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JÜLICH FORSCHUNGSZENTRUM

Modelling Viscosity of Molten Oxides (HotVeGas)

02.07.2015 Guixuan Wu

GTT Annual Users' Meeting 2015

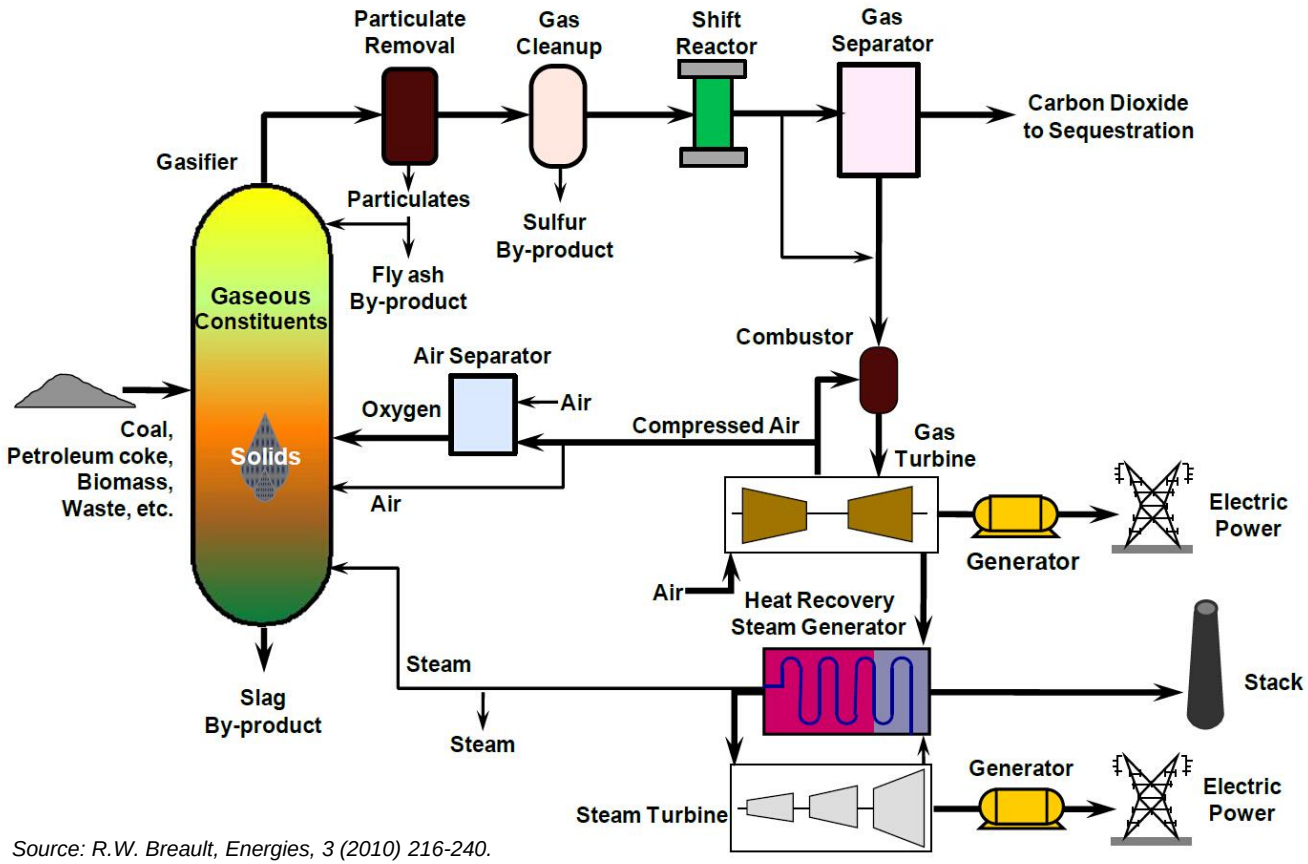
Outline

1. Introduction & motivation
2. Dependence of viscosity
3. Modelling
4. Validation
5. Application of the model
6. Conclusion & outlook

1 Introduction & motivation

The **IGCC** technology (**Integrated Gasification Combined Cycle**) based Coal power plants:

- a **high efficiency** (ca. 45% currently, >50% in 5 years, >55% in 12 years);
- an opportunity for effective **CO_2 capture and storage**;

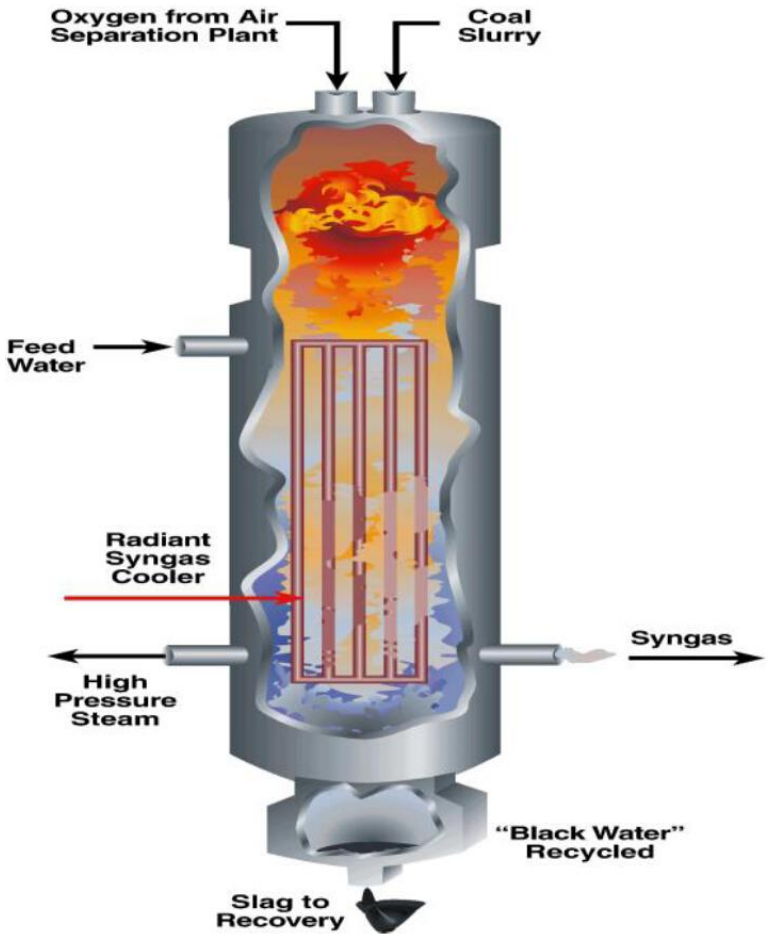


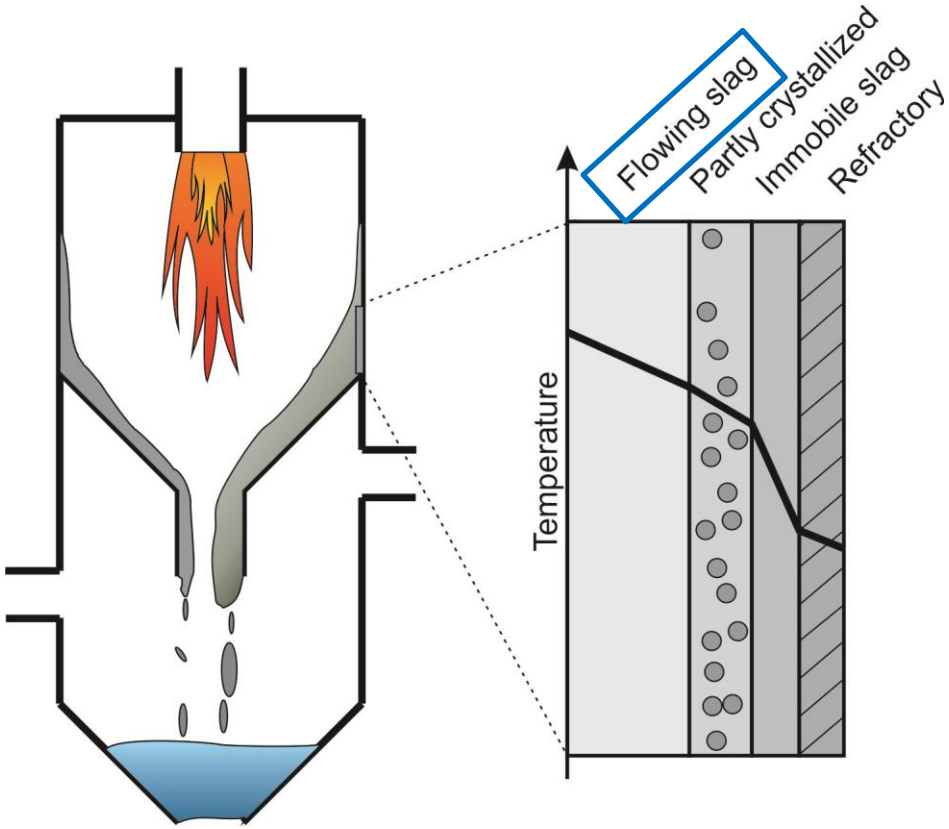
Source: R.W. Breault, Energies, 3 (2010) 216-240.

- the **core** of an IGCC power plant is the **gasifier**.

1 Introduction & motivation

The majority of the successful coal gasification processes developed after 1950 are performed by **entrained-flow slagging gasifiers**, such as **GE Energy Gasifier**.





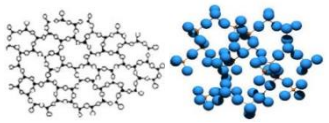
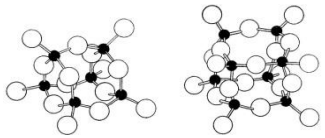
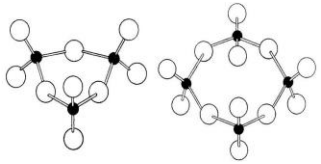
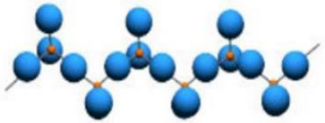
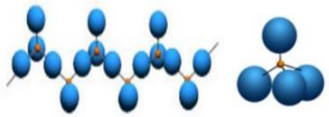
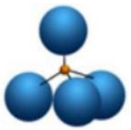
Source: R.W. Breault, Energies, 3 (2010) 216-240.

