JÜLICH
FORSCHUNGSZENTRUM

Further progress in modelling slag viscosities on the basis of the HotVeGas Oxide database

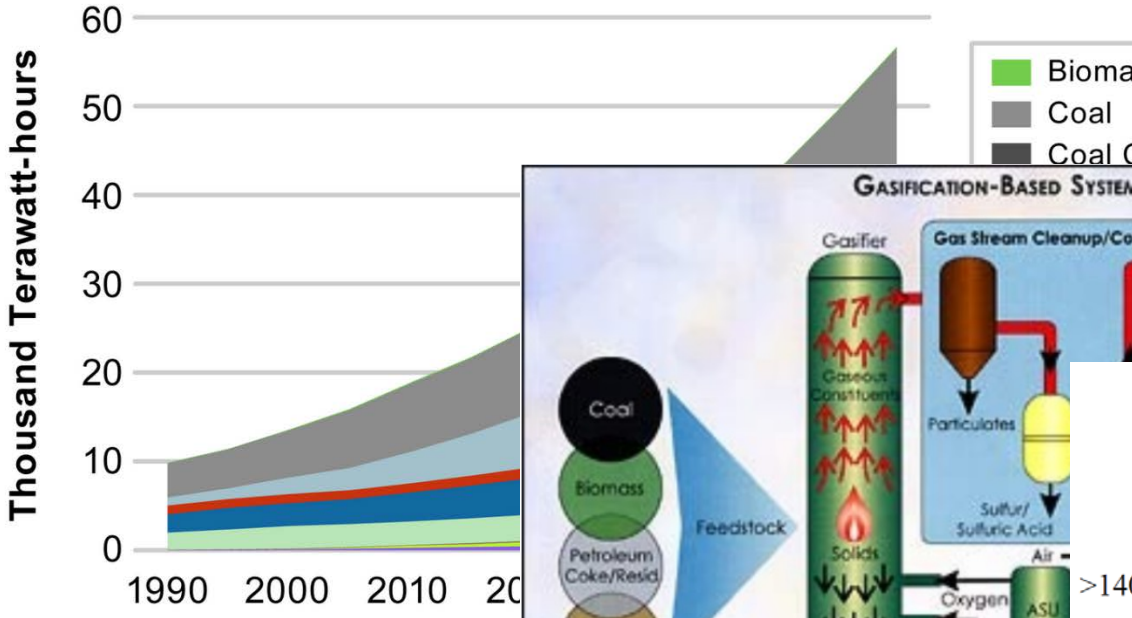
03.07.2014 Guixuan Wu

GTT Annual Users' Meeting 2014

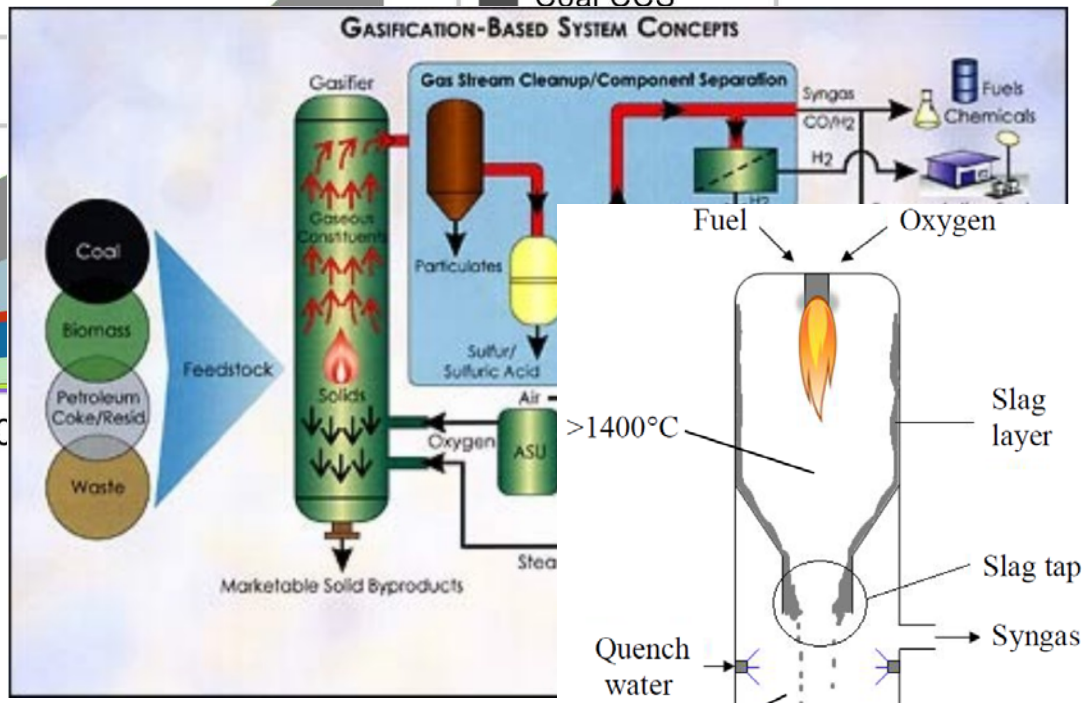
Outline

- Background and motivation
- Challenging viscosity behaviors
- Viscosity model development
- Results
- Application of 3-D viscosity surface
- Conclusions and outlook

Background and motivation



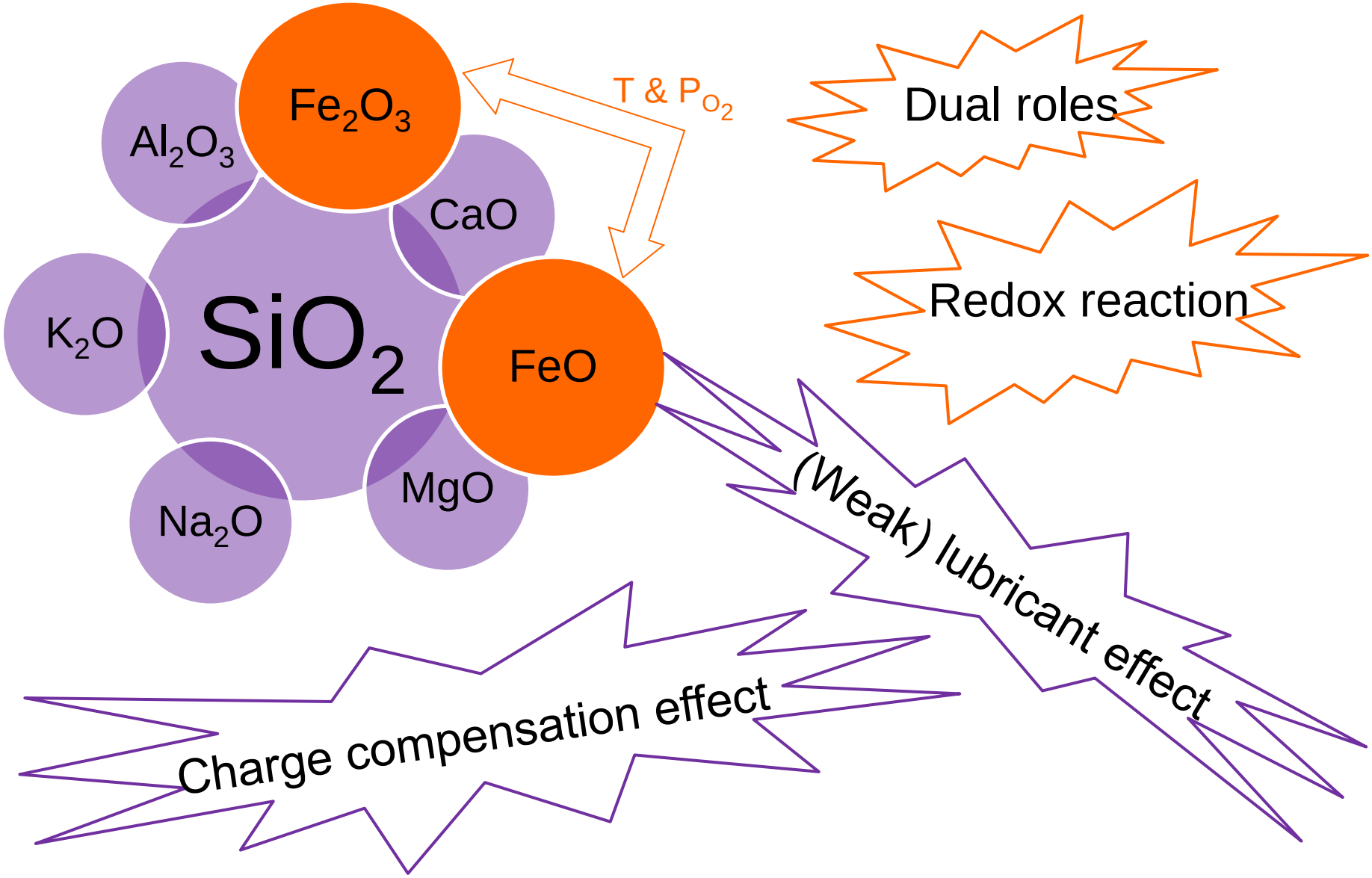
Source: SEI International



Source: HotVeGas

Source: Marc A. Duchesne, Slagging in entrained-flow gasifiers, 2012.

