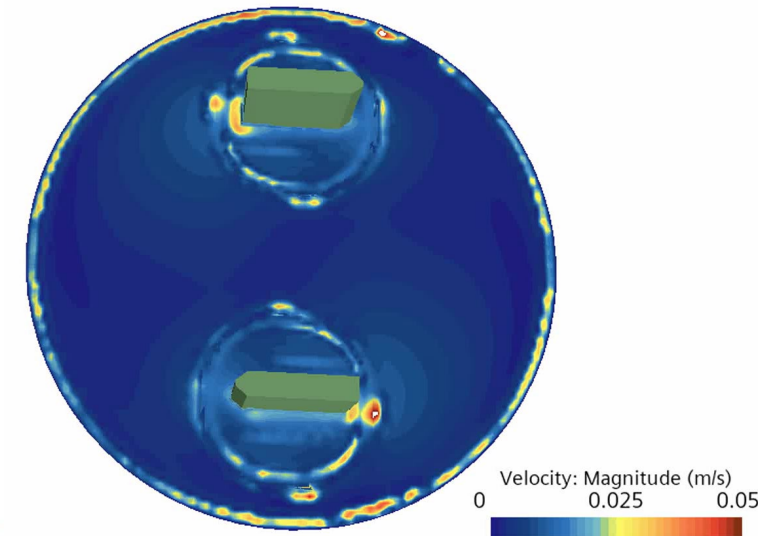


Photo of the dynamic corrosion setup after a finished test – refractory coupons are lifted from rotating Pt crucible with glass melt.

CFD model of the rotating crucible providing melt flow velocity distribution around the refractory coupons



Experimental – dynamic corrosion test



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- ▶ After the test is completed, the slabs are removed from the glass, embedded in epoxy resin, sectioned, and analyzed by optical microscopy, SEM-EDS and image analysis.
- ▶ Melt Line Corrosion Rate in mm/year is calculated from measured neck thickness.
- ▶ Mean value of slab thicknesses measured at 5 positions is used for calculation of Subsurface Corrosion Rate in mm/year

			
LORP 1150°C 0 mm/s 25 hours	LORP 1150°C 6,28 mm/s 25 hours	LORP 1150°C 9,42 mm/s 24 hours	LORP 1150°C 15,7 mm/s 23 hours

Neck

Subsurface 1

Subsurface 2

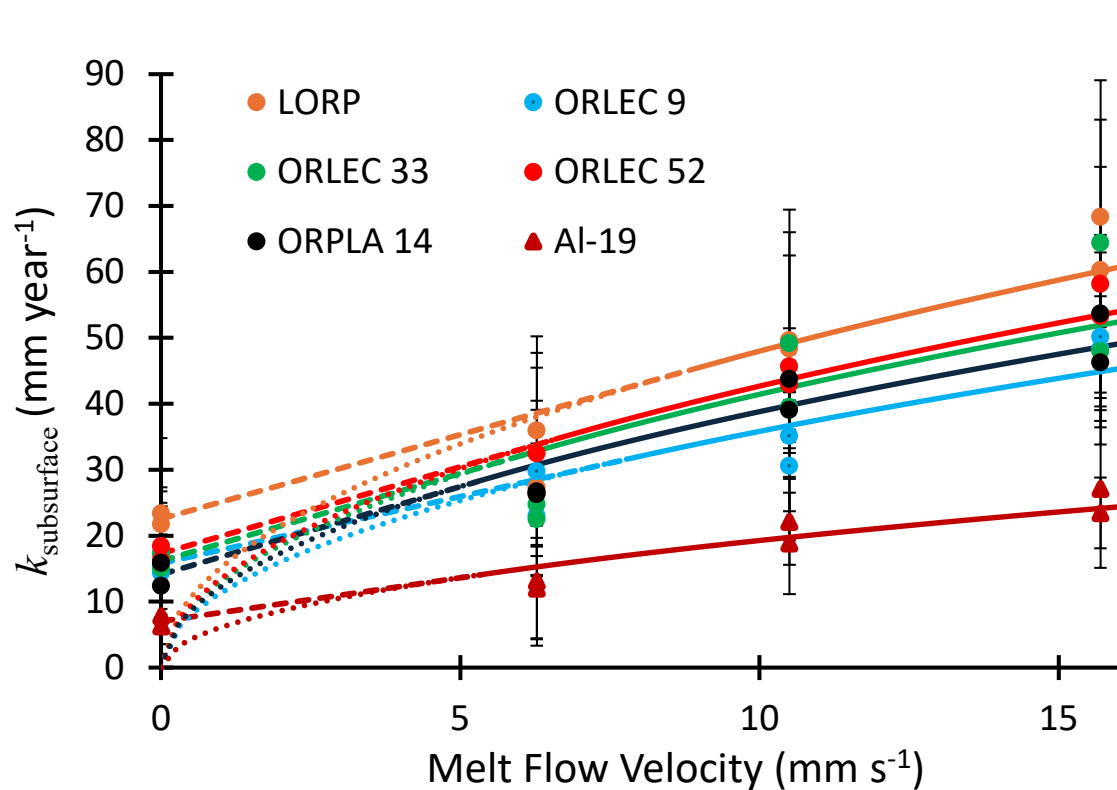
Subsurface 3

Subsurface 4

Subsurface 5

Sectioned K-3 refractory
samples after the test

Effect of melt convection - Subsurface corrosion

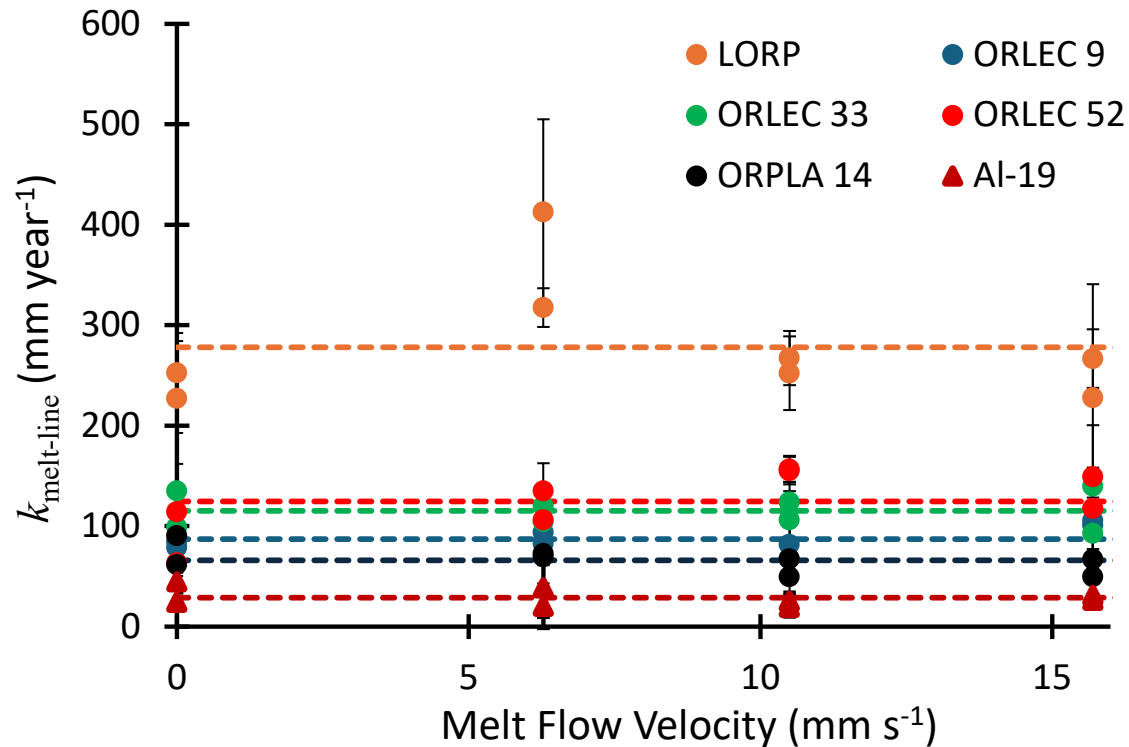


$$j_i = \frac{1}{3} \Delta c_i \sqrt{\frac{v_\infty}{y}}^3 \sqrt{\frac{D_i^2}{\sqrt{v}}}$$

- ❑ Subsurface corrosion rates increase with the square root of melt flow velocity v_∞ .
- ❑ In static melt free convection develops along the sample due to density gradient, leading to a non-zero dissolution rate.
- ❑ For the six waste glasses tested, corrosion rate increases by 10% for each 1 mm/s increase in melt flow velocity