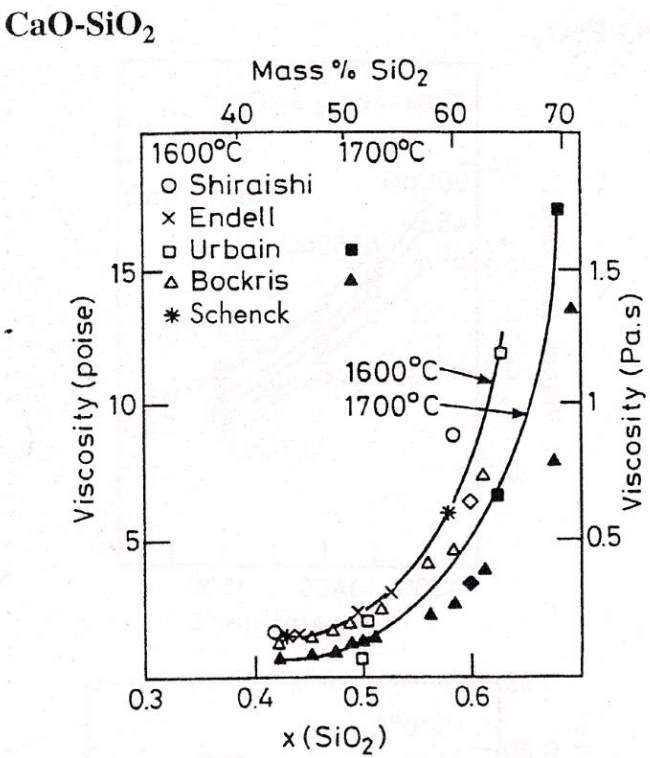
1 Introduction & motivation

Single phase slag systems		
Temperature-related models	**Temperature & Composition-related models**	
	Non-structure based models	**Structure based models**
Arrhenius model	Shaw model	Zhang-Jahanshahi model
Vogel-Fulcher-Tammann model	Lakatos model	Reddy model
Adam-Gibbs model	Urbain model	Iida model
Eyring model	Riboud model	KTH model
Weymann-Frenkel model	Kalmanovitch-Frank model	Avramov model
Bockris-Reddy model	Hurst model	Quasi-chemical viscosity model
AM model	Kondratiev-Jak model	FactSage model

- Applicable in a **limited** range of **temperatures** and **compositions**;
- Many **mathematical fitting** model parameters;
- **Non self-consistent** prediction;
- Lack of an effective description of **slag structure**.

2 Dependence of viscosity

CaO, mol %	Structural features of the system $CaO\text{-}SiO_2$	
$X_{CaO} \leq 12$	3-dimentional network in the form of $[Si_nO_{3n}]^{-2n}$	
$12 < X_{CaO} \leq 33$	Anion complexes in the form of $[Si_{n \cdot r}O_{n \cdot (2r+1)}]^{-2n}$	
$33 < X_{CaO} \leq 50$	Ring structure in the form of $[Si_nO_{3n}]^{-2n}$	
$50 < X_{CaO} \leq 67$	Chain structure in the form of $[Si_nO_{3n+1}]^{-2(n+1)}$	
$67 < X_{CaO} \leq 75$	Chain structure and monomer $[SiO_4]^{4-}$ and O^{2-}	
$X_{CaO} > 75$	monomer $[SiO_4]^{4-}$ and O^{2-}	



Source: K. C. Mills, Slag atlas, 1995 , pp. 359.

3 Modelling

Gibbs energy ⟷ **Associate species model**

Associate species

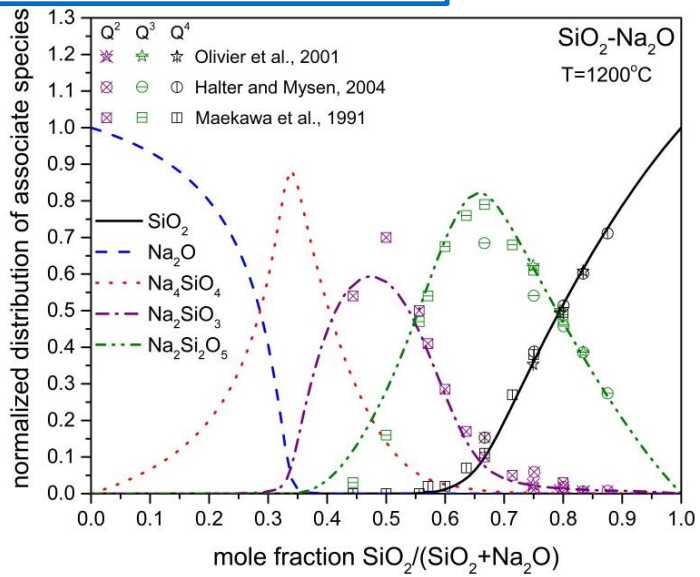
$$nSiO_2 \longleftrightarrow (SiO_2)_n$$

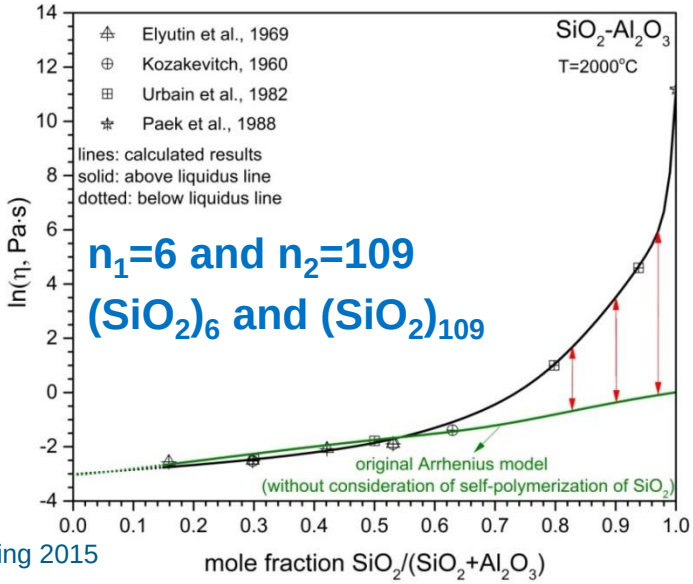
Building structural units

Determination of viscosity contribution

$$\ln \eta_i = A_i + B_i/T$$

$$\ln \eta = \sum X_i \cdot \ln \eta_i$$





3 Modelling

Comp. Temp. → Associate species → Structure → Viscosity

Partial pressure of oxygen
(for FeO/Fe_2O_3 containing system)

Modified Arrhenius model

$$\ln \eta = \ln \eta_{ideal} + \ln \eta_{excess}$$

$$= \left(\sum X_i \cdot \ln \eta_i\right) + \left(\ln \eta_{self-pol.} + \ln \eta_{inter-pol.}\right)$$

where: $\ln \eta_i = A_i + B_i/T$ ⟶ basic structural units

larger structural units

$$\ln \eta_{self-pol.} = \sum\left(A_{j,SiO_2} + B_{j,SiO_2}/T\right) \cdot \left(X^{n_j}{}_{SiO_2}\right)$$

$$+ \sum_k\left(A_{(Si-Al)_k} + B_{(Si-Al)_k}/T\right) \cdot \left(X^{n_k}_{(Si-Al)_k}\right)$$

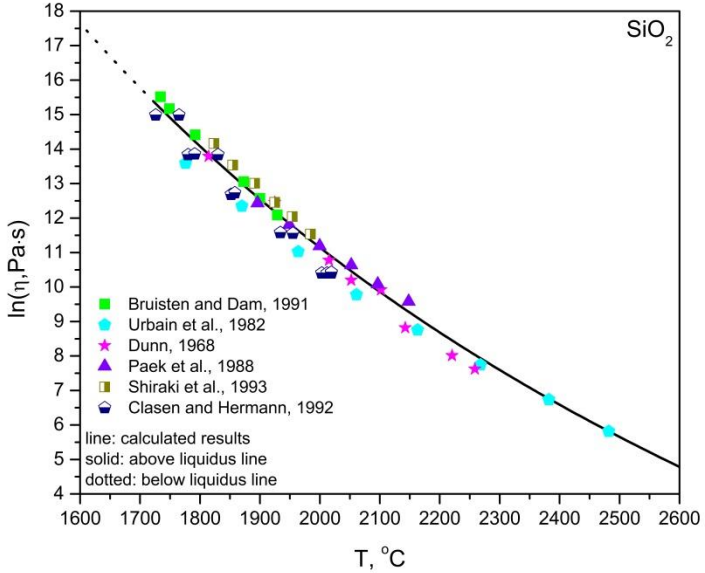
$$\ln \eta_{inter-pol.} = \sum_m\left(A_{(Si-Al)_m} + B_{(Si-Al)_m}/T\right) \cdot \left(X_{(Si-Al)_m} \cdot X^{n_m}_{SiO_2}\right)$$

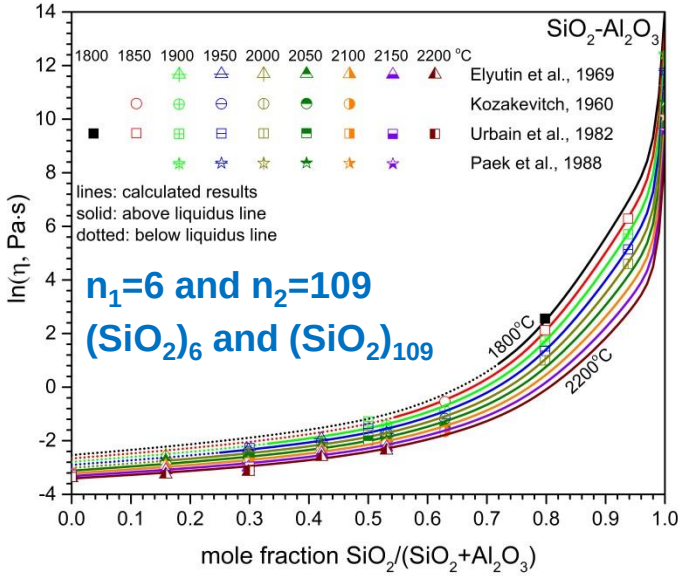
3 Model performance

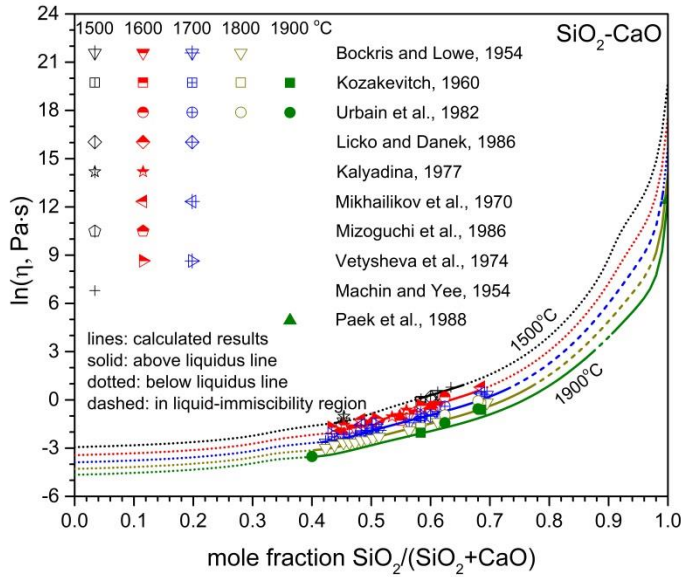
- Evaluation formula: $\Delta_n = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{(\eta_i)_{cal.}-(\eta_i)_{exp.}}{(\eta_i)_{exp.}}\right|$