The challenging viscosity behaviors



The viscosity model

Classical model:

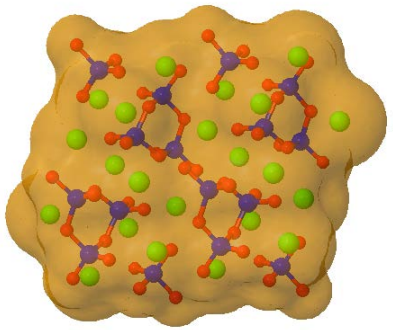
The story of current model :

- For FeO/Fe_2O_3 containing systems, partial pressure of oxygen is also taken into account in the current model.

The current viscosity model I

Comp. Temp. → Associate species → Viscosity

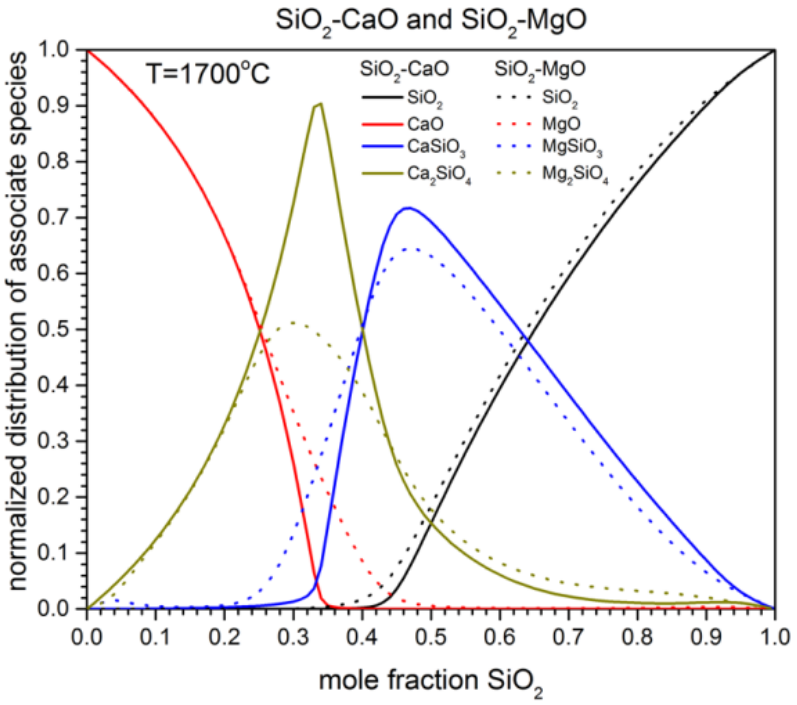
Partial pressure of oxygen
(for FeO/Fe_2O_3 containing system)



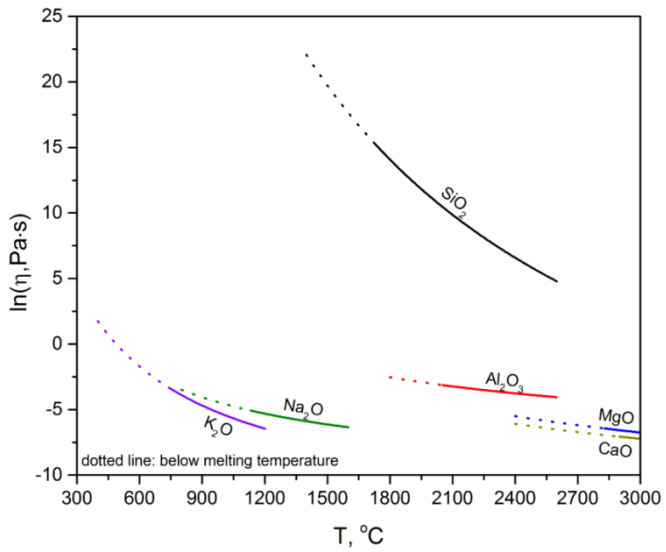
$CaSiO_3$

SiO_2-CaO-MgO

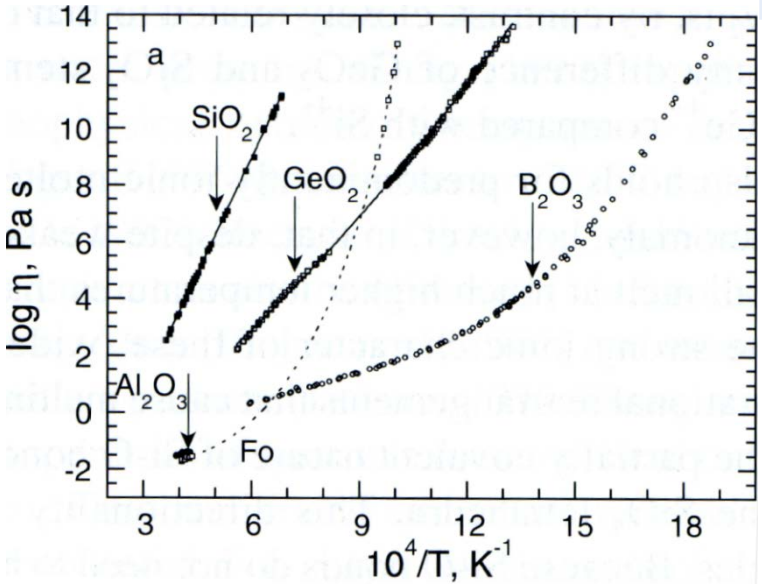
Compounds	Associate species
SiO_2	Si_2O_4
CaO	Ca_2O_2
$CaSiO_3$	$CaSiO_3$
Ca_2SiO_4	$\frac{2}{3}\cdot Ca_2SiO_4$
$MgSiO_3$	$MgSiO_3$
Mg_2SiO_4	$\frac{2}{3}\cdot Mg_2SiO_4$



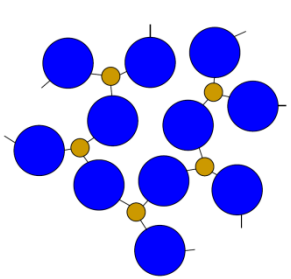
Pure oxides



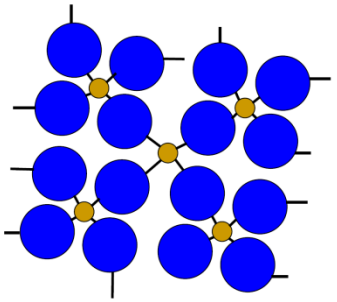
Sun's Bond Strength Model			
M in MO_x	Valence	Coordination number	Single-bond strength (kcals/mol)
B	3	3	119
Si	4	4	106
Al	3	6	53-67
Mg	2	6	37
Ca	2	8	32
Na	1	6	20
K	1	9	13



Network Dimensionality:

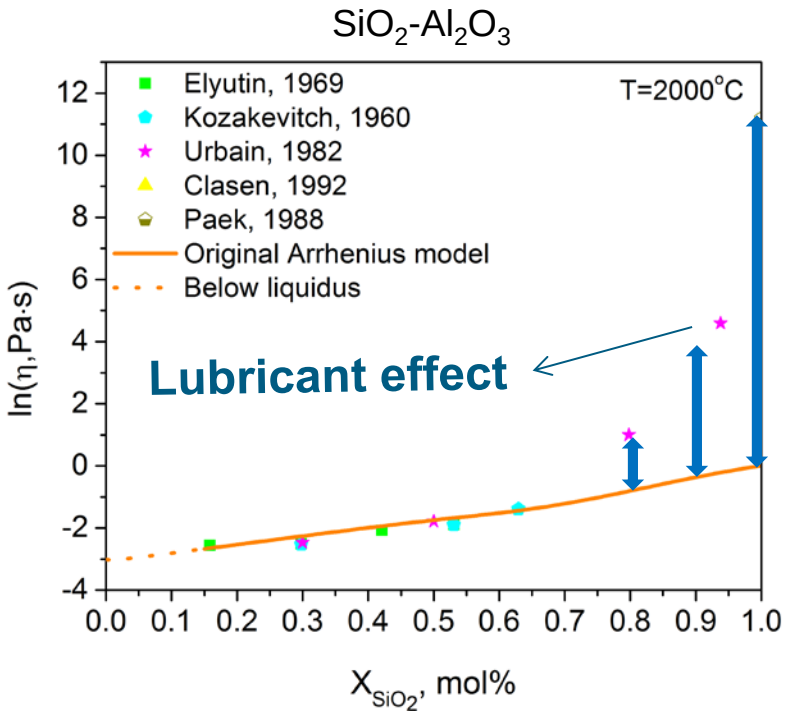


2D: B_2O_3



3D: SiO_2

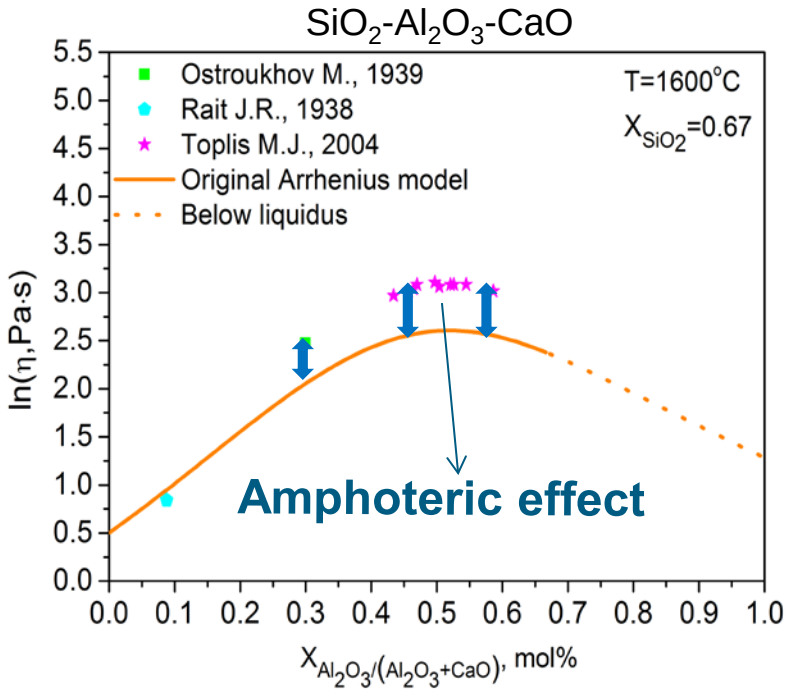
The results of the current viscosity model I



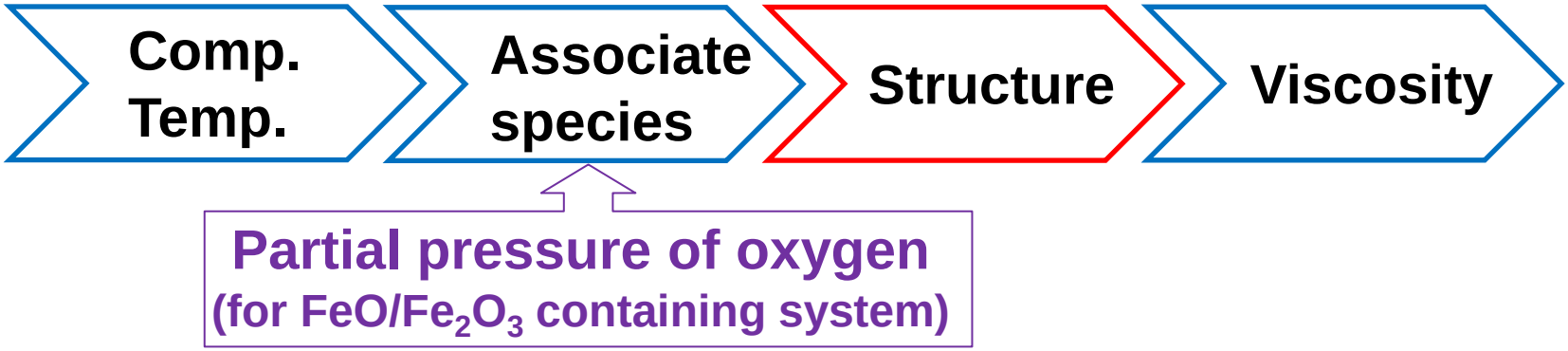
$$\ln \eta = (\sum X_i \cdot \ln \eta_i)$$

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

i: associate species



The idea of current viscosity model II



SiO_2-CaO-MgO

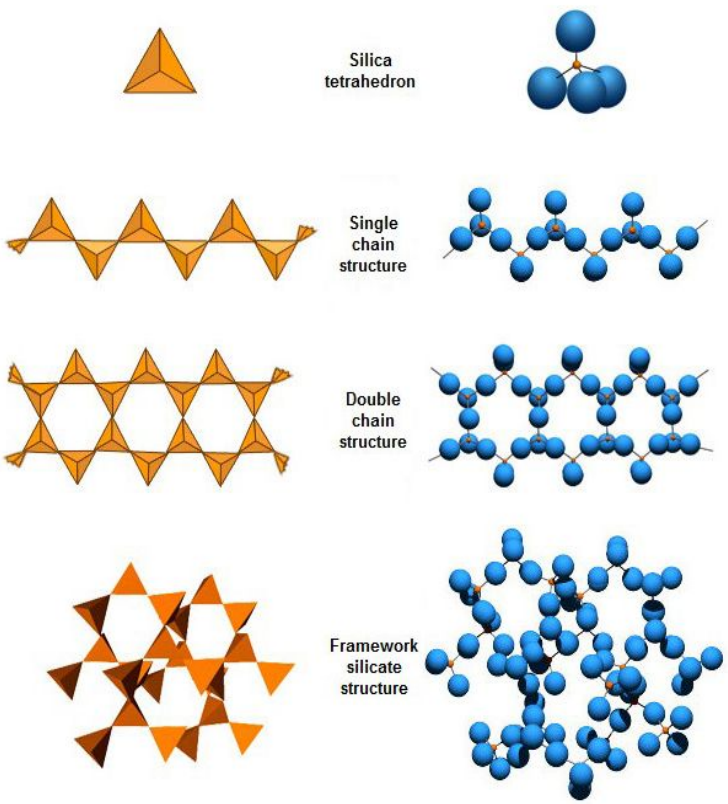
Compounds	Associate species	Structural units
SiO_2	Si_2O_4	**Si**O_2
CaO	Ca_2O_2	**Ca**O
$CaSiO_3$	$CaSiO_3$	Ca**Si**O_3
Ca_2SiO_4	$\frac{2}{3}\cdot Ca_2SiO_4$	Ca_2**Si**O_4
$MgSiO_3$	$MgSiO_3$	Mg**Si**O_3
Mg_2SiO_4	$\frac{2}{3}\cdot Mg_2SiO_4$	Mg_2**Si**O_4