Constant temperature 1150°C

Effect of melt convection – Melt-line corrosion



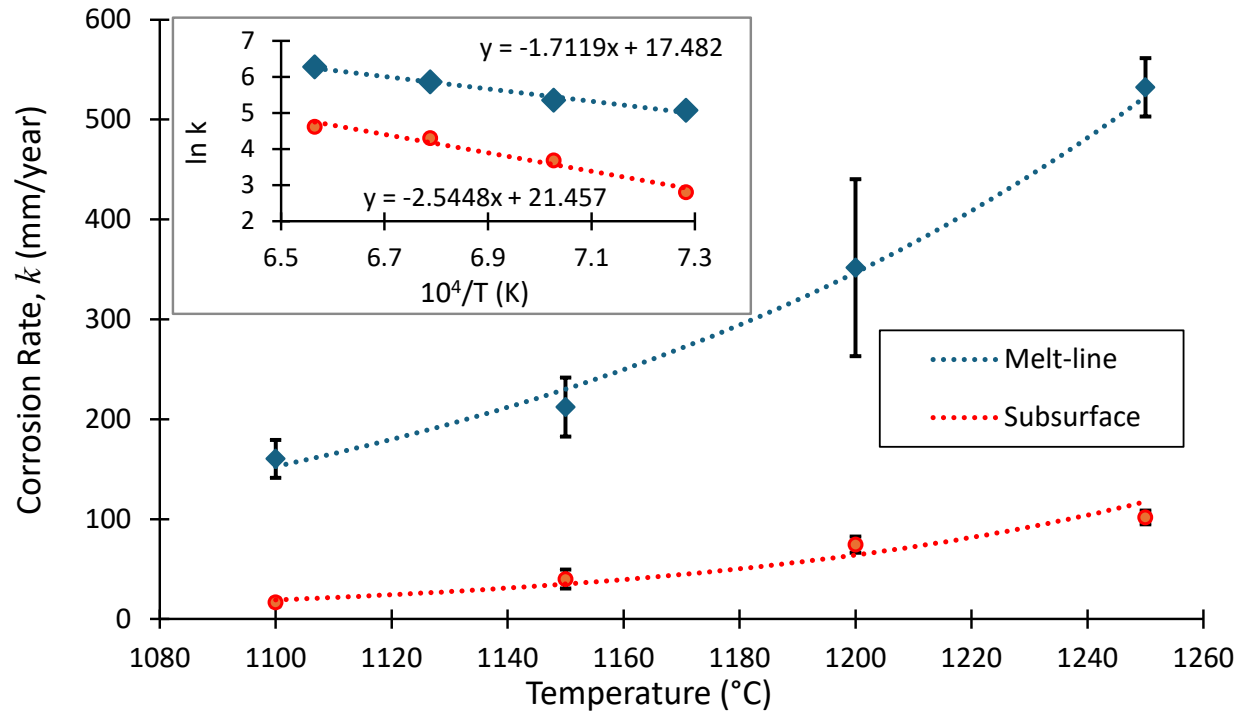
- ☐ Melt-line corrosion appears to be virtually independent of melt flow velocity
- ☐ Corrosion losses are evident also in the static melt.
- ☐ The intensity of melt convection at the meniscus is determined solely by the surface tension gradient at the melt surface contact with refractory (Marangoni convection).
- ☐ A melt flow velocity greater than 90 mm s⁻¹ is required for the bulk melt to overcome the effects of Marangoni convection*.

*Fagerlund, K., S. Sun, and S. Jahanshahi, Effect of Marangoni-induced flow on the rate of refractory dissolution in molten slags. *Scandinavian Journal of Metallurgy*, 2002. 31(6): p. 359-366.

Effect of temperature



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Both subsurface and melt-line corrosion rate increase with increasing temperature, following the Arrhenius law

$$k = Ae^{-B/T}$$

A the pre-exponential factor

B the activation energy

$$B_{\text{subsurface}} = 2.54 \times 10^4 \text{ K and } B_{\text{meltline}} = 1.71 \times 10^4 \text{ K}$$

Effect of temperature (viscosity)

Subsurface

$$j_i = \frac{1}{3} \Delta c_i \sqrt{\frac{v_\infty}{y}} \sqrt[3]{\frac{D_i^2}{\sqrt{v}}}$$

$$j \sim D^{2/3} v^{-1/6}$$

Stokes-Einstein ($D \sim v^{-1}$)

$$j \sim v^{-5/6}$$

Melt-line

$$j_i = B \Delta c_i \left(\frac{D_i^2 \Delta \sigma^* g}{v} \right)^{\frac{1}{3}}$$

$$j \sim D^{2/3} v^{-1/3} \Delta \sigma^{1/3}$$

Stokes-Einstein ($D \sim v^{-1}$)

$$j \sim v^{-1} \Delta \sigma^{1/3}$$

- ❑ Corrosion rate is approximately inversely proportional to viscosity
- ❑ $\Delta \sigma$ is only a weak function of temperature
- ❑ Viscosity-composition relationship developed for Hanford LAW glasses by Ferkl et al.
- ❑ The viscosity activation energy for LORPM14R1 glass is $B_{\text{visc}} = 1.78 \times 10^4 \text{ K}$ - close to the B_{meltline}

$$B_{\text{subsurface}} = 2.54 \times 10^4 \text{ K and } B_{\text{meltline}} = 1.71 \times 10^4 \text{ K}$$

Ferkl, P., P. Hřma, and A.A. Kruger, Augmented Adam-Gibbs model for glass melt viscosity and configuration entropy as functions of temperature and composition. *Journal of Non-Crystalline Solids*, 2022. 595: p. 121832.

Glasses

☐ 1100 – 1250 °C

☐ 3 rpm (9.42 mm/s)

☐ Additional Glasses:

☐ **ORLEC9**

☐ **APPS2-1**

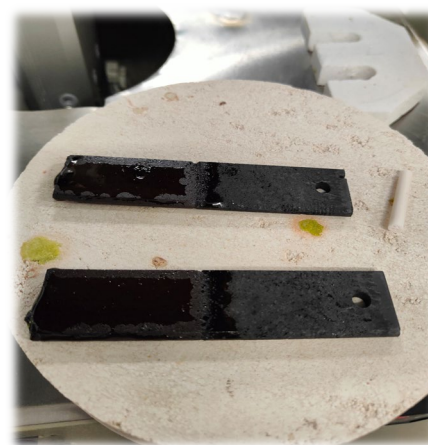
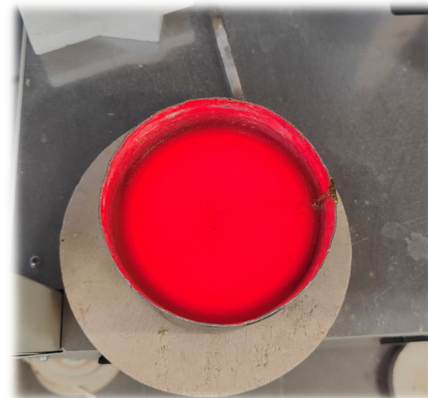
☐ **APPS2-2**

☐ **APPS2-4**

☐ **APPS2-16**

Glass composition (wt.%)

Component	APPS2-1	APPS2-2	APPS2-4	APPS2-16	LORPM14R1	ORLEC9
SiO ₂	45.352	43.83	45.197	43.784	38.4	40.71
Ag ₂ O	0	0.005	0.009	0.014	0	0
Al ₂ O ₃	5.778	12.748	5.428	11.671	5.57	7.8
B ₂ O ₃	5.833	15.33	4.975	13.012	7.546	10
BaO	0	0	0	0	0.00025	0
Bi ₂ O ₃	0.003	0.014	0.007	0.007	0	0
CaO	2.833	0.213	6.249	0.278	9.792	9.17
CdO	0	0	0	0	0.00025	0
Cl	0.197	0.219	0.222	0.152	0.020005	0.2
Cr ₂ O ₃	0.608	0.167	0.602	0.603	0.008035	0.08
F	1.616	0.1	1.293	0.173	0.007485	0.08
Fe ₂ O ₃	1.67	0.13	7.156	1.116	2.395	1
K ₂ O	0.073	0.963	0.06	2.525	4.726	0.5
Li ₂ O	0	0.012	0	0.016	3.611	2.48
MgO	0.007	0.095	0.068	0.087	3.5	1
MnO	0.17	0.007	0.661	0.269	0	0
Na ₂ O	22.369	25.08	20.22	24.027	13.273	16
Nd ₂ O ₃	1.174	0.217	0.328	0.445	0	0
NiO	0.522	0.017	0.263	0.046	0.00075	0.01
P ₂ O ₅	1.827	0.357	0.549	0.134	0.012475	0.12
PbO	0.094	0.058	0.272	0.165	0.00075	0.01
RuO ₂	0	0	0.037	0.004	0	0
SnO	0	0	0	0	3.622	0
SO ₃	1.205	0.369	1.206	0.153	0.24	1.47
TiO ₂	0	0	0	0	0.6	1
V ₂ O ₅	5.144	0.049	5.101	0.005	2.875	1.87
ZnO	1.66	0.008	0.013	1.248	1.8	3
ZrO ₂	1.865	0.012	0.084	0.066	2	3.5
Total	100	100	100	100	100	100