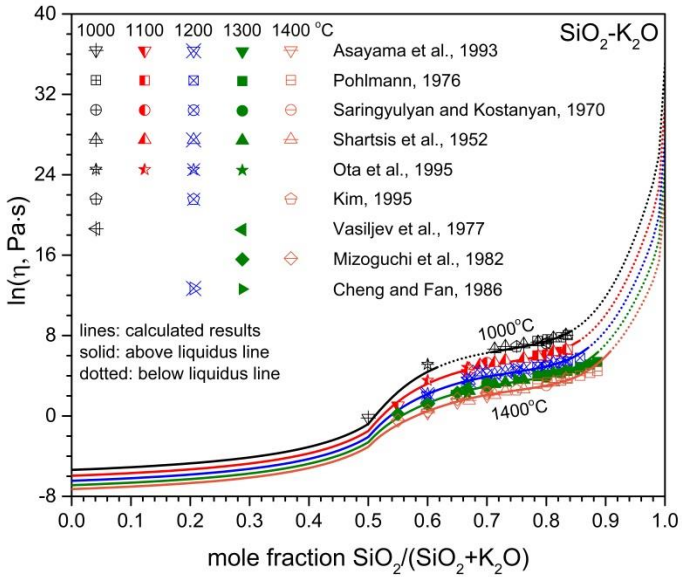
System	No. of data points	Range of viscosities, Pa·s	Δ_n
SiO_2–Al_2O_3	73	0.03–537.76	0.122
SiO_2–MgO	56	0.002–0.59	0.135
Al_2O_3–CaO	136	0.05–1.30	0.175
SiO_2–CaO–MgO	426	0.03–3.85	0.130
SiO_2–Na_2O–K_2O	48	7.59–2951.21	0.208
SiO_2–Al_2O_3–CaO	1717	0.03–1995.26	0.281
SiO_2–Al_2O_3–MgO	357	0.04–94.17	0.217
SiO_2–Al_2O_3–K_2O	33	1.02–6165.95	0.263
SiO_2–Al_2O_3–CaO–MgO	1253	0.09–83.10	0.250
SiO_2–Al_2O_3–Na_2O–K_2O	45	15.49–79432.82	0.212
SiO_2–CaO–MgO–Na_2O–K_2O	29	10.00–23442.29	0.312
SiO_2–Al_2O_3–CaO–MgO–Na_2O–K_2O	43	10.72–1412.54	0.320

3 Modelling

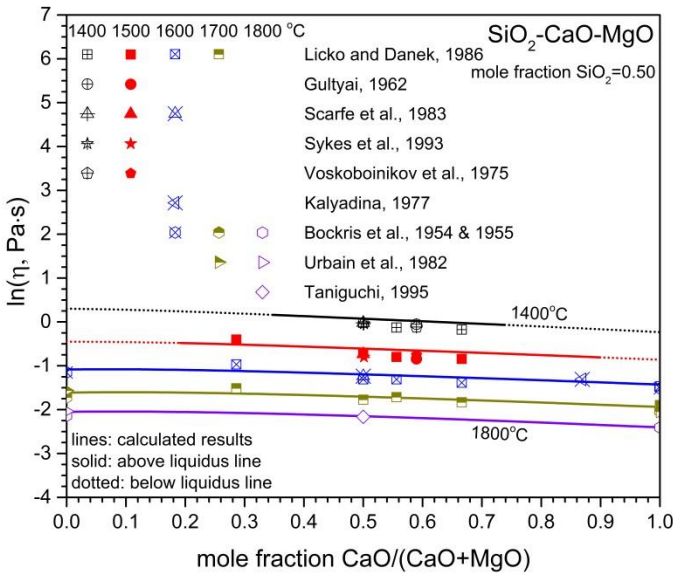

SiO2
ln(η,Pa·s)
T, °C
Bruisten and Dam, 1991
Urbain et al., 1982
Dunn, 1968
Paek et al., 1988
Shiraki et al., 1993
Clasen and Hermann, 1992
line: calculated results
solid: above liquidus line
dotted: below liquidus line

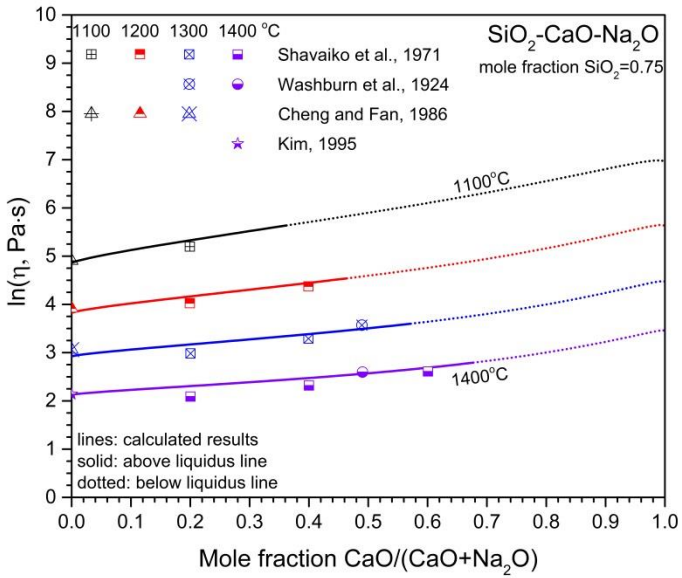

SiO2-Al2O3
1800 1850 1900 1950 2000 2050 2100 2150 2200 °C
Elyutin et al., 1969
Kozakevitch, 1960
Urbain et al., 1982
Paek et al., 1988
lines: calculated results
solid: above liquidus line
dotted: below liquidus line
n1=6 and n2=109
(SiO2)6 and (SiO2)109
1800°C
2200°C
ln(η, Pa·s)
mole fraction SiO2/(SiO2+Al2O3)

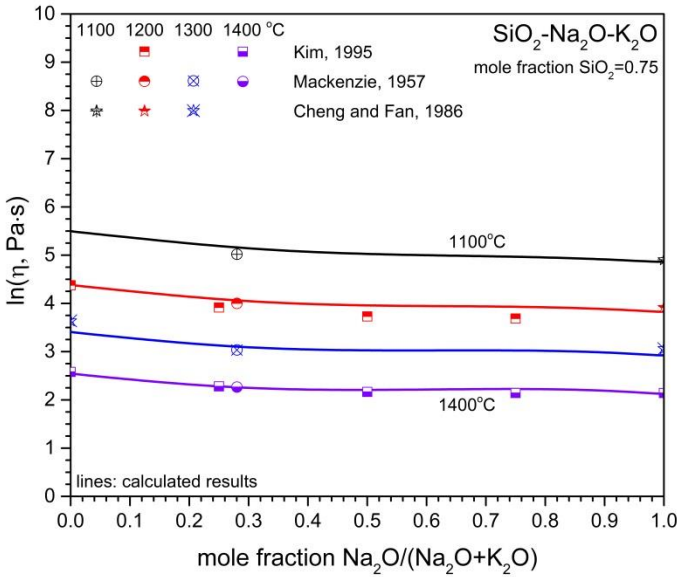

SiO2-CaO
1500 1600 1700 1800 1900 °C
Bockris and Lowe, 1954
Kozakevitch, 1960
Urbain et al., 1982
Licko and Danek, 1986
Kalyadina, 1977
Mikhailikov et al., 1970
Mizoguchi et al., 1986
Vetysheva et al., 1974
Machin and Yee, 1954
Paek et al., 1988
lines: calculated results
solid: above liquidus line
dotted: below liquidus line
dashed: in liquid-immiscibility region
1500°C
1900°C
ln(η, Pa·s)
mole fraction SiO2/(SiO2+CaO)

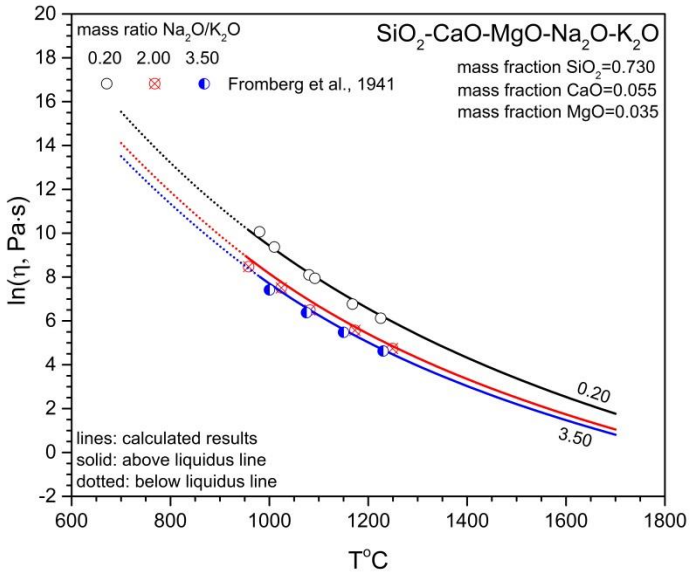

SiO2-K2O
1000 1100 1200 1300 1400 °C
Asayama et al., 1993
Pohlmann, 1976
Saringyulyan and Kostanyan, 1970
Shartsis et al., 1952
Ota et al., 1995
Kim, 1995
Vasiljev et al., 1977
Mizoguchi et al., 1982
Cheng and Fan, 1986
lines: calculated results
solid: above liquidus line
dotted: below liquidus line
1000°C
1400°C
ln(η, Pa·s)
mole fraction SiO2/(SiO2+K2O)