CaO-Fe_2O_3

Compounds	Associate species	Structural units
CaO	Ca_2O_2	**Ca**O
FeO	Fe_2O_2	**Fe**O
Fe_2O_3	Fe_2O_3	**Fe**$O_{1.5}$
$CaFe_2O_4$	$\frac{2}{3}\cdot CaFe_2O_4$	$Ca_{0.5}$**Fe**O_2

basic structural units

Larger structural units



$S: SiO_2, A: Al_2O_3, N: Na_2O$

$$S_1+S_1=S_2$$
$$S_1+S_2=S_3$$
$$\dots\ \dots$$
$$S_1+S_{k-1}=S_k$$

self-pol. of SiO_2

$$A_1N_1S_1 + S_1 = A_1N_1S_2$$
$$A_1N_1S_1 + S_2 = A_1N_1S_3$$
$$\dots\ \dots$$
$$A_1N_1S_1 + S_{k-1} = A_1N_1S_k$$

inter-pol.

$$A_1N_1S_1 + A_1N_1S_1 = A_2N_2S_2$$
$$A_2N_2S_2 + A_1N_1S_1 = A_3N_3S_3$$
$$\dots\ \dots$$
$$A_{k-1}N_{k-1}S_{k-1} + A_1N_1S_1 = A_kN_kS_k$$

self-pol. of silicon-aluminum based ternary associate species

The current viscosity model II

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

Arrhenius model (modified)

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

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

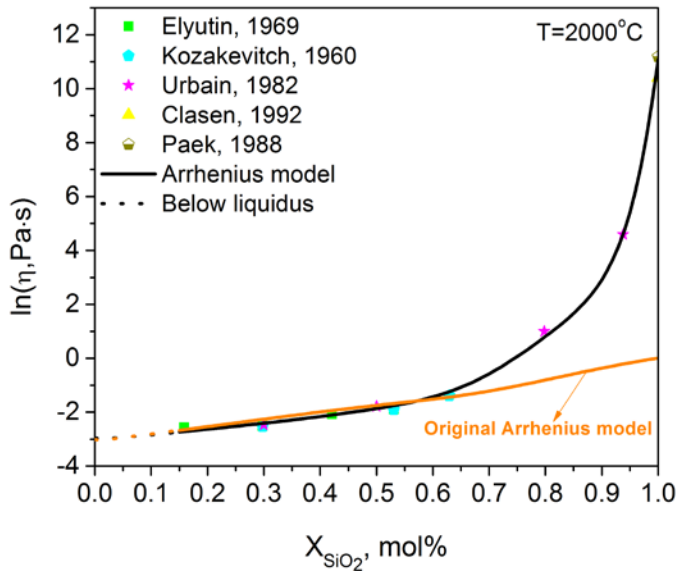
where: $\ln \eta_i = A_i + B_i/T$ ⟶ basic structural units

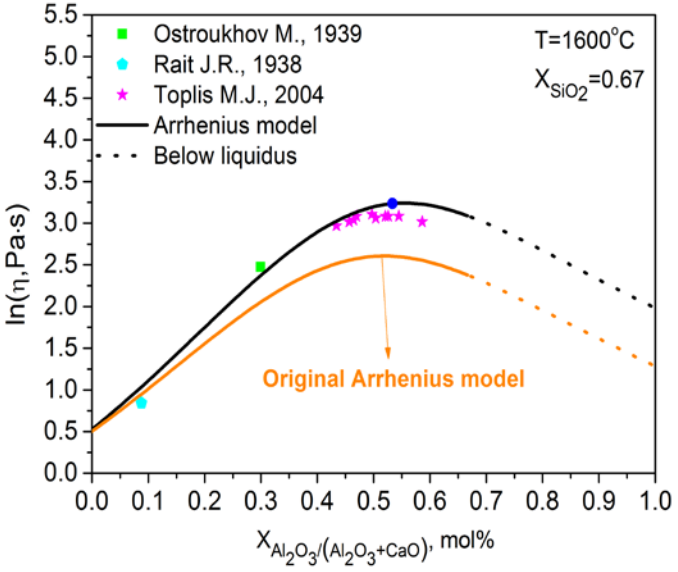
$$\ln \eta_{self-pol.} = \sum \left(A^*_{j,SiO_2} + B^*_{j,SiO_2}/T\right) \cdot \left(X^{n_j}_{SiO_2}\right) + \sum (A^*_k + B^*_k/T) \cdot (X^{n_k}_k)$$

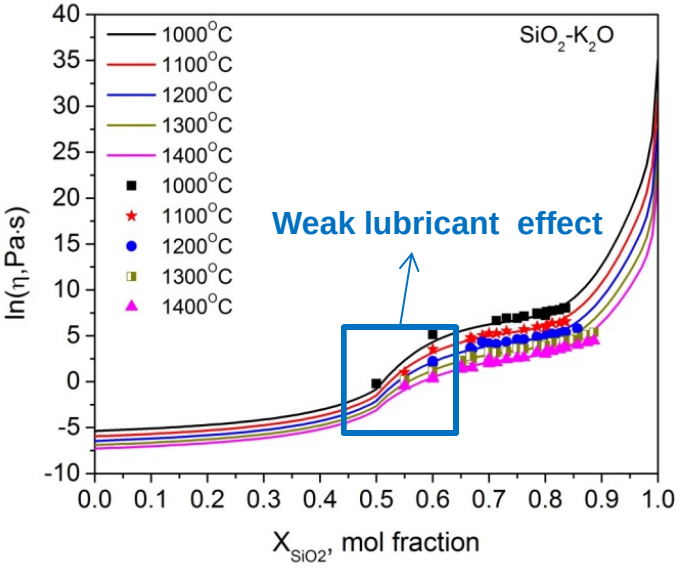
$$\ln \eta_{inter-pol.} = \sum (A^*_m + B^*_m/T) \cdot (X_m \cdot X^{n_m}_{SiO_2})$$