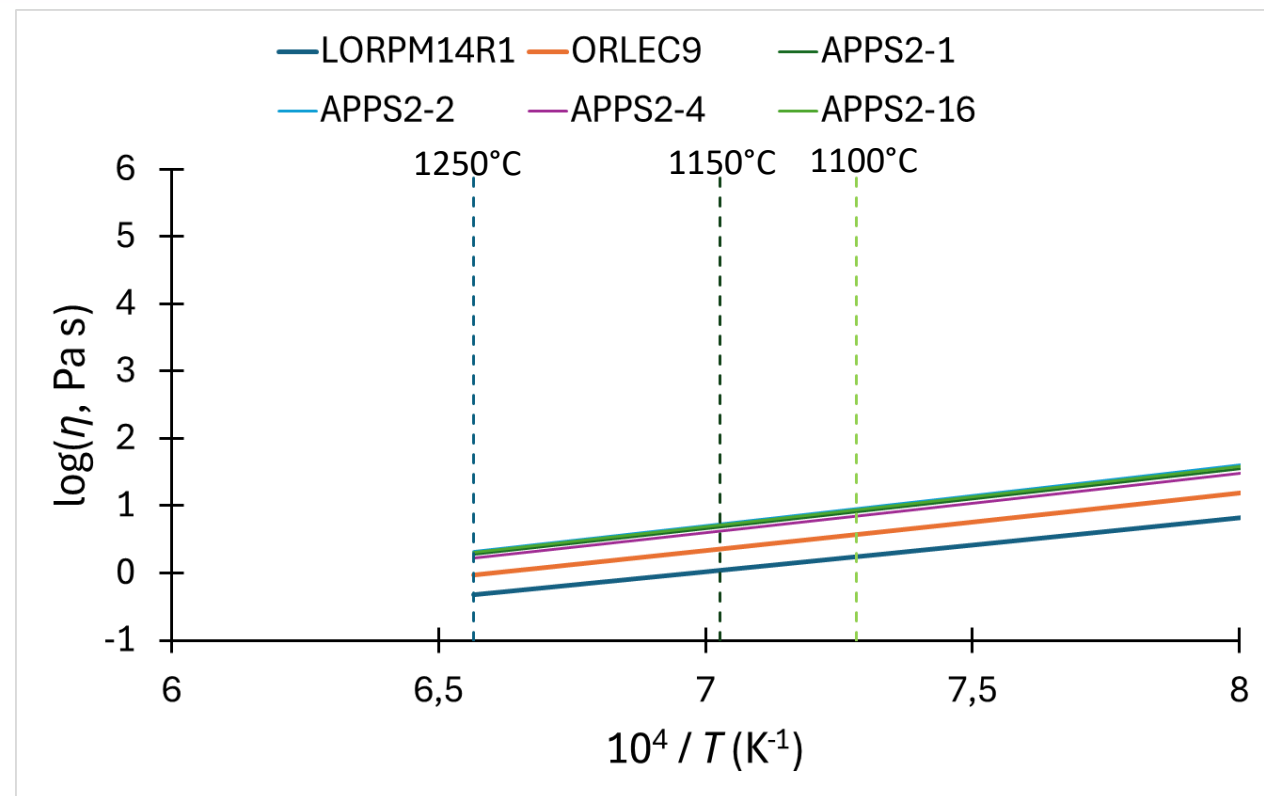
Glass viscosity



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LORPM14R1	ORLEC9	APPS2-1	APPS2-2	APPS2-4	APPS2-16
Viscosity 1100 C (Pa s)					
1.74	3.80	8.19	9.21	7.02	8.65
Viscosity 1150 C (Pa s)					
1.09	2.31	4.87	5.44	4.20	5.13
Viscosity 1200 C (Pa s)					
0.71	1.46	3.01	3.34	2.60	3.16
Viscosity 1250 C (Pa s)					
0.47	0.95	1.92	2.12	1.67	2.01

- Overall, the viscosity ranges from about 1 to 10 Pa·s.
- LORPM14R1 exhibiting the overall lowest viscosity.

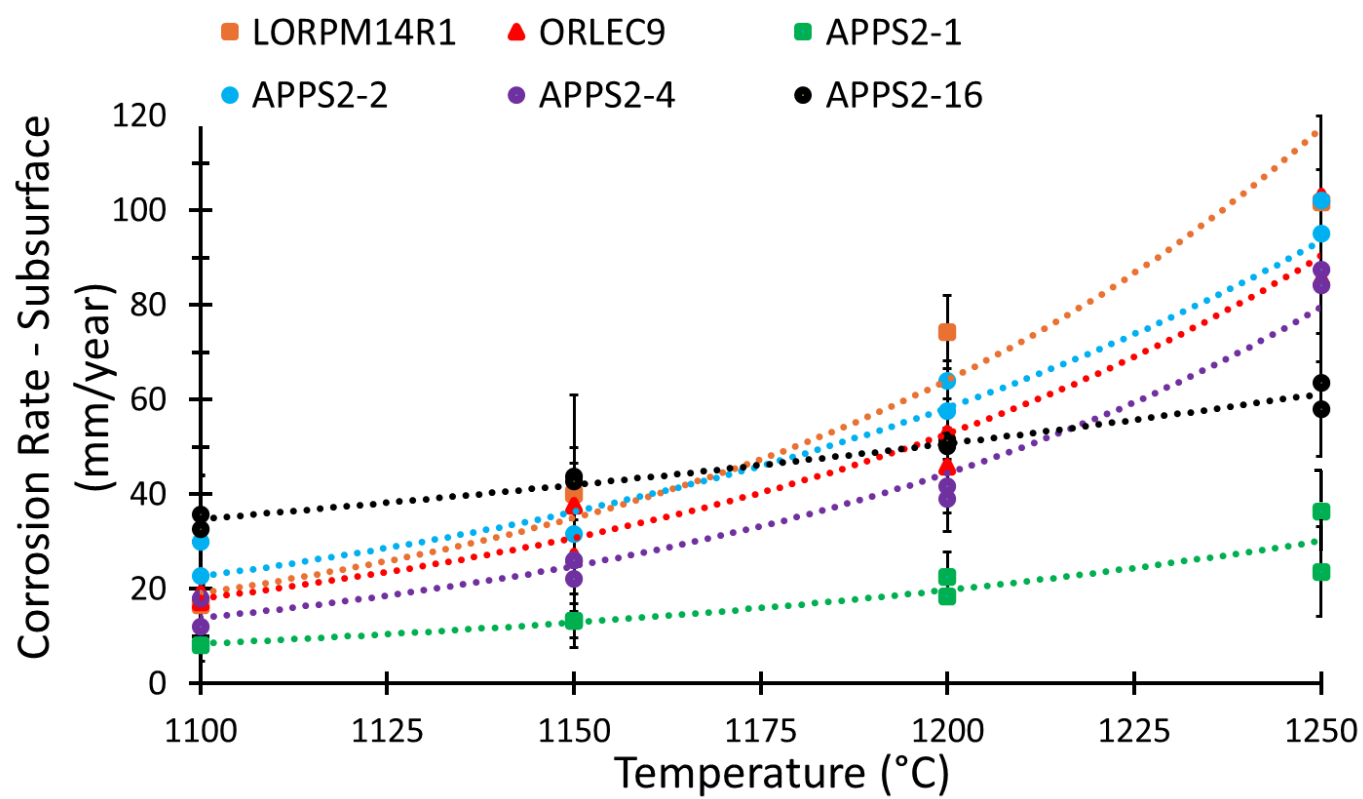


Glass viscosity calculated using Model LAW(A) from P. Ferkl, P. Hrma, A.A. Kruger, Augmented Adam-Gibbs model for glass melt viscosity and configuration entropy as functions of temperature and composition

Effect of Temperature – Subsurface



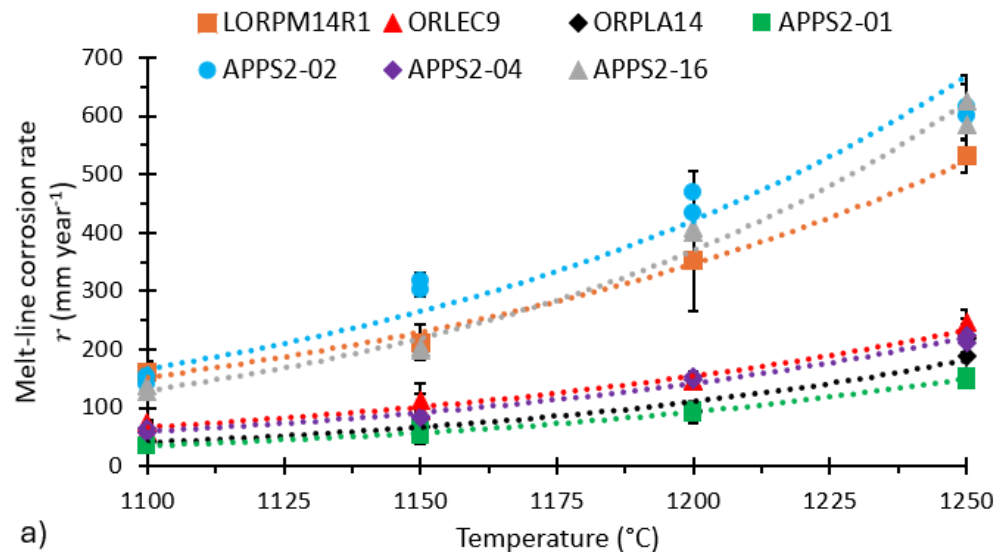
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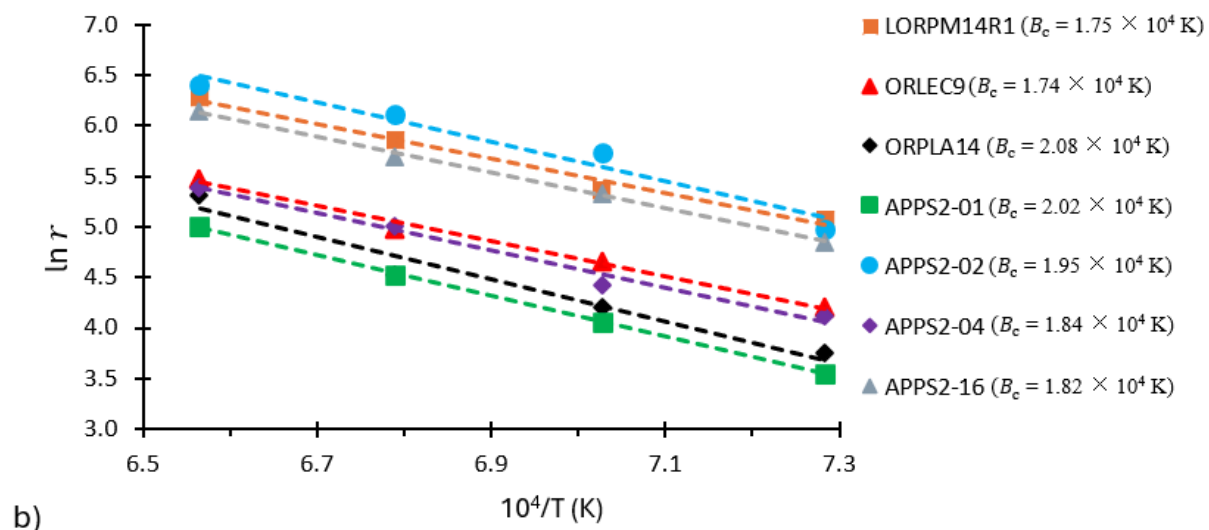
$$k = Ae^{-B/T}$$