3 Modelling

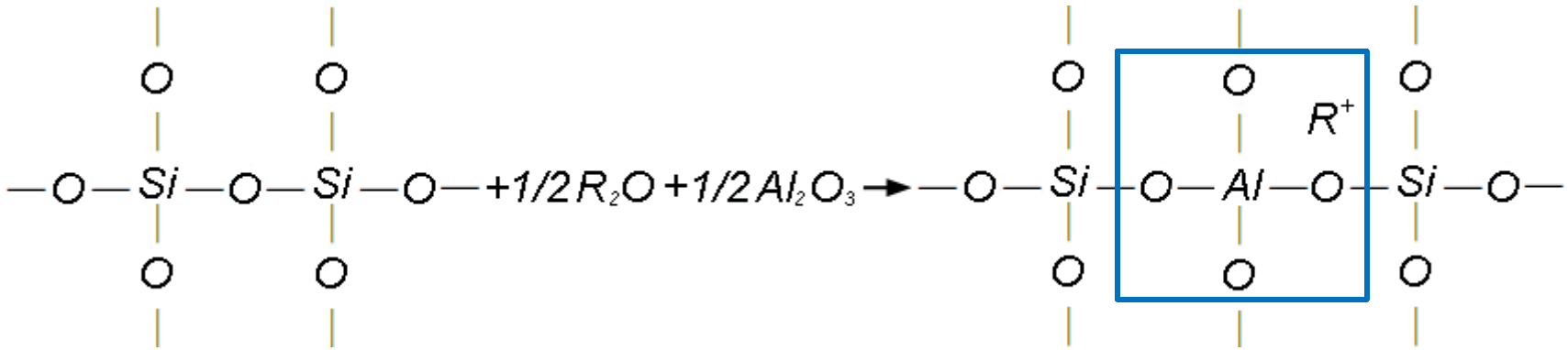

1400 1500 1600 1700 1800 °C
SiO2-CaO-MgO
mole fraction SiO2=0.50
Licko and Danek, 1986
Gultyai, 1962
Scarfe et al., 1983
Sykes et al., 1993
Voskoboinikov et al., 1975
Kalyadina, 1977
Bockris et al., 1954 & 1955
Urbain et al., 1982
Taniguchi, 1995
1400°C
1800°C
lines: calculated results
solid: above liquidus line
dotted: below liquidus line
ln(η, Pa·s)
mole fraction CaO/(CaO+MgO)


1100 1200 1300 1400 °C
SiO2-CaO-Na2O
mole fraction SiO2=0.75
Shavaiko et al., 1971
Washburn et al., 1924
Cheng and Fan, 1986
Kim, 1995
1100°C
1400°C
lines: calculated results
solid: above liquidus line
dotted: below liquidus line
ln(η, Pa·s)
Mole fraction CaO/(CaO+Na2O)

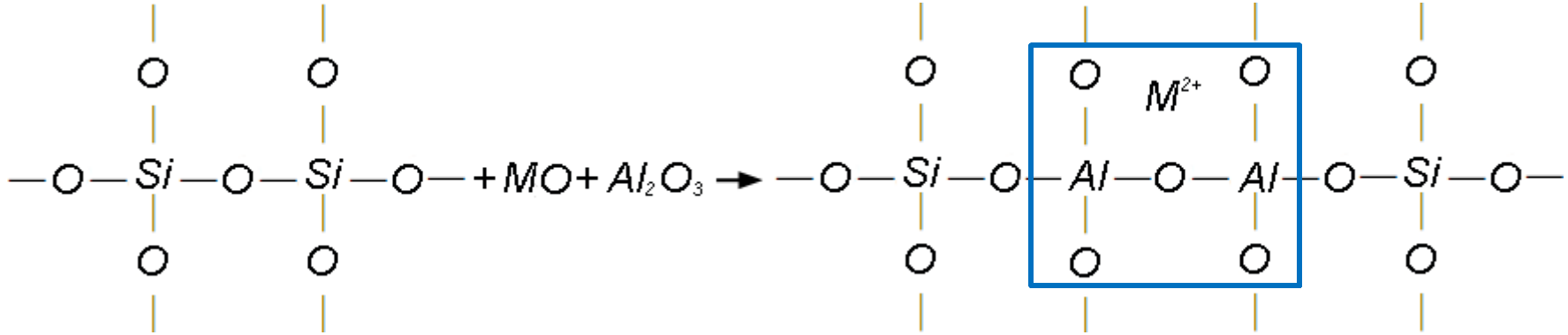

1100 1200 1300 1400 °C
SiO2-Na2O-K2O
mole fraction SiO2=0.75
Kim, 1995
Mackenzie, 1957
Cheng and Fan, 1986
1100°C
1400°C
lines: calculated results
ln(η, Pa·s)
mole fraction Na2O/(Na2O+K2O)


mass ratio Na2O/K2O
0.20 2.00 3.50
Fromberg et al., 1941
SiO2-CaO-MgO-Na2O-K2O
mass fraction SiO2=0.730
mass fraction CaO=0.055
mass fraction MgO=0.035
0.20
3.50
lines: calculated results
solid: above liquidus line
dotted: below liquidus line
ln(η, Pa·s)
T°C

3 Modelling

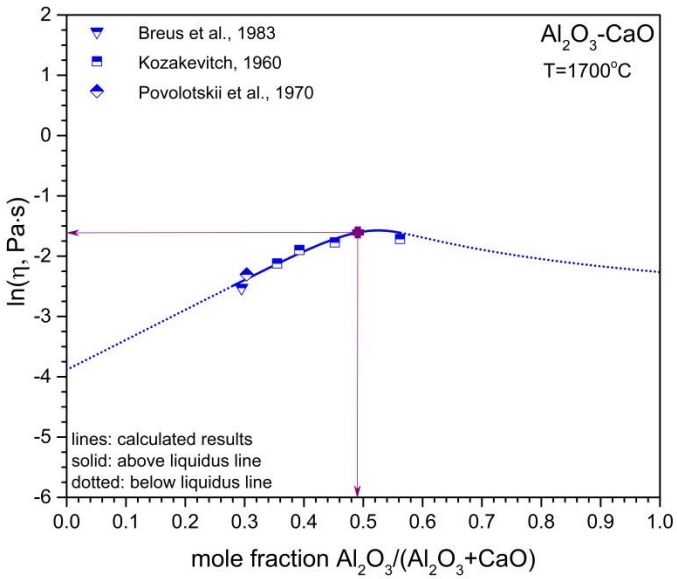


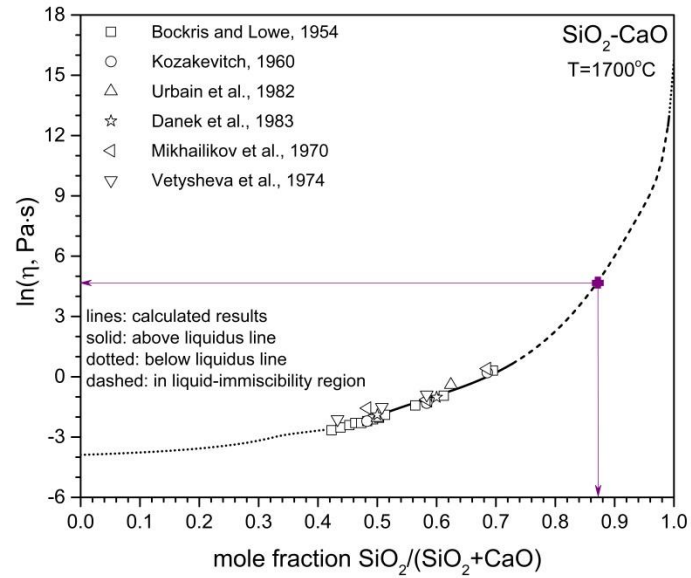
$RAlO_2$, $RSiAlO_4$, RSi_3AlO_8 or RSi_2AlO_6
R: Na, K

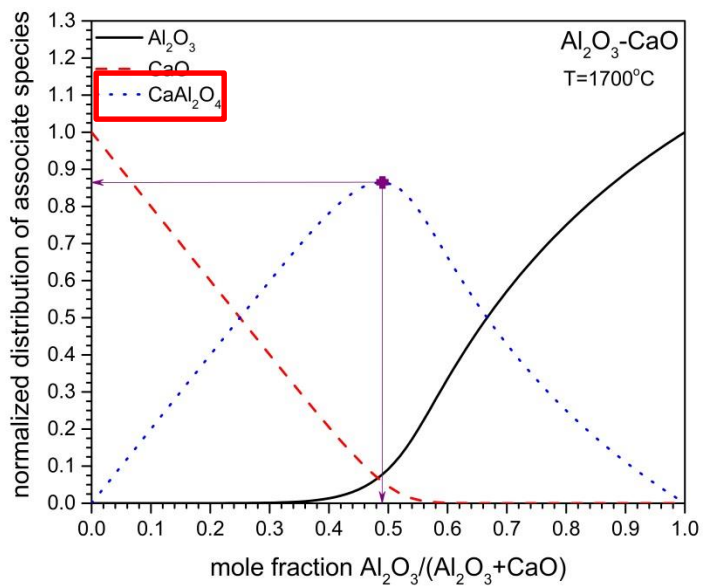


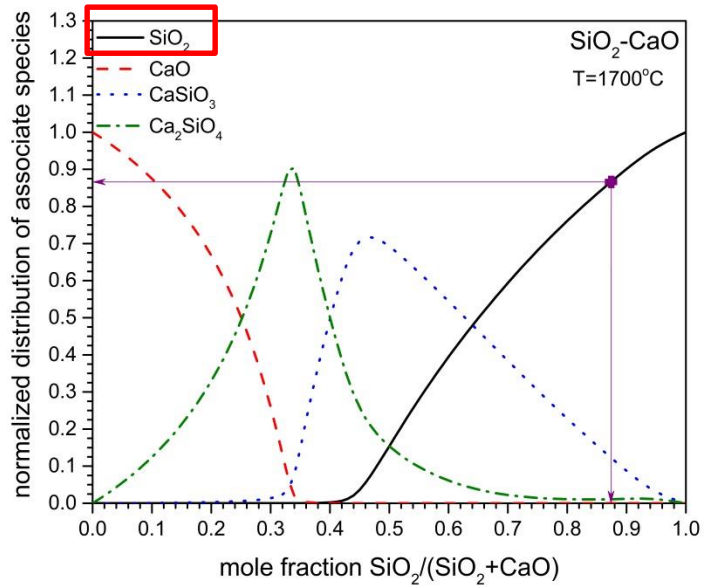
MAl_2O_4, $MSi_2Al_2O_8$ or $M_2Si_5Al_4O_{18}$
M: Ca, Mg

3 Modelling

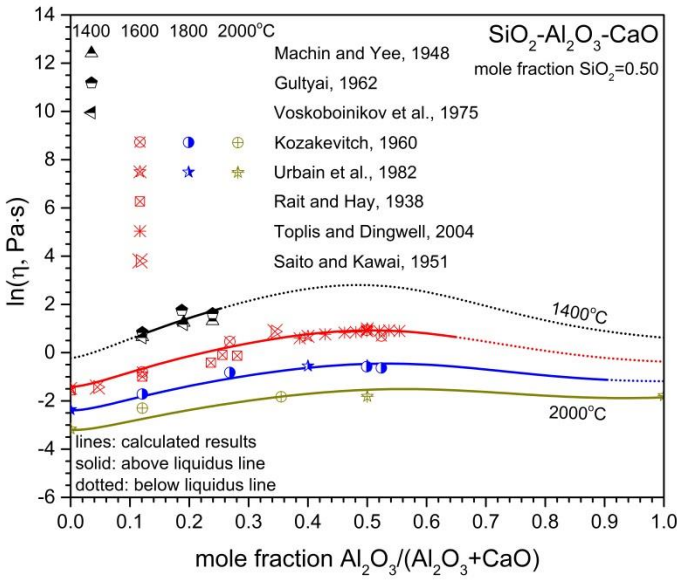

Breus et al., 1983
Kozakevitch, 1960
Povolotskii et al., 1970
Al_2O_3-CaO
T=1700°C
ln(η, Pa·s)
lines: calculated results
solid: above liquidus line
dotted: below liquidus line
mole fraction $Al_2O_3/(Al_2O_3+CaO)$