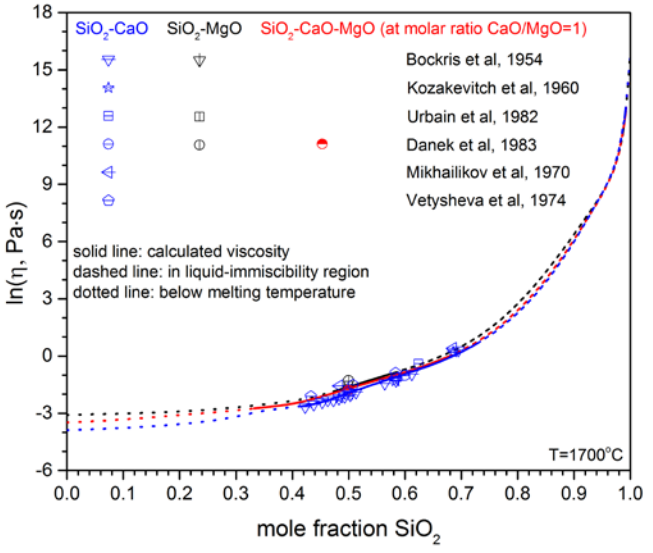
larger structural units

The results of the current viscosity model II

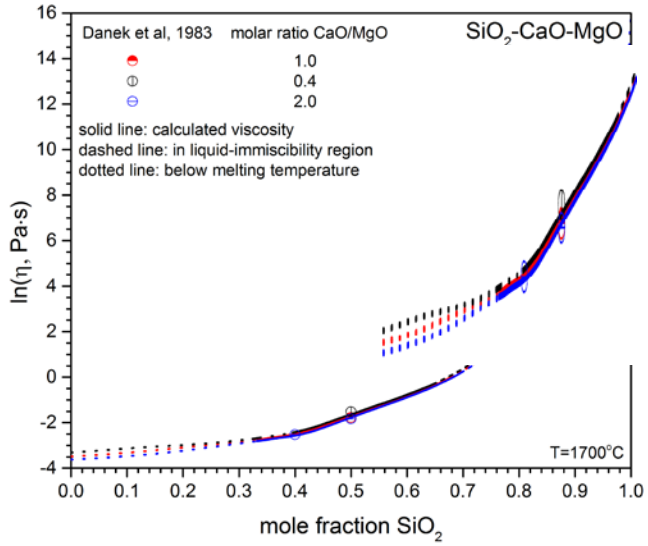


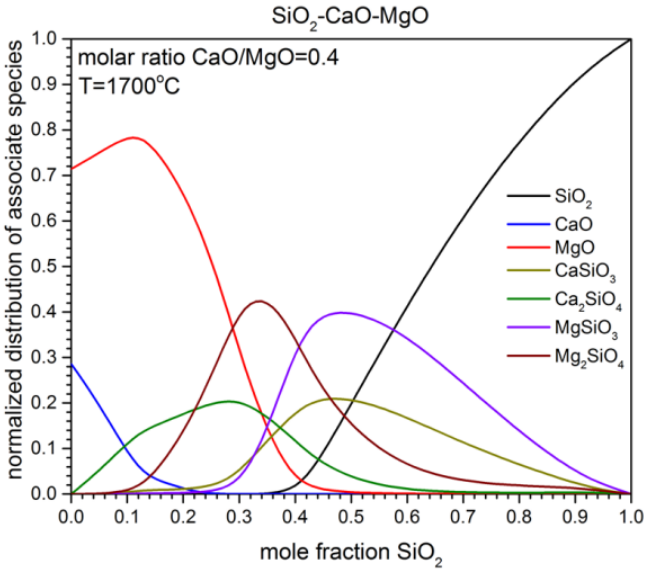


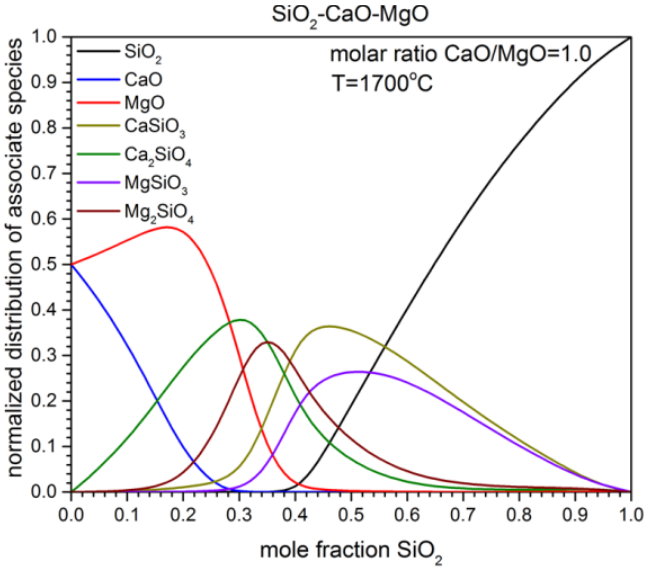


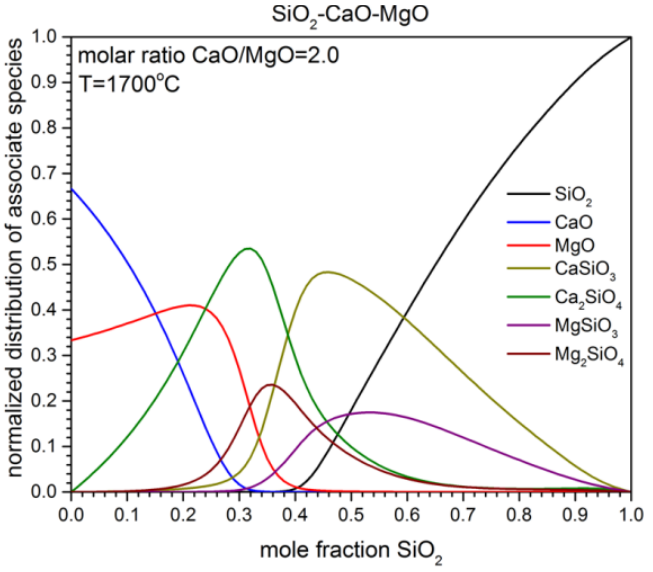


The distribution of structural units

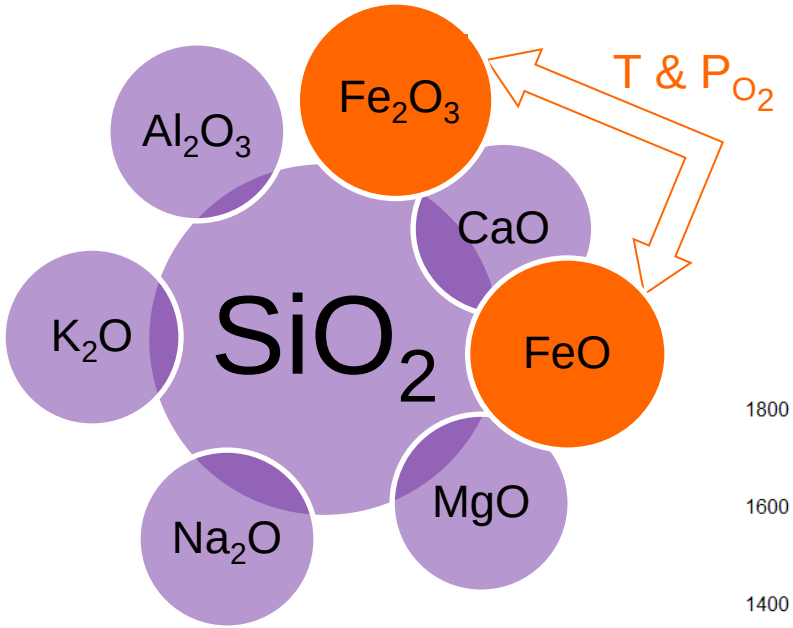






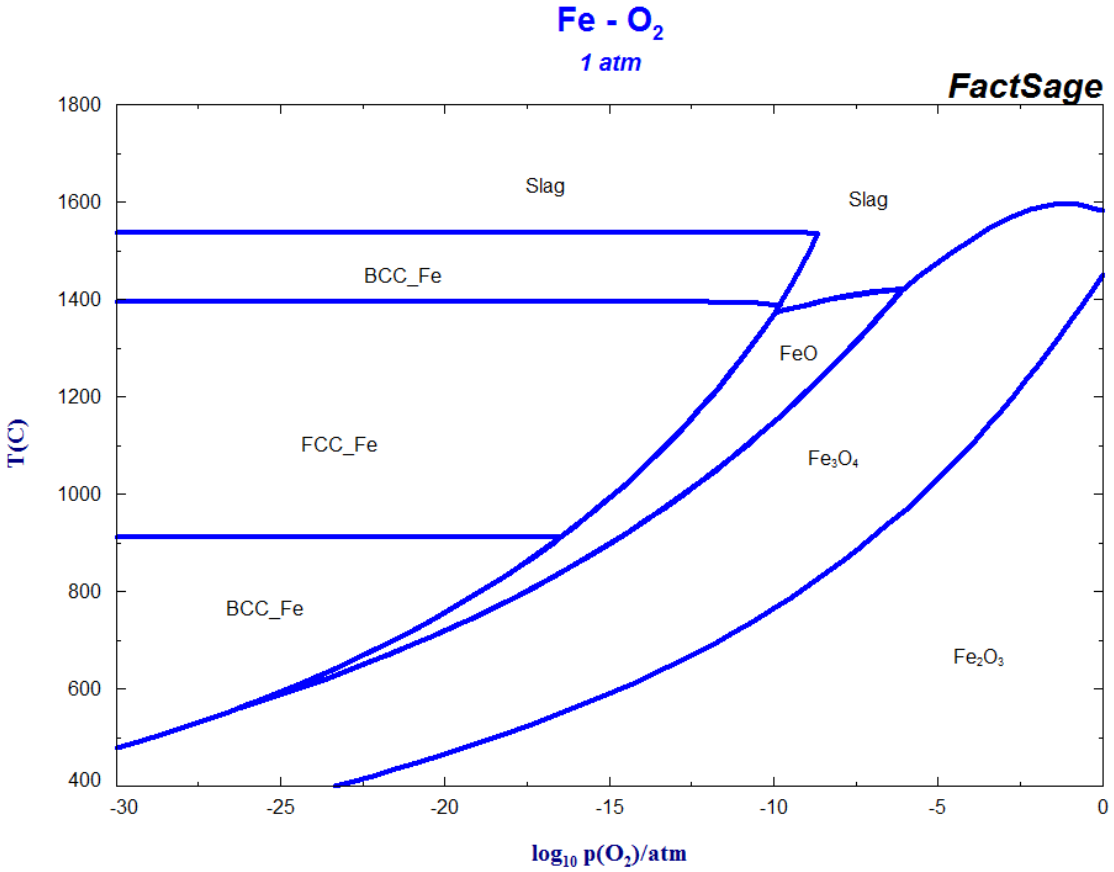


Influence of the T and P_{O_2}

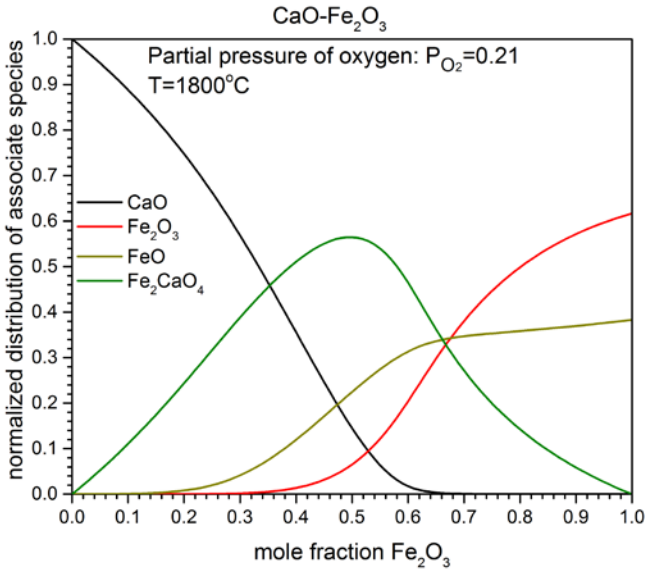


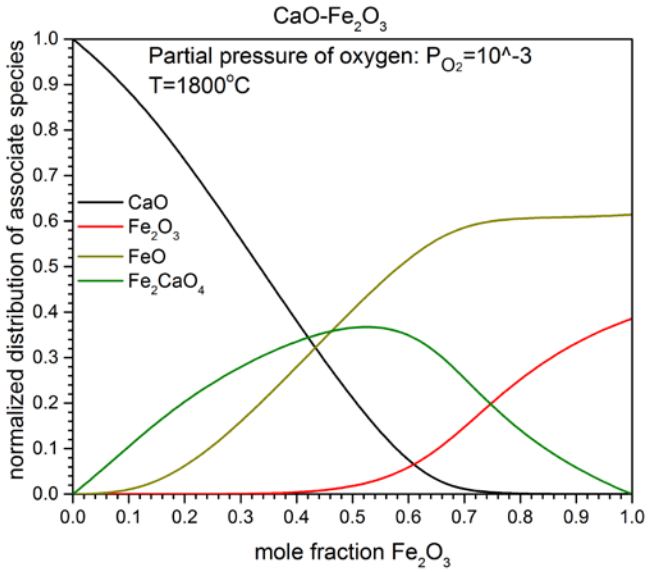
Dual roles

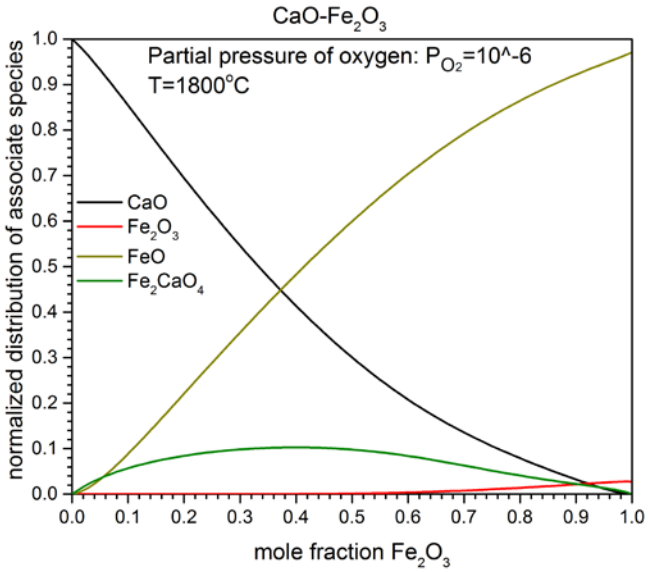
Redox reaction

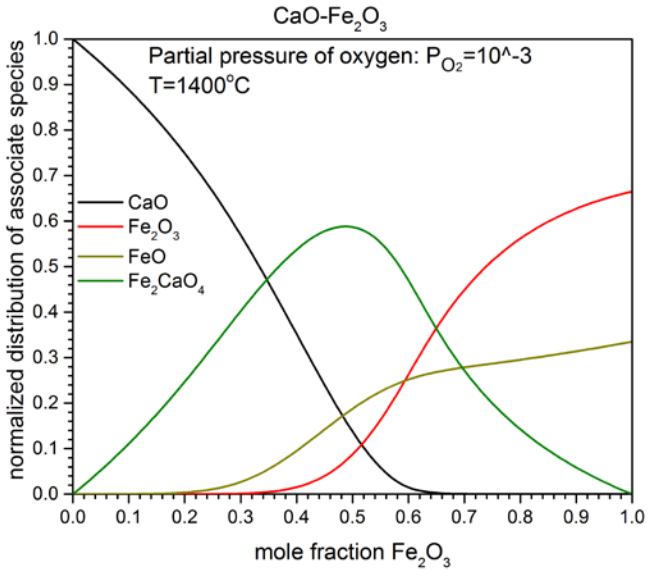


Influence of the T and P_{O_2}









The modified Urbain model

$$\eta = \mathrm{ATexp(B/RT)},$$

$$\ln(\eta) = \ln(\mathrm{A}) + \ln(\mathrm{T}) + \mathrm{B/RT},$$