- Corrosion experiments show an Arrhenius-type increase in corrosion rate with rising temperature.
- APPS2-16 exhibits behavior distinct from the other glasses:
 - shows higher corrosion rates at lower temperatures
 - only a minimal increase in corrosion rate as temperature increase

Effect of Temperature – Melt-line



The melt-line corrosion rate also follows a trend consistent with Arrhenius-type behavior.

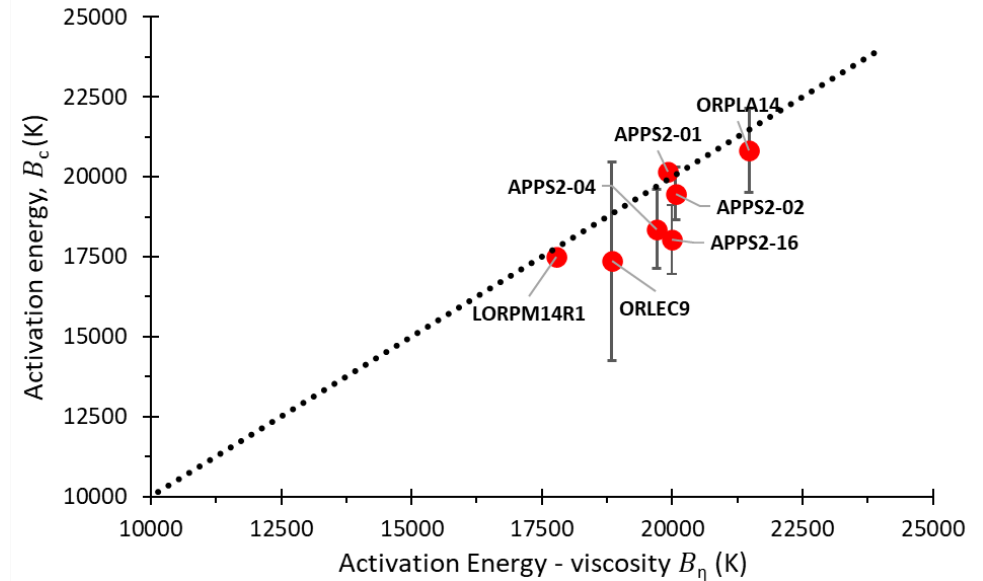


Activation energy



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Glass sample	$10^{-4} \times B_c$ (K)	$10^{-4} \times B_\eta$ (K)	$B_c/B_\eta - 1$
APPS2-01	2.02	1.99	0.015
LORPM14R1	1.75	1.78	-0.016
APPS2-02	1.95	2.01	-0.030
ORPLA14	2.08	2.15	-0.033
APPS2-04	1.84	1.97	-0.066
ORLEC9	1.74	1.88	-0.075
APPS2-16	1.82	2.00	-0.090



- Values of activation energy of corrosion B_c are close to those of activation energy of glass melt viscosity B_η . The differences are within 10% for all glasses.
- For most glasses, B_c is slightly lower than B_η
- This agreement suggests that the temperature dependence of Monofrax® K-3 melt-line corrosion is controlled primarily by the temperature dependence of glass melt viscosity.

- ❑ The close agreement between B_c and B_η provides a practical way to include the temperature dependence of melt-line corrosion in CFD-based melter models.
- ❑ Instead of determining the corrosion activation energy experimentally for each glass composition, the temperature correction can be estimated from the viscosity activation energy calculated from existing glass-property models.

$$r(T) = r(T_{\text{ref}}) \frac{\eta(T_{\text{ref}})}{\eta(T)}$$

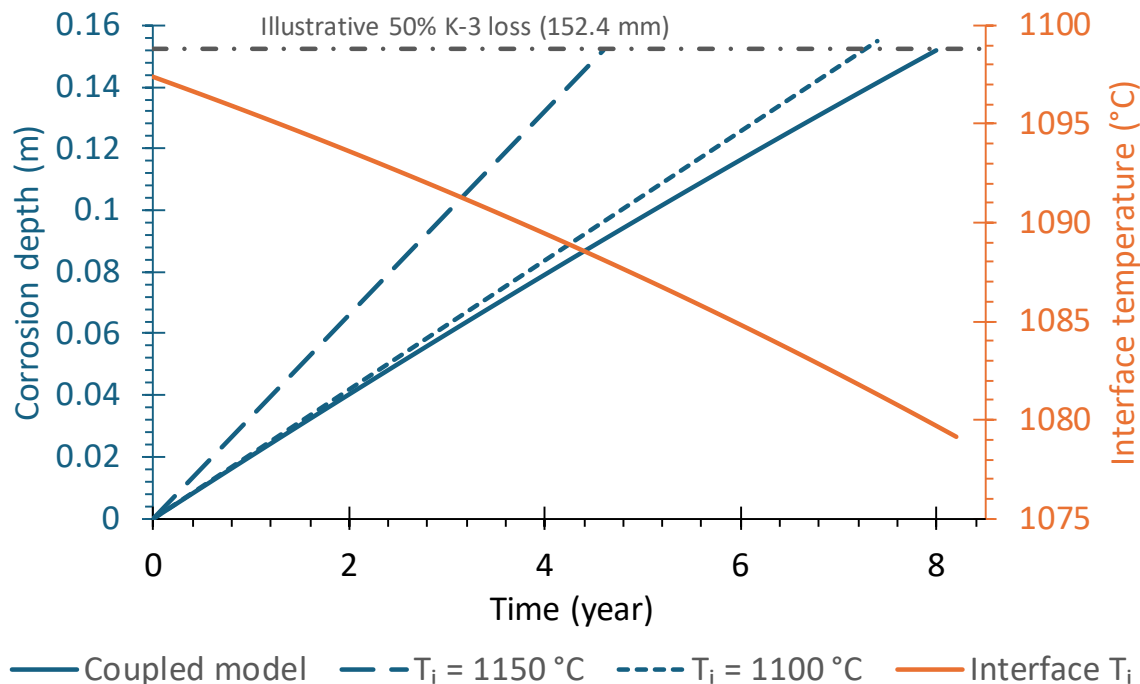
- ❑ $r(T)$ - melt line corrosion rate
- ❑ T_{ref} – reference temperature (measured corrosion rate)
- ❑ T – local melter temperature

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- ❑ T_{ref} – reference temperature (measured corrosion rate)
- ❑ T – local melter temperature

- ❑ Local corrosion - simplified one-dimension sidewall calculation
 - ❑ Sidewall layers - K3, AZS backup refractory, insulation panel, water cooling
 - ❑ Calculated heat flux under constant heat transfer coefficient
 - ❑ Initial thickness of K3 layer – 305 mm
 - ❑ $r_{\text{ref}} = 200 \text{ mm/year}$ at $T_{\text{ref}} = 1150^\circ\text{C}$