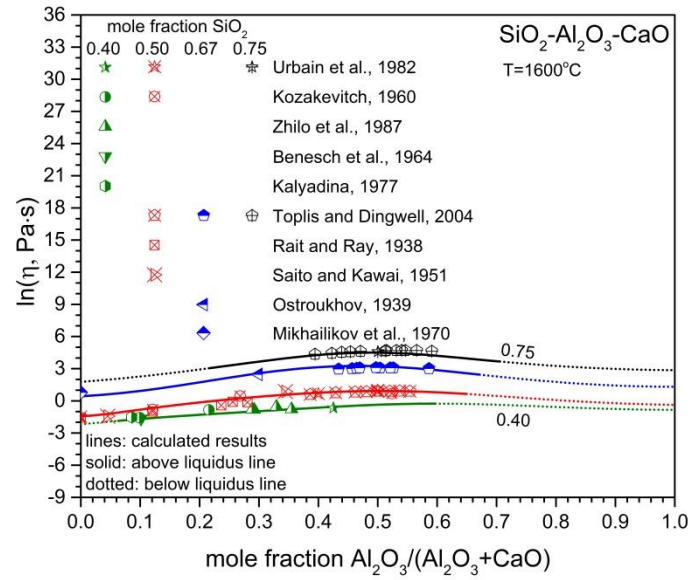

Bockris and Lowe, 1954
Kozakevitch, 1960
Urbain et al., 1982
Danek et al., 1983
Mikhailikov et al., 1970
Vetysheva et al., 1974
SiO_2-CaO
T=1700°C
ln(η, Pa·s)
lines: calculated results
solid: above liquidus line
dotted: below liquidus line
dashed: in liquid-immiscibility region
mole fraction $SiO_2/(SiO_2+CaO)$

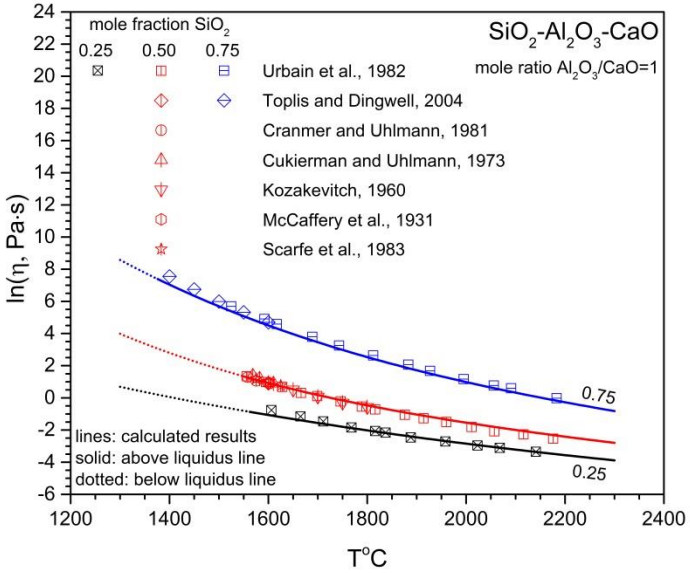

Al_2O_3
CaO
$CaAl_2O_4$
Al_2O_3-CaO
T=1700°C
normalized distribution of associate species
mole fraction $Al_2O_3/(Al_2O_3+CaO)$

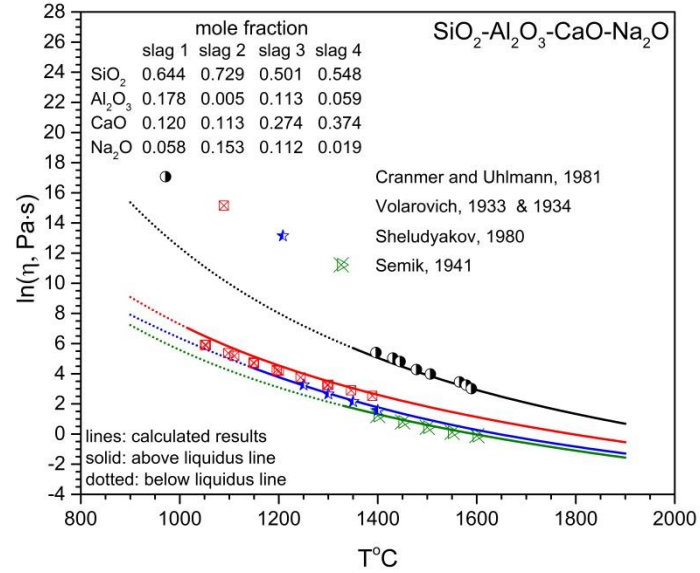

SiO_2
CaO
$CaSiO_3$
Ca_2SiO_4
SiO_2-CaO
T=1700°C
normalized distribution of associate species
mole fraction $SiO_2/(SiO_2+CaO)$

3 Modelling

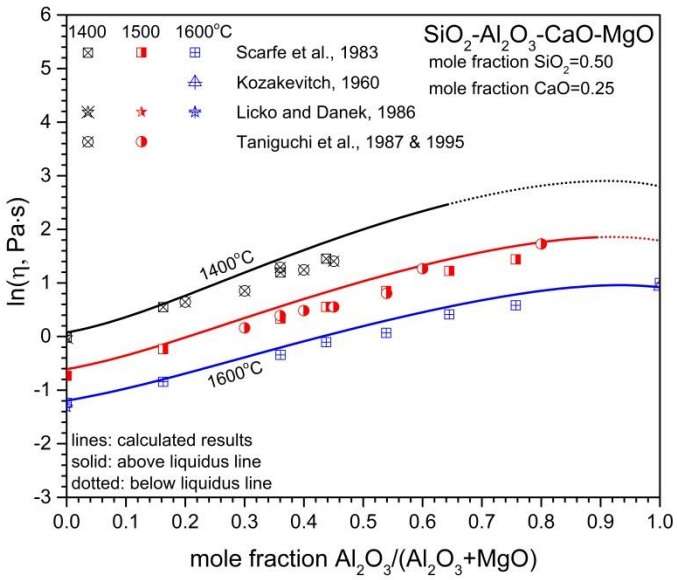

1400 1600 1800 2000°C
SiO2-Al2O3-CaO
mole fraction SiO2=0.50
Machin and Yee, 1948
Gultyai, 1962
Voskoboinikov et al., 1975
Kozakevitch, 1960
Urbain et al., 1982
Rait and Hay, 1938
Toplis and Dingwell, 2004
Saito and Kawai, 1951
1400°C
2000°C
lines: calculated results
solid: above liquidus line
dotted: below liquidus line
ln(η, Pa·s)
mole fraction Al2O3/(Al2O3+CaO)

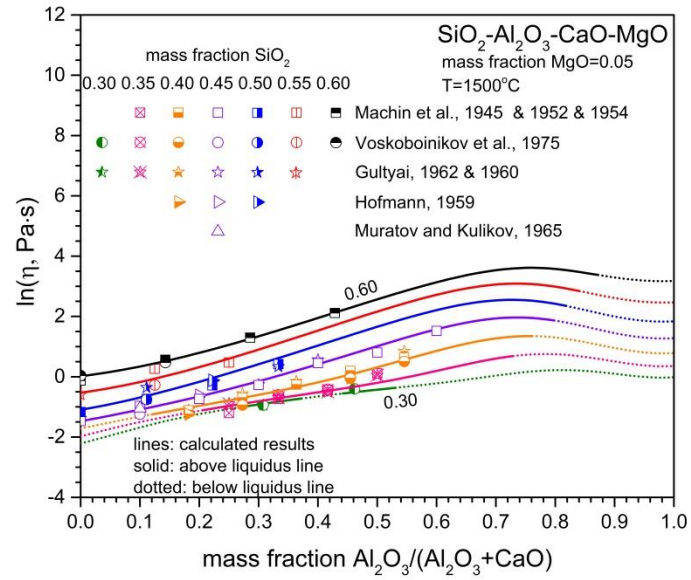

mole fraction SiO2
0.40 0.50 0.67 0.75
SiO2-Al2O3-CaO
T=1600°C
Urbain et al., 1982
Kozakevitch, 1960
Zhilo et al., 1987
Benesch et al., 1964
Kalyadina, 1977
Toplis and Dingwell, 2004
Rait and Ray, 1938
Saito and Kawai, 1951
Ostroukhov, 1939
Mikhailikov et al., 1970
0.75
0.40
lines: calculated results
solid: above liquidus line
dotted: below liquidus line
ln(η, Pa·s)
mole fraction Al2O3/(Al2O3+CaO)

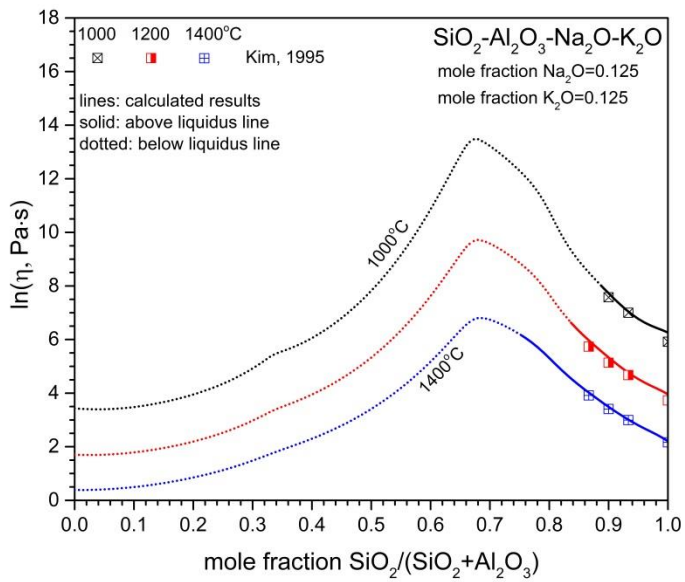

mole fraction SiO2
0.25 0.50 0.75
SiO2-Al2O3-CaO
mole ratio Al2O3/CaO=1
Urbain et al., 1982
Toplis and Dingwell, 2004
Cranmer and Uhlmann, 1981
Cukierman and Uhlmann, 1973
Kozakevitch, 1960
McCaffery et al., 1931
Scarfe et al., 1983
0.75
0.25
lines: calculated results
solid: above liquidus line
dotted: below liquidus line
ln(η, Pa·s)
T°C