$$\ln(\eta) = a_0 + a_1 y + a_2 y^2 + a_3 x + a_4 xy + a_5 xy^2 + a_6 x^2 + a_7 x^2 y$$

$$+ a_8 x^2 y^2 + a_9 x^3 + a_{10} x^3 y + a_{11} x^3 y^2,$$

where: x and y are the normalized mole fractions $m_s/(m_s + m_a + m_c + m_f)$ and $(m_c + m_f)/(m_a + m_c + m_f)$, respectively.

s: SiO_2, a: Al_2O_3, c: CaO, f: FeO

*Source: Hurst, H. J.; Novak, F.; Patterson, J. H., Fuel **1999,** 78, 1831-1840.*

Parameters for the modified Urbain model

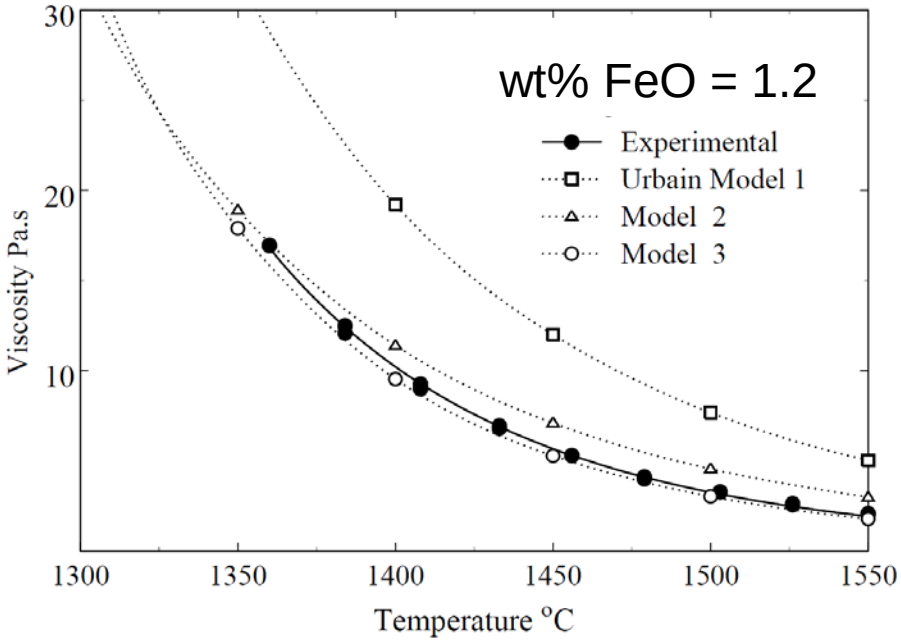
Model 1	Urbain model [4]
Model 2	Synthetic slag SAC model [3]
Model 3	Coal ash slag model for <2.5% FeO
Model 4	Synthetic slag SACF model for 5% FeO [5]
Model 5	Coal ash slag SACF model for 2.5–5% FeO
Model 6	Coal ash slag SACF model for 5–7.5% FeO
Model 7	Synthetic slag SACF model for 10% FeO [5]
Model 8	Coal ash slag SACF model for 7.5–10% FeO