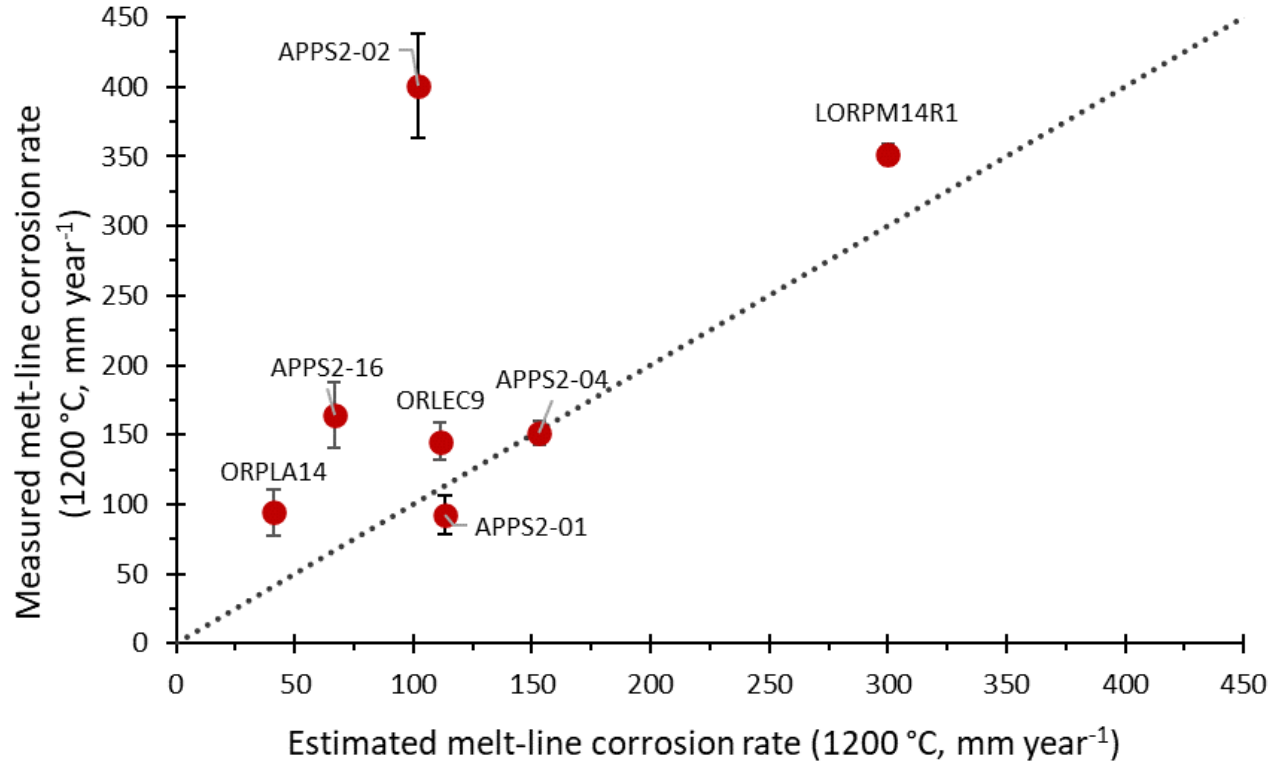


- ❑ The predicted time to reach a corrosion depth of 50% of the initial K-3 thickness, is 8.05 years
- ❑ Calculations with constant interface temperatures of 1150 and 1100 $^\circ\text{C}$ gave 4.61 and 7.27 years, respectively.
- ❑ The example demonstrates that using the nominal bulk melt temperature instead of the local interface temperature can overpredict corrosion.
- ❑ It also shows that as the K-3 wall becomes thinner, its thermal resistance decreases, the heat flux increases, and the hot-face temperature decreases, which slows the temperature-dependent corrosion rate.

Effect of sulfate layer on melt-line corrosion



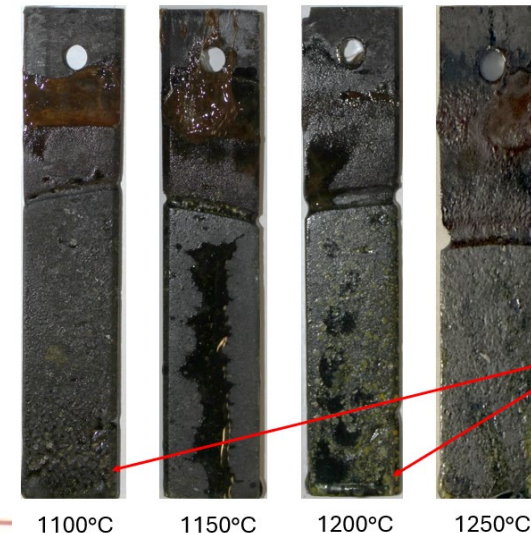
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Melt-line corrosion rate of Monofrax K-3 by waste glasses at 1200°C, measured (this work) versus model estimated by Vienna et al.

Vienna, J.D., et al., Glass Property-Composition Models Update for use in Direct Feed High Level Waste Flowsheet Development: EWG2.6, PNNL-37762, Rev.0. 2025, Pacific Northwest National Laboratory: Richland, WA, United States.

- ❑ The exceptionally high corrosion rate measured for the APPS2-02 glass could be explained by the formation of segregated molten sulfate layer at the glass melt surface.
- ❑ Molten sulfate phases are expected to be chemically aggressive toward glass contact
- ❑ Sulfate presence at the three-phase boundary could alter surface tension gradients that drive Marangoni convection.



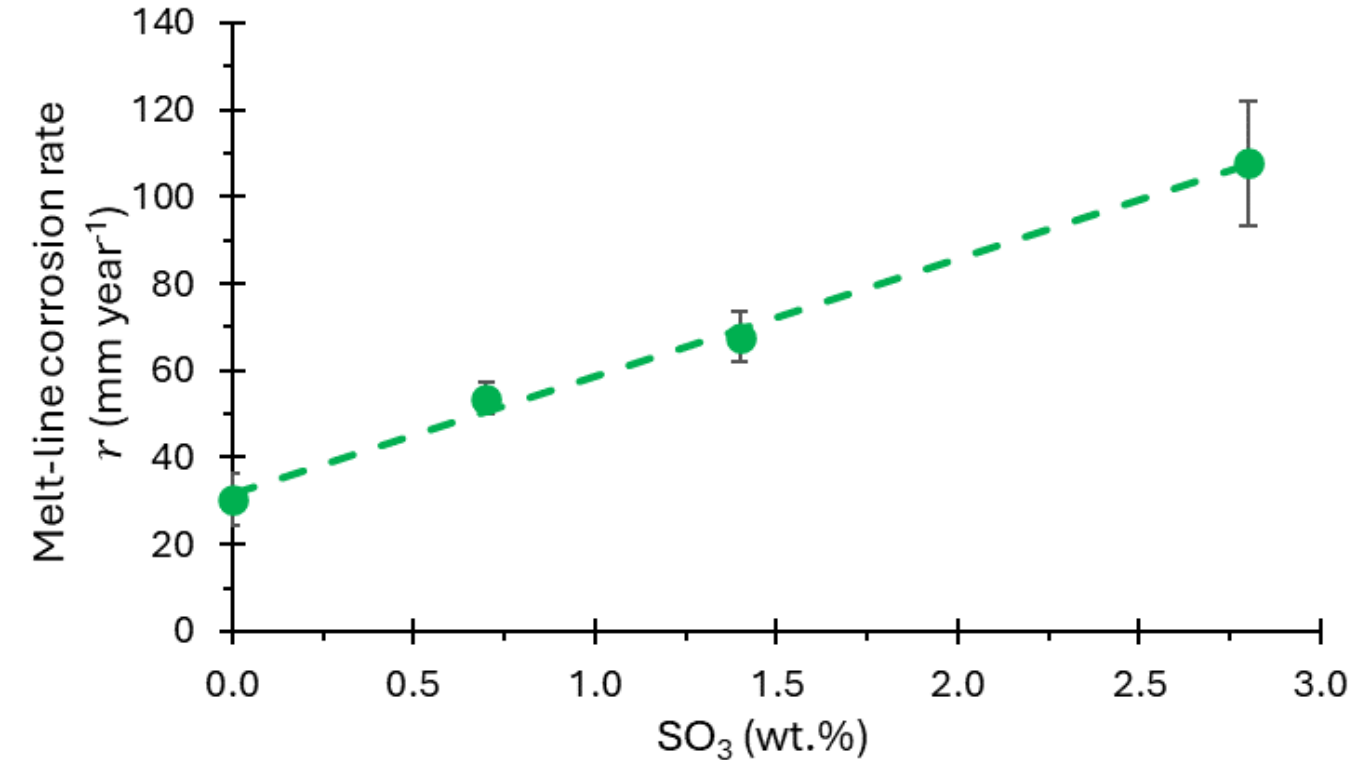
Side view of the K-3 coupons after corrosion testing with APPS2-02 glass at different temperatures with yellowish sulfate/chromate layer.

Sulfate / Chromate

Effect of sulfate layer on melt-line corrosion



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Melt line corrosion rate as a function of sulfate content in APPS2-07 waste glass.