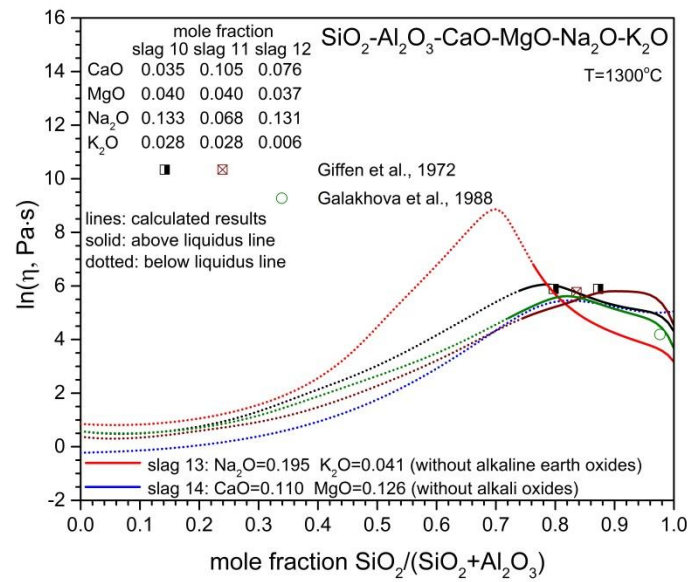

mole fraction
slag 1 slag 2 slag 3 slag 4
SiO2 0.644 0.729 0.501 0.548
Al2O3 0.178 0.005 0.113 0.059
CaO 0.120 0.113 0.274 0.374
Na2O 0.058 0.153 0.112 0.019
SiO2-Al2O3-CaO-Na2O
Cranmer and Uhlmann, 1981
Volarovich, 1933 & 1934
Sheludyakov, 1980
Semik, 1941
lines: calculated results
solid: above liquidus line
dotted: below liquidus line
ln(η, Pa·s)
T°C

3 Modelling

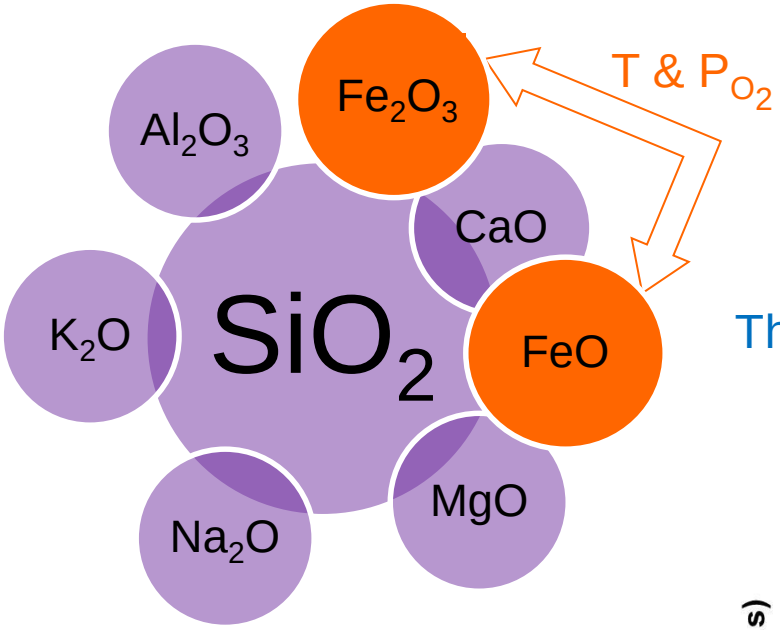

1400 1500 1600°C
Scarfe et al., 1983
Kozakevitch, 1960
Licko and Danek, 1986
Taniguchi et al., 1987 & 1995
SiO2-Al2O3-CaO-MgO
mole fraction SiO2=0.50
mole fraction CaO=0.25
1400°C
1600°C
lines: calculated results
solid: above liquidus line
dotted: below liquidus line
ln(η, Pa·s)
mole fraction Al2O3/(Al2O3+MgO)


mass fraction SiO2
0.30 0.35 0.40 0.45 0.50 0.55 0.60
Machin et al., 1945 & 1952 & 1954
Voskoboinikov et al., 1975
Gultyai, 1962 & 1960
Hofmann, 1959
Muratov and Kulikov, 1965
SiO2-Al2O3-CaO-MgO
mass fraction MgO=0.05
T=1500°C
0.60
0.30
lines: calculated results
solid: above liquidus line
dotted: below liquidus line
ln(η, Pa·s)
mass fraction Al2O3/(Al2O3+CaO)


1000 1200 1400°C
Kim, 1995
SiO2-Al2O3-Na2O-K2O
mole fraction Na2O=0.125
mole fraction K2O=0.125
lines: calculated results
solid: above liquidus line
dotted: below liquidus line
1000°C
1400°C
ln(η, Pa·s)
mole fraction SiO2/(SiO2+Al2O3)


mole fraction
slag 10 slag 11 slag 12
CaO 0.035 0.105 0.076
MgO 0.040 0.040 0.037
Na2O 0.133 0.068 0.131
K2O 0.028 0.028 0.006
SiO2-Al2O3-CaO-MgO-Na2O-K2O
T=1300°C
Giffen et al., 1972
Galakhova et al., 1988
lines: calculated results
solid: above liquidus line
dotted: below liquidus line
slag 13: Na2O=0.195 K2O=0.041 (without alkaline earth oxides)
slag 14: CaO=0.110 MgO=0.126 (without alkali oxides)
ln(η, Pa·s)
mole fraction SiO2/(SiO2+Al2O3)

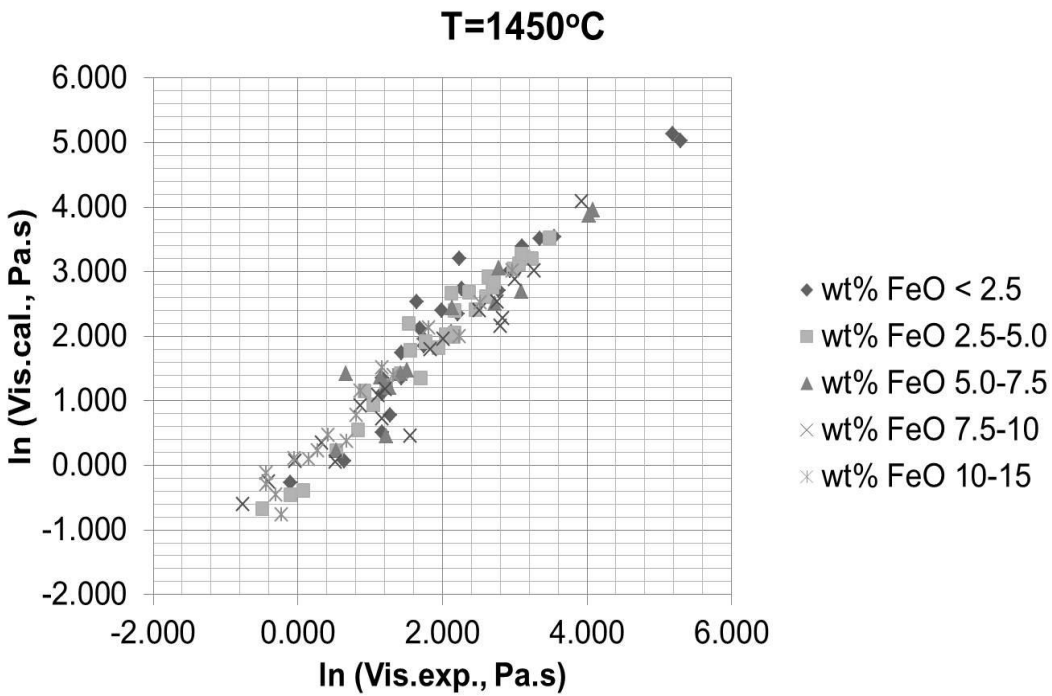
3 Modelling



Dual roles

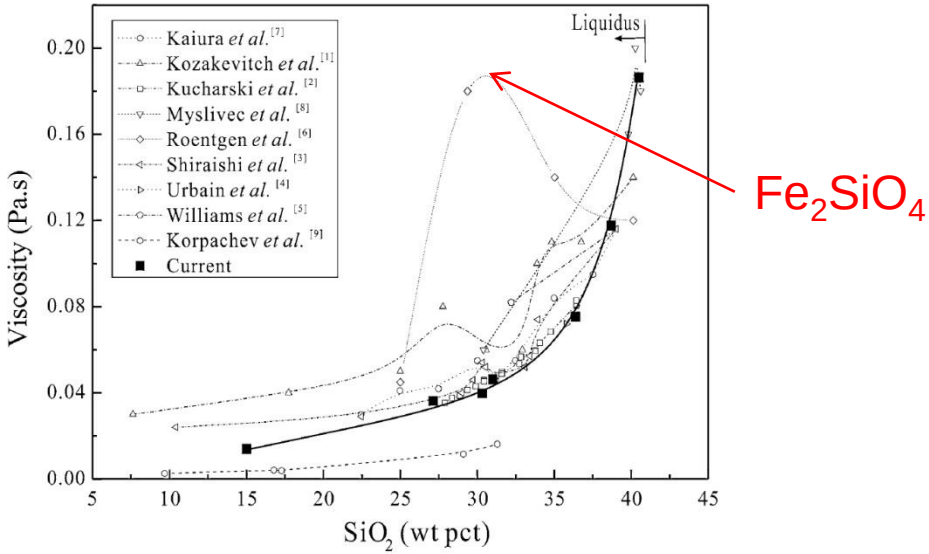
Redox reaction

The current model **VS.** The Hurst model*



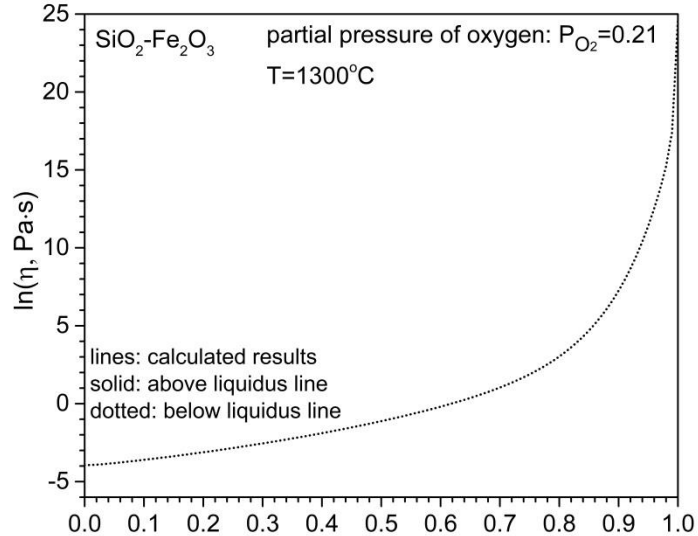
Source: H.J. Hurst, F. Novak, J.H. Patterson, Proc. V International Conference on Molten Slags, Fluxes and Salts, Sydney, Australia, 1997, pp. 873-876