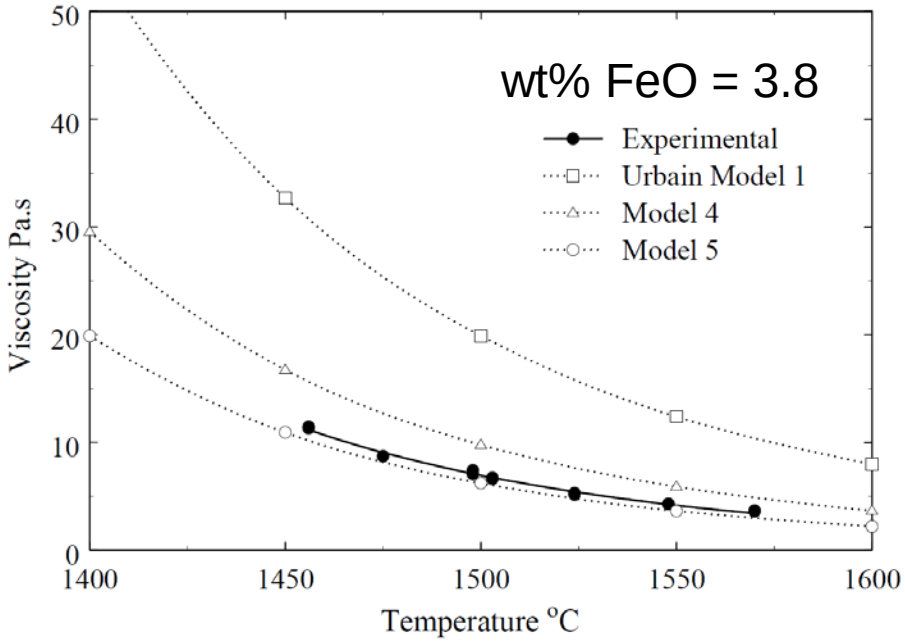
Coeff.	Model 3, < 2.5 wt% FeO	
	1450°C	1500°C
a_0	−7.402775E + 03	−7.817323E + 03
a_1	2.133864E + 04	2.241419E + 04
a_2	−1.539507E + 04	−1.607130E + 04
a_3	4.133813E + 04	4.361551E + 04
a_4	−1.190597E + 06	−1.248887E + 05
a_5	8.582252E + 04	8.941590E + 04
a_6	−7.623803E + 04	−8.039671E + 04
a_7	2.193927E + 04	2.298908E + 05
a_8	−1.580125E + 04	−1.643712E + 05
a_9	4.651861E + 04	4.903991E + 04
a_{10}	−1.336966E + 04	−1.399871E + 05
a_{11}	9.619190E + 04	9.994213E + 04
s^2	0.44	0.51

Slag	Ash	Model	Normalised composition			
			SiO_2	Al_2O_3	CaO	FeO
1	1	3	62.7	11.6	25.6	0.1
2	2	3	50.1	23.6	26.1	0.2
3	2	3	52.1	24.7	22.9	0.2
4	1	3	71.1	13.2	15.3	0.4
5	3	3	61.7	9.1	28.7	0.5
6	3	3	55.9	9.8	33.8	0.5
7	1	3	71.0	13.3	14.8	0.9
8	4	3	40.8	20.1	38.1	1.0
9	5	3	48.1	25.3	25.4	1.2
10	5	3	51.6	27.9	19.2	1.3
11	5	3	54.7	28.6	15.3	1.4
12	6	3	46.4	18.2	33.8	1.5
13	7	3	39.3	26.9	32.3	1.6
14	6	3	49.4	26.9	29.4	1.7
15	8	3	49.2	22.6	26.4	1.8
16	7	3	43.8	29.7	24.7	1.8
17	7	3	50.3	33.0	14.7	1.9
18	9	3	40.9	30.7	26.5	1.9
19	6	3	53.0	21.0	24.1	1.9
20	10	3	47.5	28.1	22.	2.0
21	11	3	57.0	17.0	23.9	2.1
22	12	3	65.2	14.0	19.3	1.55
23	13	3	60.8	17.9	19.0	2.2
24	14	3	55.2	17.7	24.6	2.5

*Source: Hurst, H. J.; Novak, F.; Patterson, J. H., Fuel **1999,** 78, 1831-1840.*

Some results





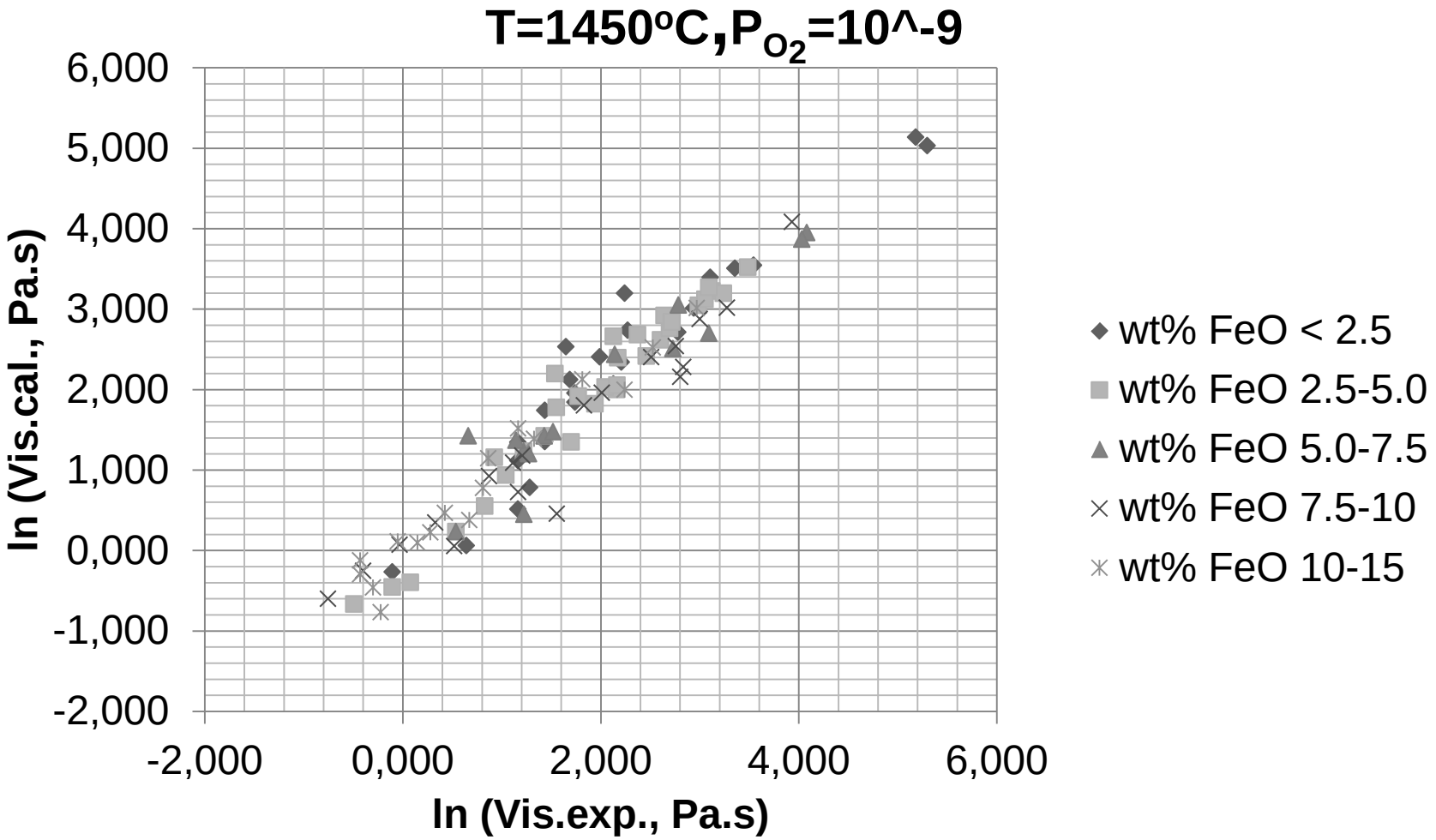
*Source: Hurst, H. J.; Novak, F.; Patterson, J. H., Fuel **1999,** 78, 1831-1840.*