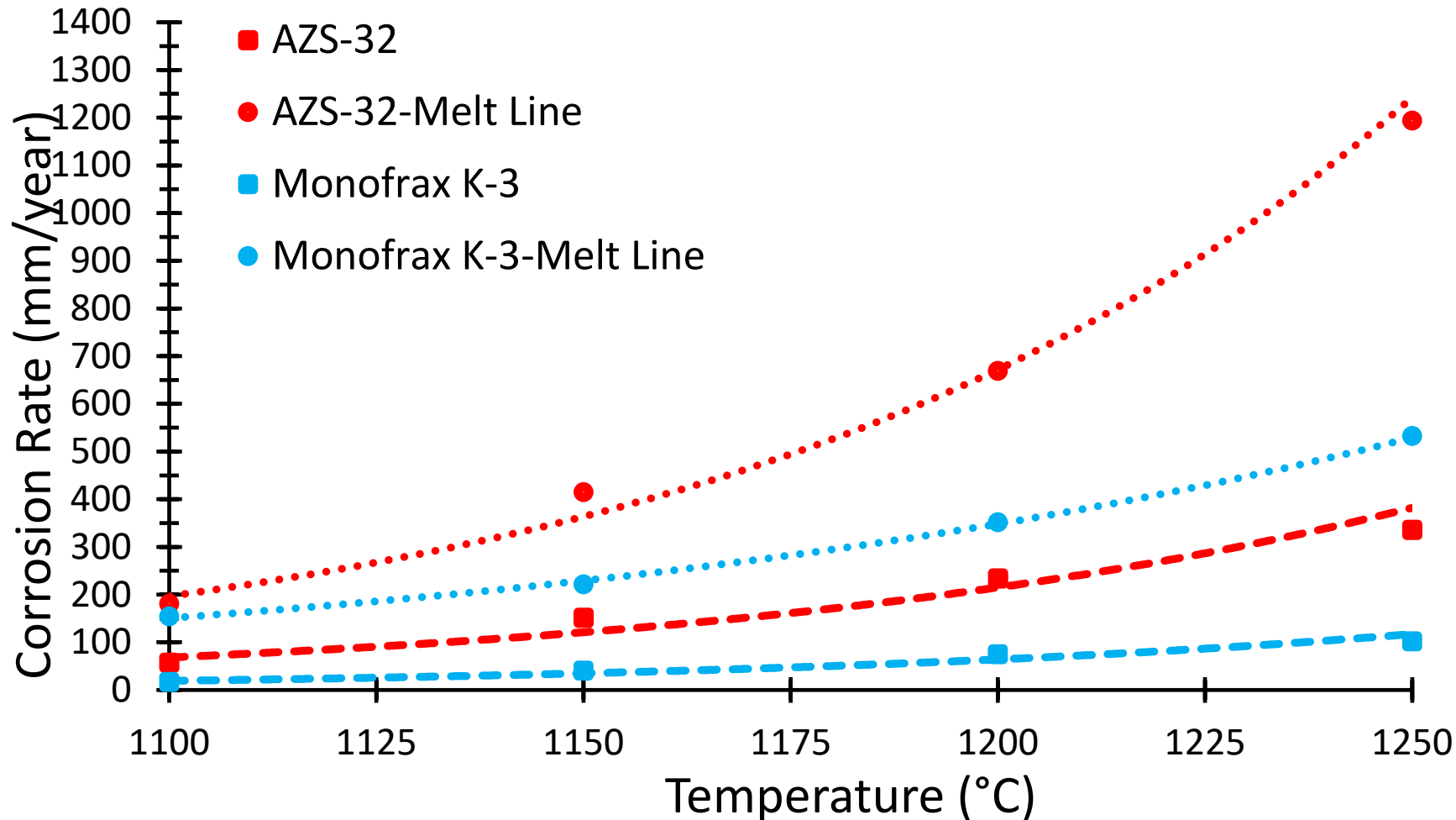
- ❑ Melt-line corrosion rate increased linearly with sulfate content.
- ❑ The precise mechanism by which the sulfate layer enhances melt-line corrosion — whether through direct chemical attack on the refractory surface, modification of the surface tension gradient driving Marangoni convection, or changes in interfacial chemistry — remains an open question

AZS-32 vs Monofrax K3

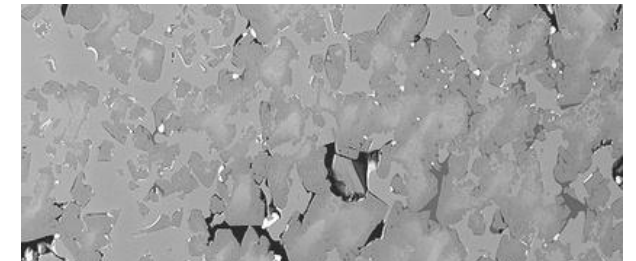


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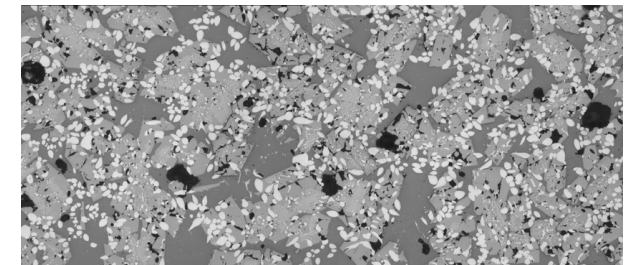
□ LORPM14R1 glass, 3 rpm (9.42 mm/s)



□ The cause of the significant differences in the corrosion rate of both materials is the glassy phase content. AZS contains about 20%, whereas K3 contains less than 1%.



MonofraxK3 microstructure



AZS32 microstructure

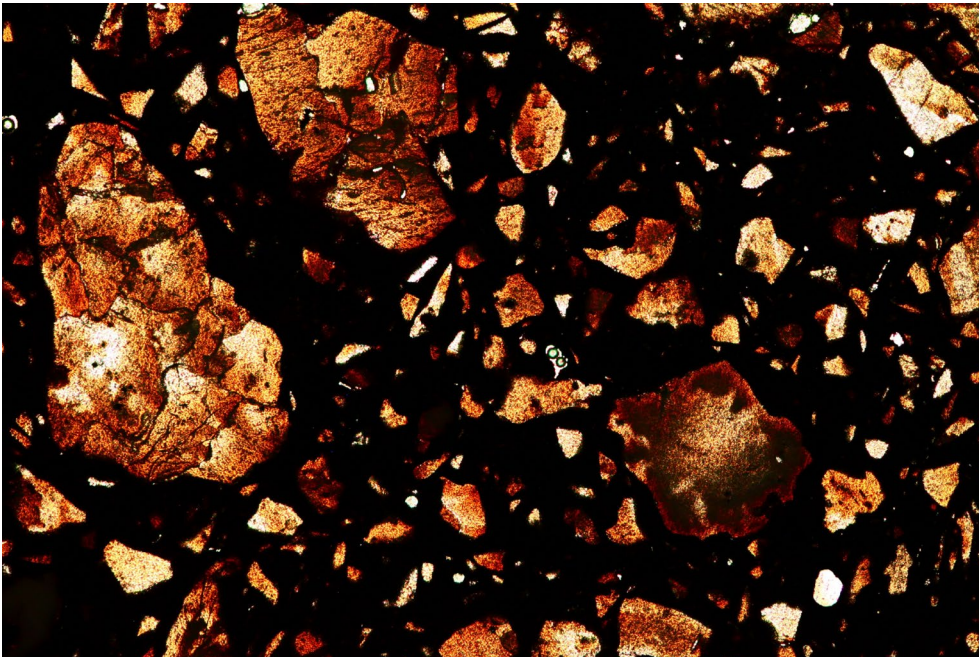
Zirchrom 60



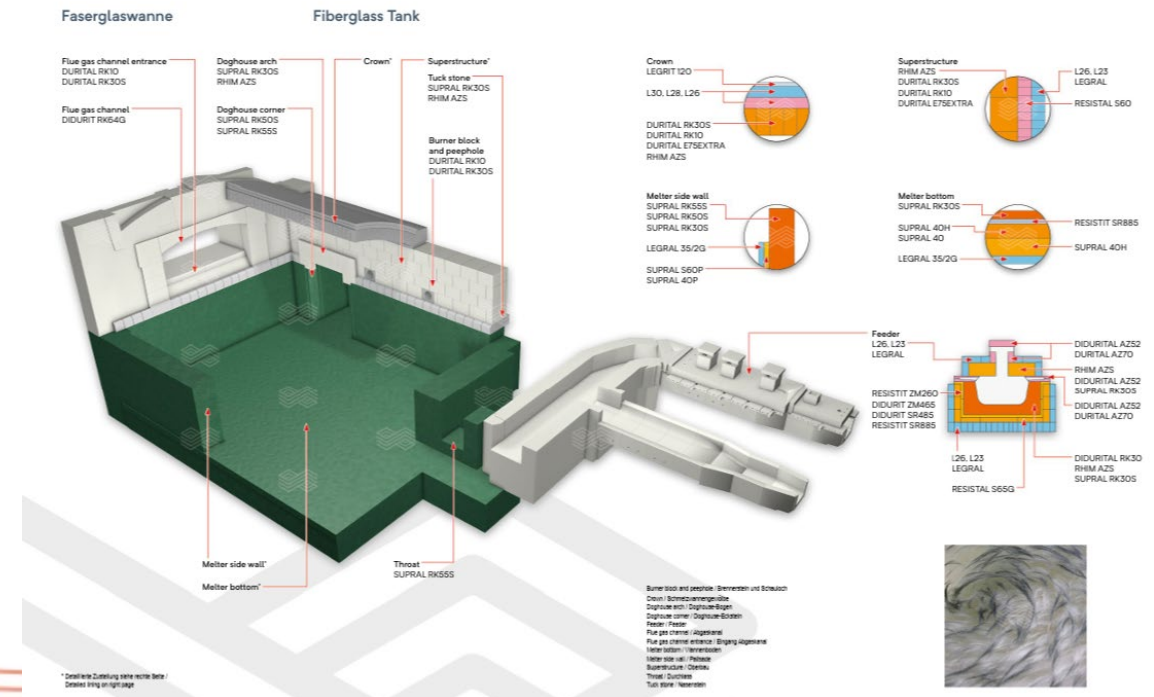
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- ❑ Chemical composition: 62% Cr_2O_3 , 17% Al_2O_3 , 12% ZrO_2 , 8% SiO_2
- ❑ Phase composition: Chromia-alumina ss, chromia, corundum, baddeleyite
- ❑ It is manufactured by dry pressing, vibrocasting and sintering
- ❑ Open porosity 18%
- ❑ Good thermal shock properties