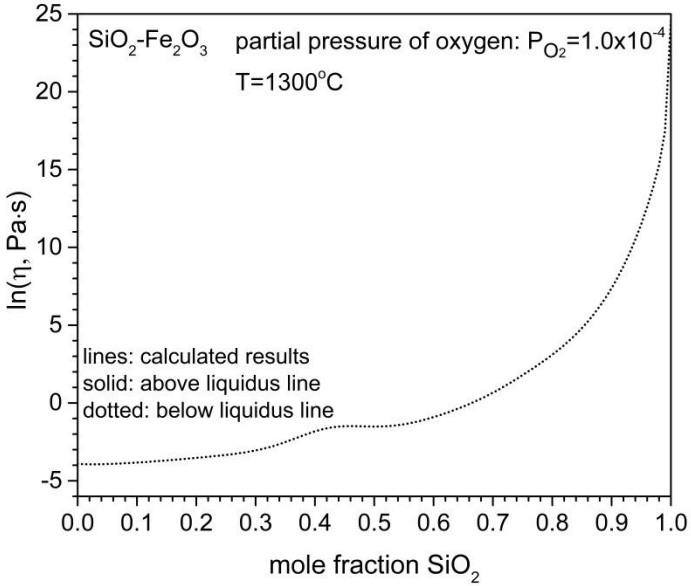
3 Modelling

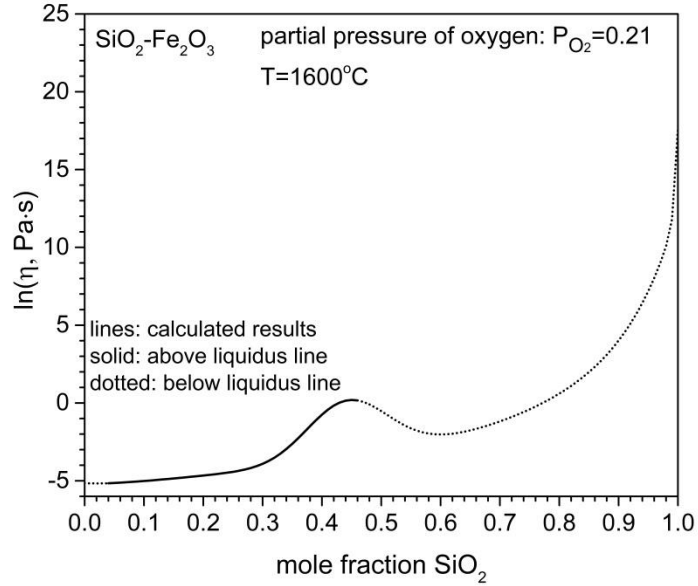


Fe_2SiO_4

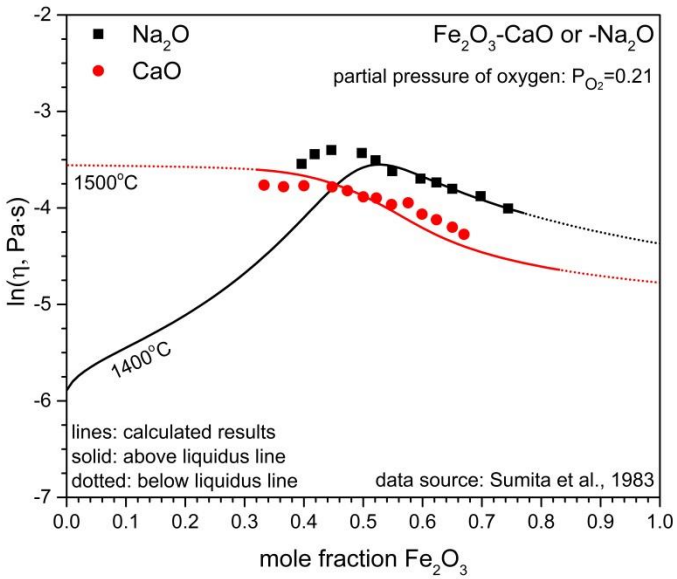
Source: M. Chen, S. Raghunath, B. Zhao, Metall. Mater. Trans. B, 44 (2013) 506-515.

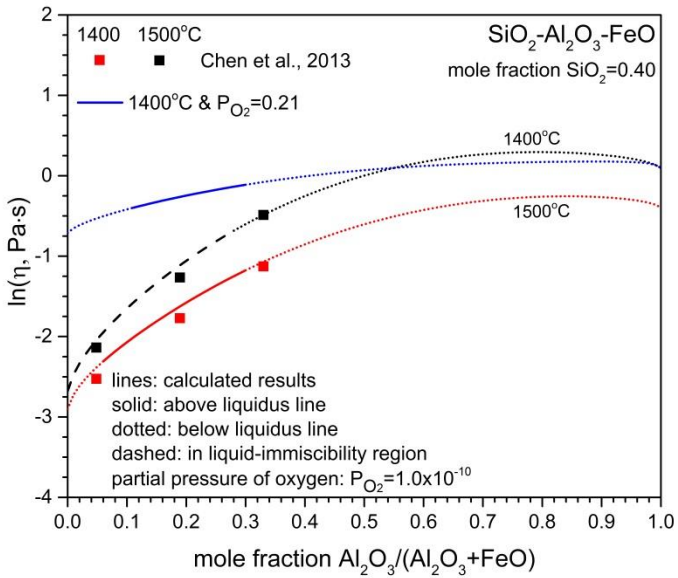


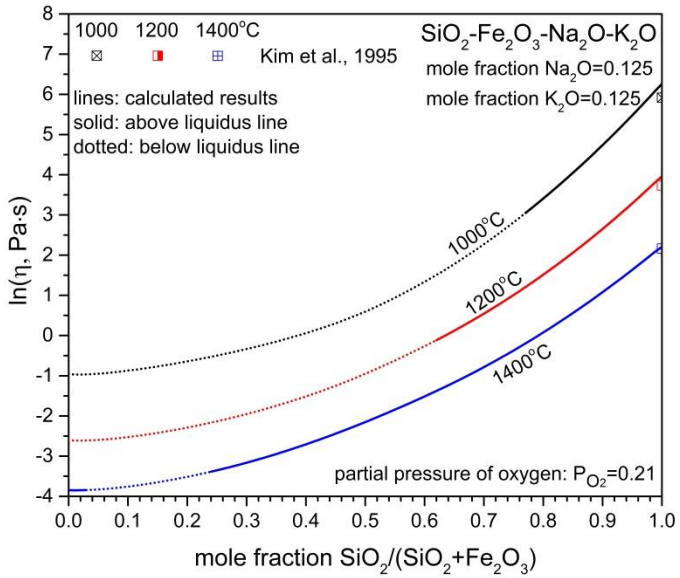




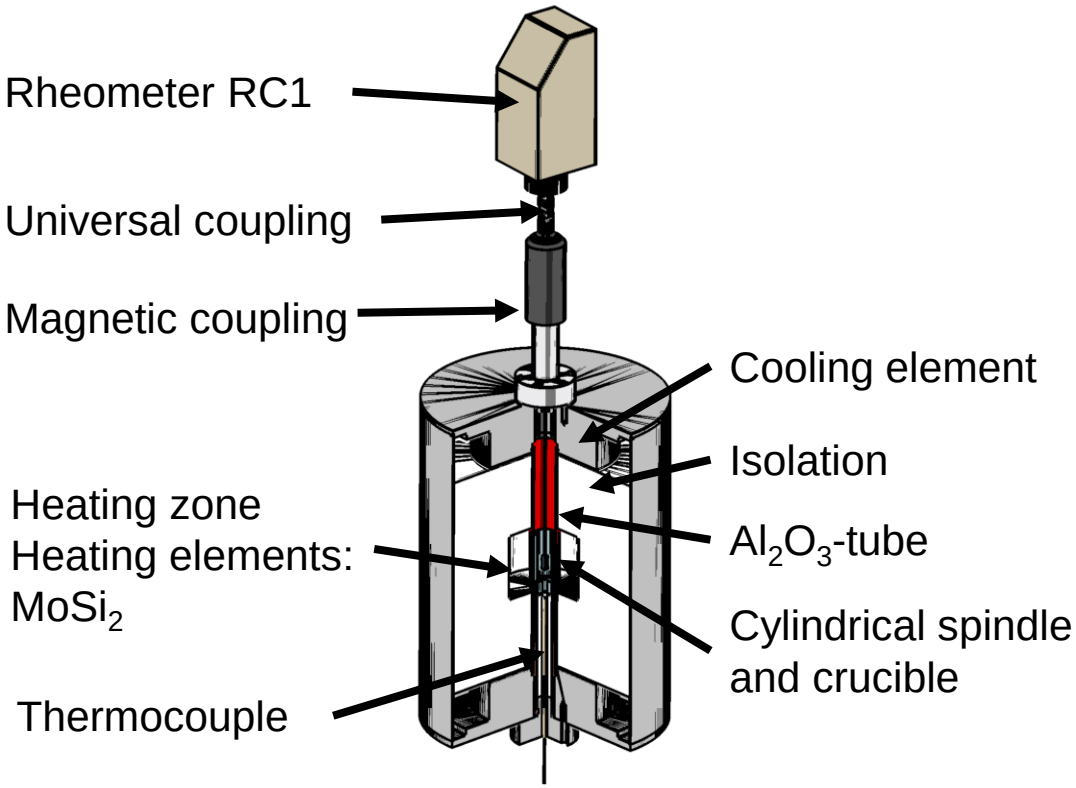
3 Modelling


Na2O
CaO
Fe2O3-CaO or -Na2O
partial pressure of oxygen: PO2=0.21
1500°C
1400°C
lines: calculated results
solid: above liquidus line
dotted: below liquidus line
data source: Sumita et al., 1983
ln(η, Pa·s)
mole fraction Fe2O3


1400 1500°C
Chen et al., 2013
1400°C & PO2=0.21
SiO2-Al2O3-FeO
mole fraction SiO2=0.40
1400°C
1500°C
lines: calculated results
solid: above liquidus line
dotted: below liquidus line
dashed: in liquid-immiscibility region
partial pressure of oxygen: PO2=1.0x10-10
ln(η, Pa·s)
mole fraction Al2O3/(Al2O3+FeO)