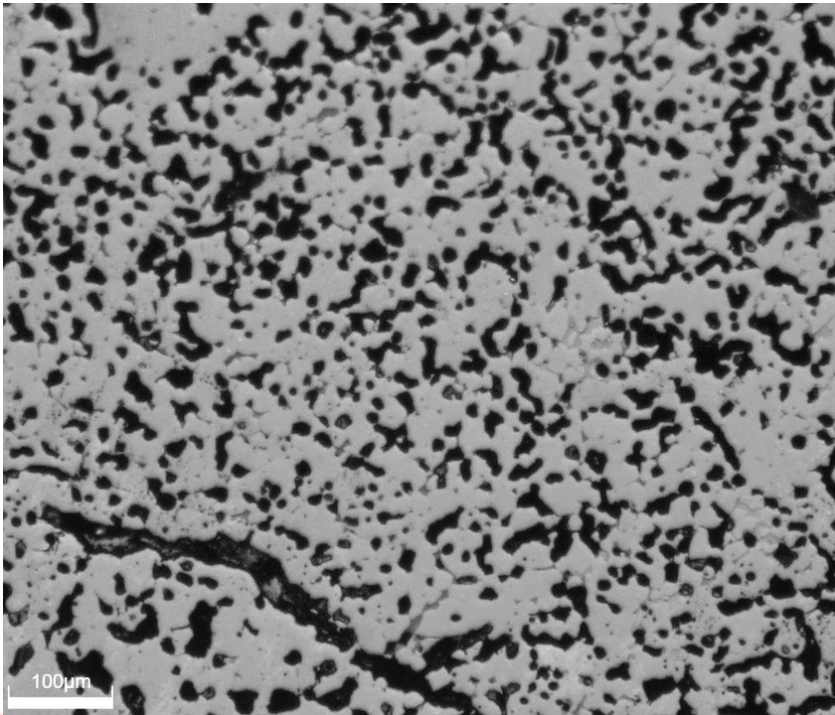
- ❑ Other materials of this group
 - ❑ Zirchrom 85, Zirchrom 50 (Sefpro)
 - ❑ Supral RK50S, Supral RK55S (RHI)
- ❑ Commercial glass melting –fiber production



Zirchrom 60 microstructure



- ❑ Chemical composition: 94% Cr_2O_3 , 4% TiO_2
- ❑ Phase composition: Eskolaite
- ❑ It is manufactured by dry pressing, vibrocasting and sintering of coarse chromia grains
- ❑ Open porosity 18%
- ❑ Good thermal shock properties



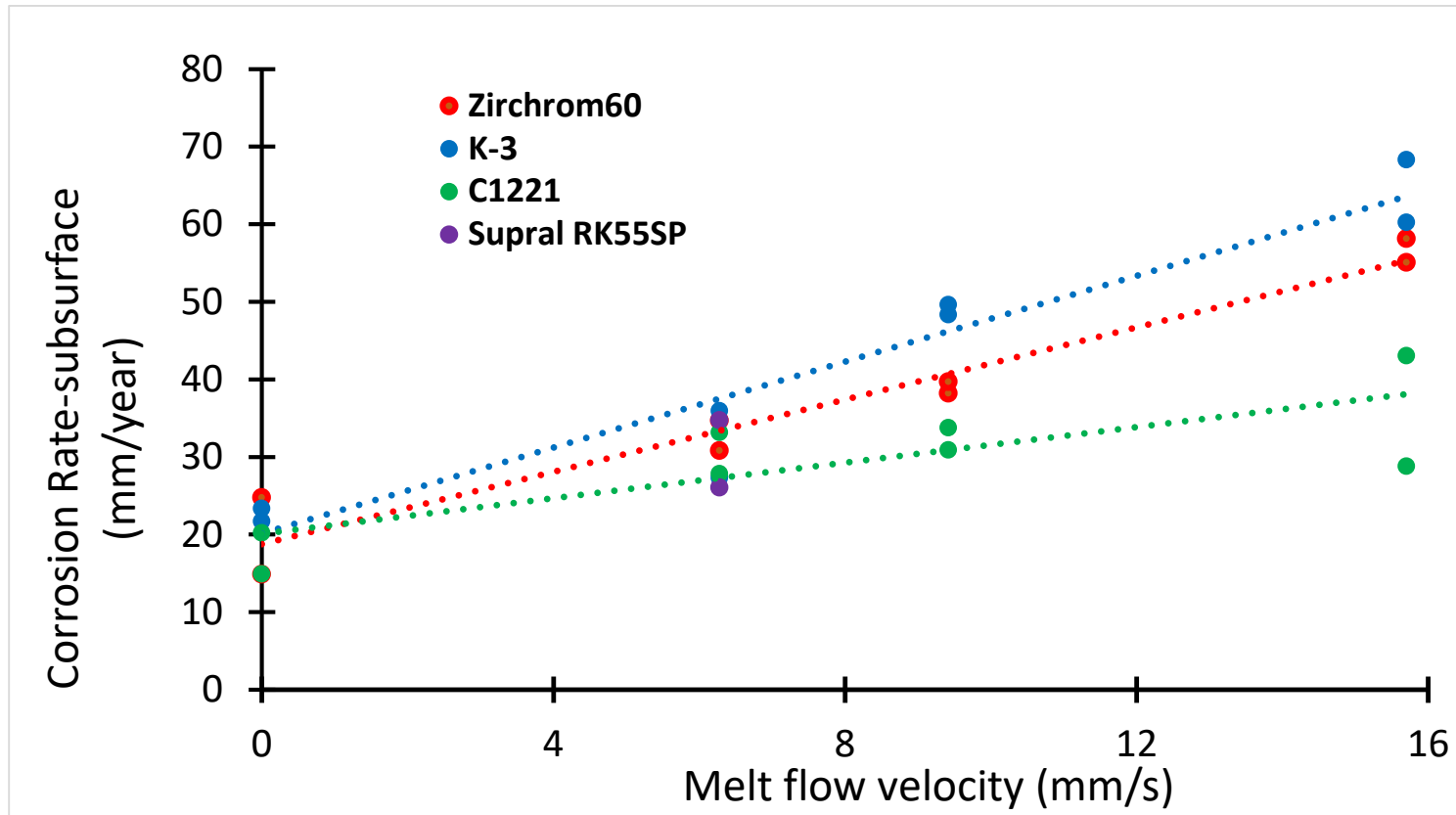
- ❑ Commercial glass melting –fiber production
 - ❑ melter throats, flow blocks, bushing blocks and doghouse areas
 - ❑ C1221 is also used in areas subject to high thermal gradient

Zirchrom 60 and C1221 vs K3 – Subsurface corrosion



UCT PRAGUE

□ LORPM14R1 glass, 1150°C



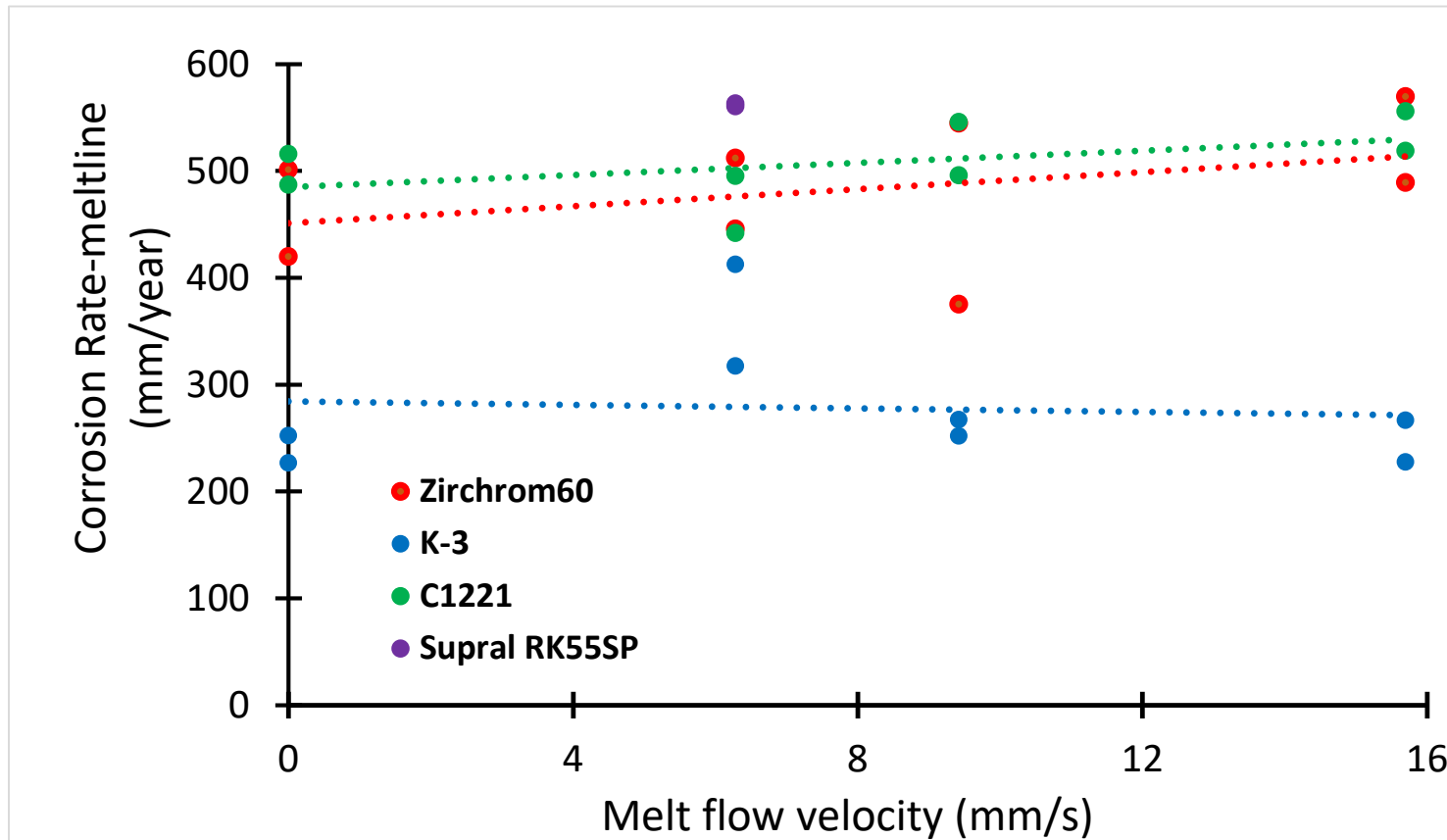
□ Both Zirchrom 60 and C1221 exhibit higher corrosion resistance compared to Monofrax K3.

Zirchrom 60 and C1221 vs K3 – Melt line corrosion



UCT PRAGUE

□ LORPM14R1 glass, 1150°C

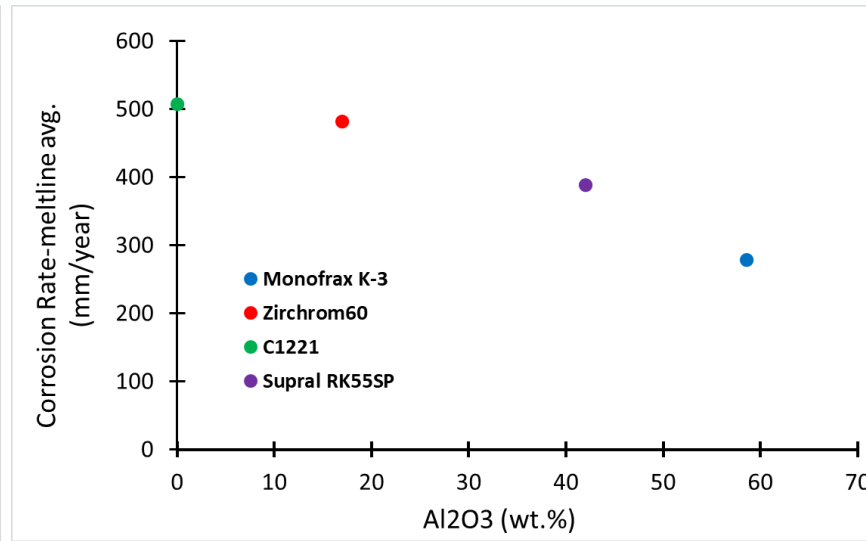
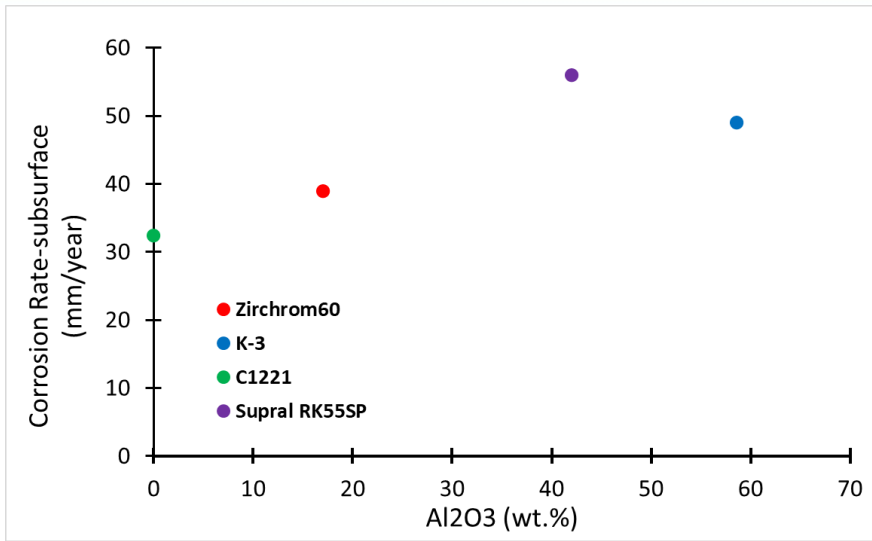


□ The melt line corrosion resistance of both Zirchrom 60 and C1221 is lower than that of Monofrax K3.

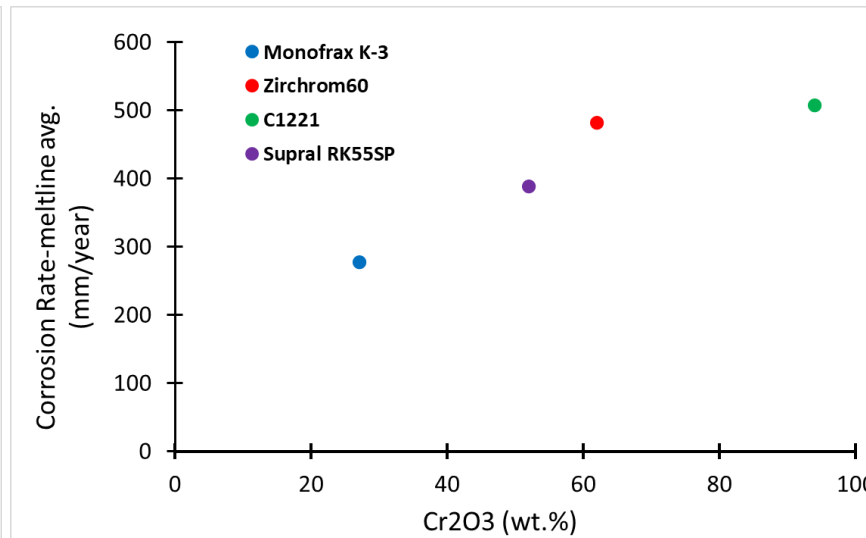
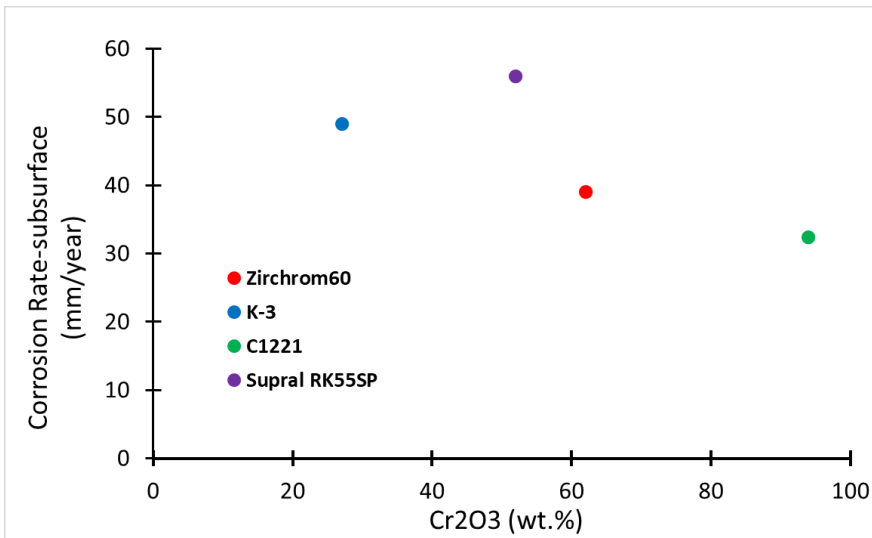
Refractory composition vs corrosion rate



UCT PRAGUE



□ With increasing Al_2O_3 content the subsurface corrosion rate increases while the melt-line corrosion rate decreases.



□ With increasing Cr_2O_3 content the subsurface corrosion rate decreases while the melt-line corrosion rate increases.

- ▶ This study investigated main types of refractory wear: subsurface corrosion and melt line corrosion.
- ▶ Corrosion tests have been performed under both static and dynamic conditions.
- ▶ The results agree with theoretical diffusion-controlled corrosion models
 - ❑ subsurface corrosion rate increased by approximately 10% for every 1 mm s^{-1} increment in melt velocity
 - ❑ melt-line corrosion remained largely unaffected by the melt velocity.
- ▶ Corrosion rate is inversely proportional to melt viscosity; the activation energy governing the corrosion rate-temperature relationship can be approximated using the viscosity activation energy, available from standard viscosity models.
- ▶ The measured data will be used directly in a CFD waste glass melter model to evaluate the effect of melter processing conditions, such as temperature, bubbling rate etc.