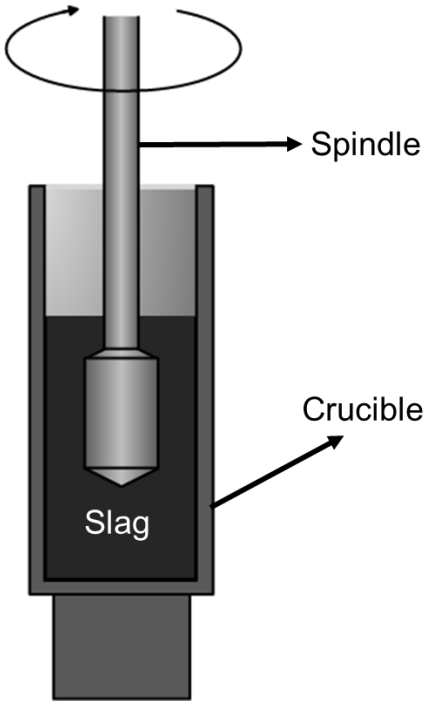

1000 1200 1400°C
Kim et al., 1995
SiO2-Fe2O3-Na2O-K2O
mole fraction Na2O=0.125
mole fraction K2O=0.125
lines: calculated results
solid: above liquidus line
dotted: below liquidus line
1000°C
1200°C
1400°C
partial pressure of oxygen: PO2=0.21
ln(η, Pa·s)
mole fraction SiO2/(SiO2+Fe2O3)

4 Validation



Spindle and crucible:

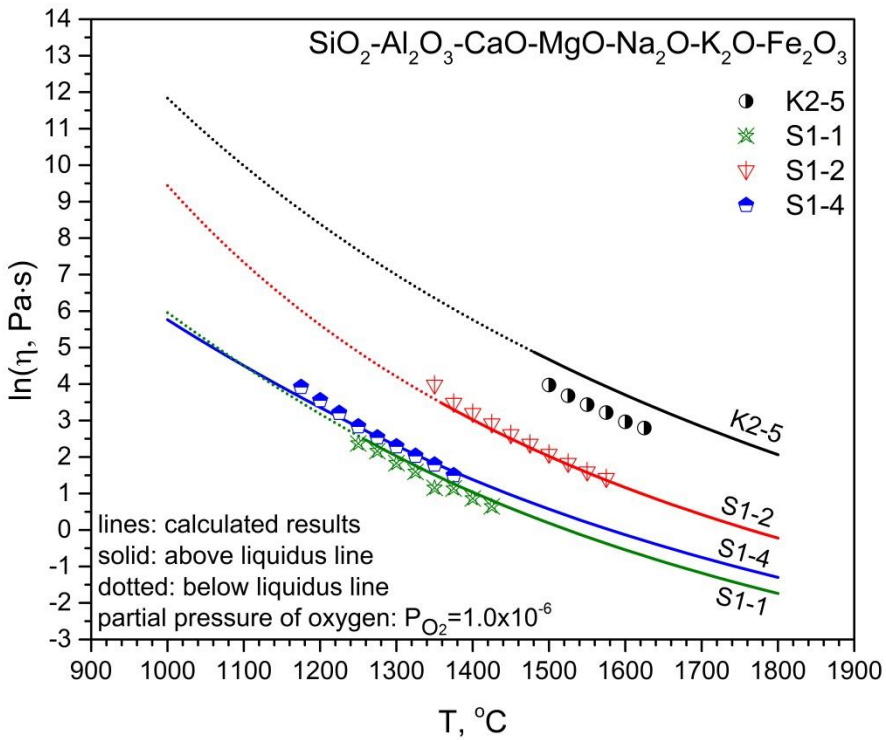
- Molybdenum type (T_m=2623°C)
- Bob diameter of 14 mm
- Crucible diameter of 29 mm
- Relative viscosity measurement



Rotational viscometer:

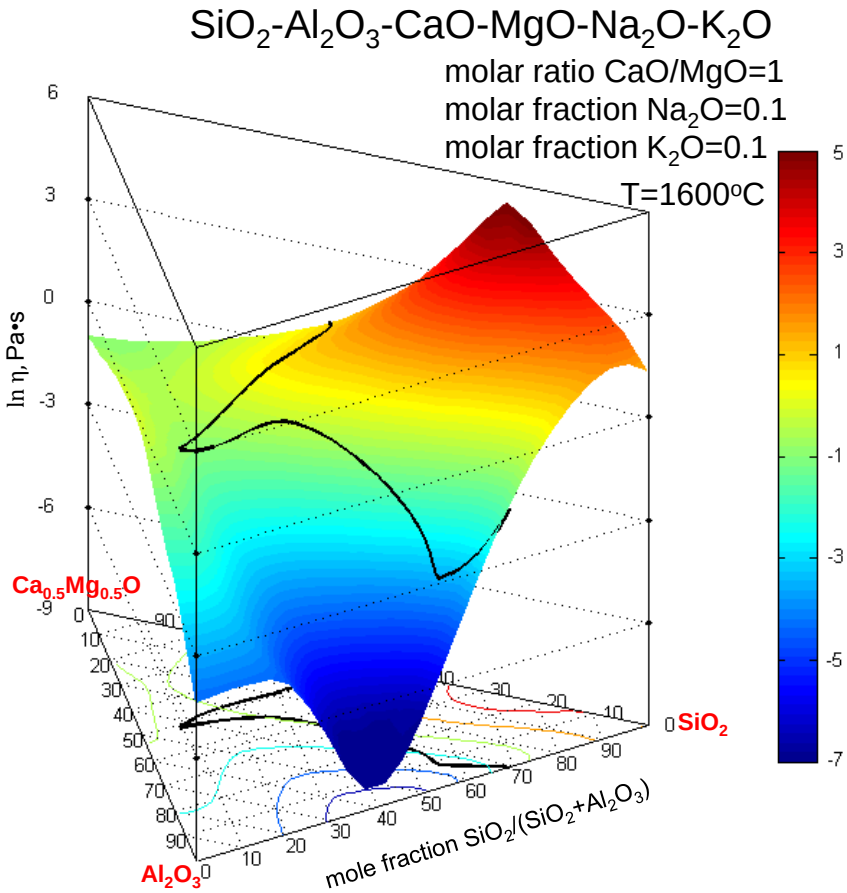
- Temperature up to 1600°C
- Pressure up to 5 bar
- Measuring range: 1~1000 Pa•s

4 Validation



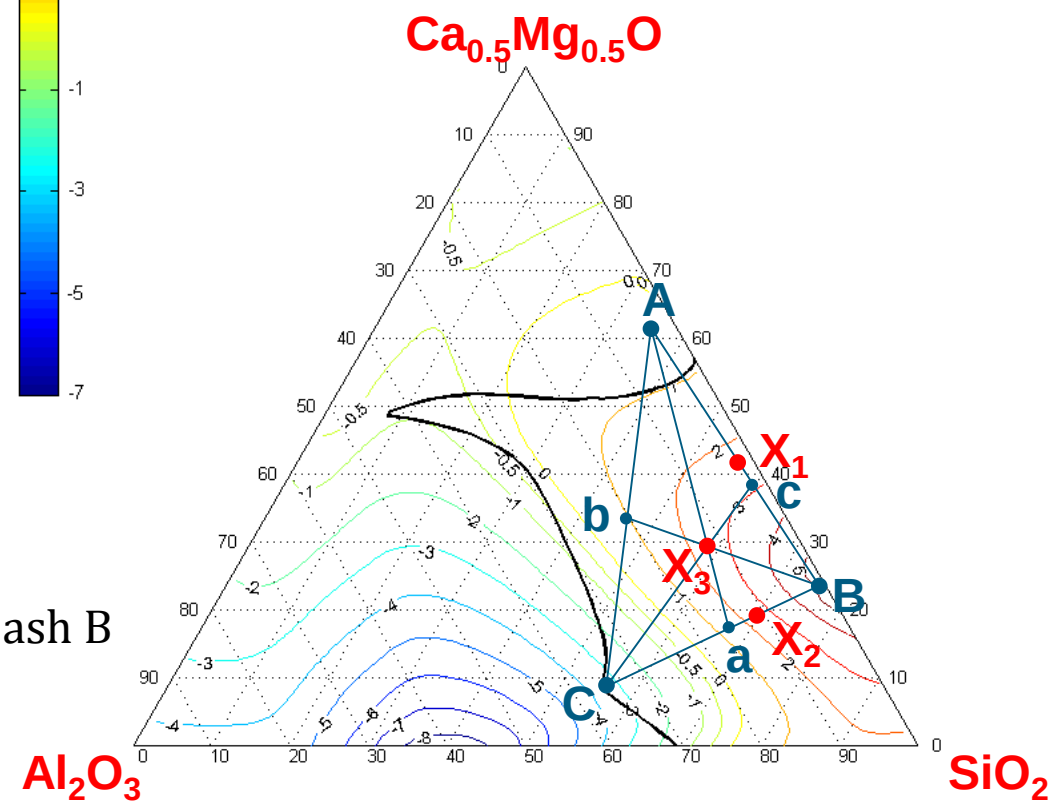
Coal ashes	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	Fe_2O_3
K2-5	0.7180	0.1747	0.0206	0.0239	0.0028	0.0320	0.0280
S1-1	0.6292	0.0185	0.2165	0.0873	0.0153	0.0018	0.0314
S1-2	0.5738	0.1739	0.1612	0.0416	0.0206	0.0071	0.0218
S1-4	0.5777	0.0798	0.1785	0.0709	0.0510	0.0105	0.0316

5 Application of the model



$$\frac{\text{Amount of Coal ash A}}{\text{Amount of Coal ash B}} = \frac{BX_1}{AX_1}$$

$$\frac{\text{Amount of Coal ash B}}{\text{Amount of Coal ash C}} = \frac{CX_2}{BX_2}$$



Amount of Coal ash A / Amount of Coal ash B / Amount of Coal ash C = $aX_3/bX_3/cX_3$

6 Conclusion & outlook

Conclusion:

- A new **structurally-based viscosity model** is developed for the fully liquid oxide system **SiO_2-Al_2O_3-CaO-MgO-Na_2O-K_2O-FeO-Fe_2O_3** over the **whole range of compositions** and a **broad range of temperatures**;
- Good performance is achieved using only **one set of model parameters**, all having a clear **physico-chemical meaning**;
- **Composition-** and **temperature-**induced viscosity behaviors are well described;
- **Extrapolated viscosities** to the regions without experimental data are **reasonable**;
- The model is **self-consistent**.

6 Conclusion & outlook

Outlook:

- Further assessing the model parameters of the **FeO/Fe_2O_3 containing systems**;
- Extending the model for fully liquid phase by **further oxides**, such as P_2O_5;
- Extending the model from fully liquid phase to **mixtures of liquid and solids**;
- Measuring viscosity in unknown region to **validate the current model**.

JÜLICH
FORSCHUNGSZENTRUM

Thank you very much for your attention!