Associate species employed for FeO/Fe_2O_3 containing systems

Compounds	Associate species	Structural units
FeO	Fe_2O_2	$\mathbf{Fe}O$
Fe_2O_3	Fe_2O_3	$\mathbf{Fe}O_{1.5}$
$FeAl_2O_4$	$\frac{2}{3}\cdot FeAl_2O_4$	$Fe_{0.5}\mathbf{Al}O_2$
$CaFe_2O_4$	$\frac{2}{3}\cdot CaFe_2O_4$	$Ca_{0.5}\mathbf{Fe}O_2$
$MgFe_2O_4$	$\frac{2}{3}\cdot MgFe_2O_4$	$Mg_{0.5}\mathbf{Fe}O_2$
Fe_2SiO_4	$\frac{2}{3}\cdot Fe_2SiO_4$	$Fe_2\mathbf{Si}O_4$
$NaFeO_2$	$NaFeO_2$	$Na\mathbf{Fe}O_2$
Na_2FeO_2	$\frac{2}{3}\cdot Na_2FeO_2$	$Na_2\mathbf{Fe}O_2$
$KFeO_2$	$KFeO_2$	$K\mathbf{Fe}O_2$
$FeSi_2MgO_6$	$\frac{1}{2}\cdot FeSi_2MgO_6$	$Fe_{0.5}\mathbf{Si}Mg_{0.5}O_3$
$FeSi_2CaO_6$	$\frac{1}{2}\cdot FeSi_2CaO_6$	$Fe_{0.5}\mathbf{Si}Ca_{0.5}O_3$
$FeSiO_3$	$FeSiO_3$	$Fe\mathbf{Si}O_3$
$Fe_2Si_5Al_4O_{18}$	$\frac{2}{11}\cdot Fe_2Si_5Al_4O_{18}$	$Fe_{0.4}\mathbf{Si}Al_{0.8}O_{3.6}$
$FeSiNa_2O_4$	$\frac{1}{2}\cdot FeSiNa_2O_4$	$Fe\mathbf{Si}Na_2O_4$

First result

The source of the experimental data: Hurst et al., Fuel 1999 & 2000



First result

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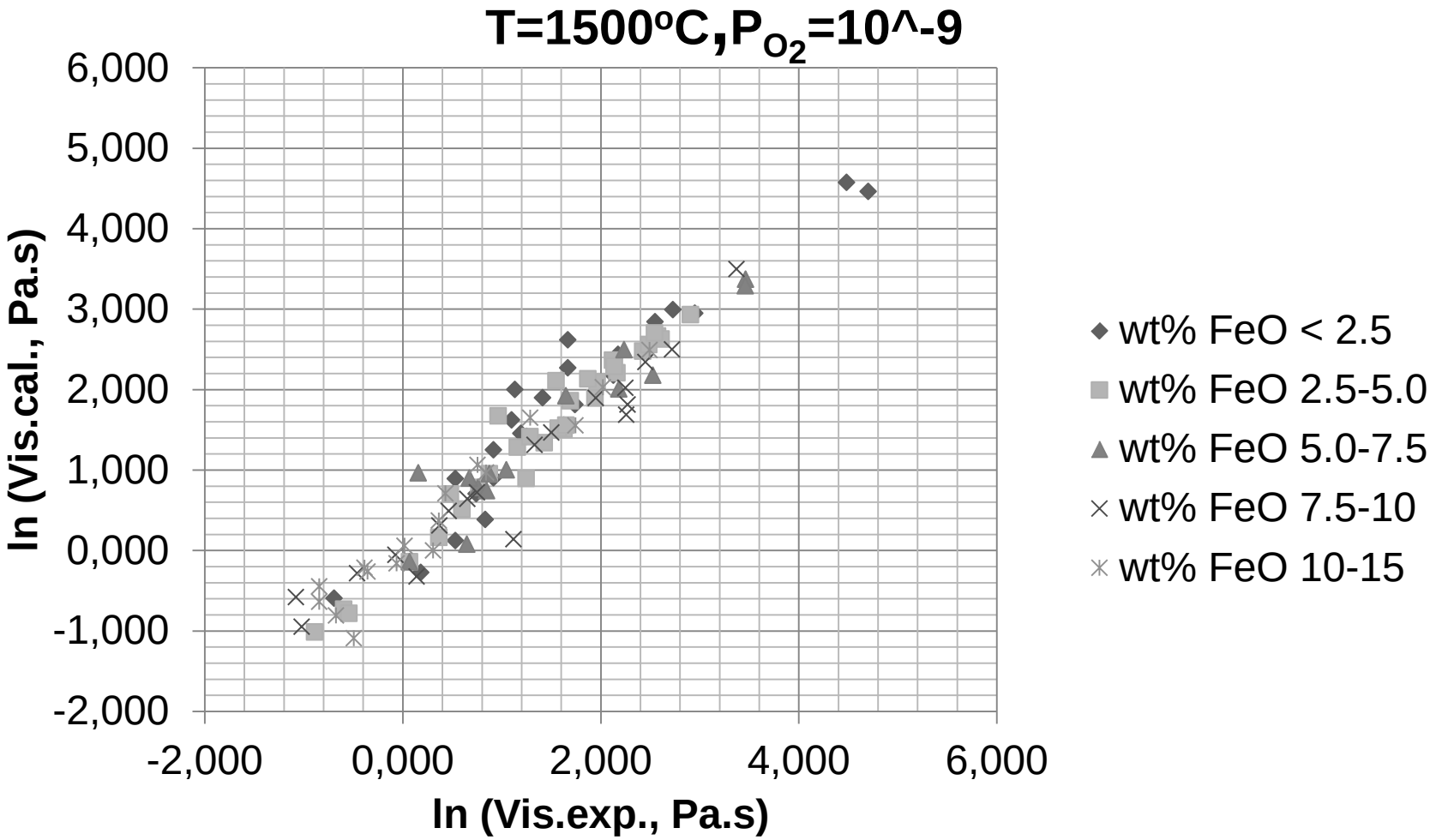
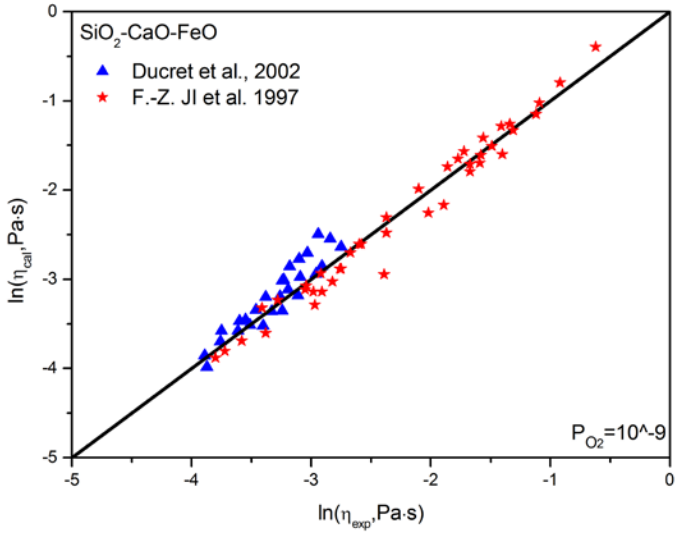
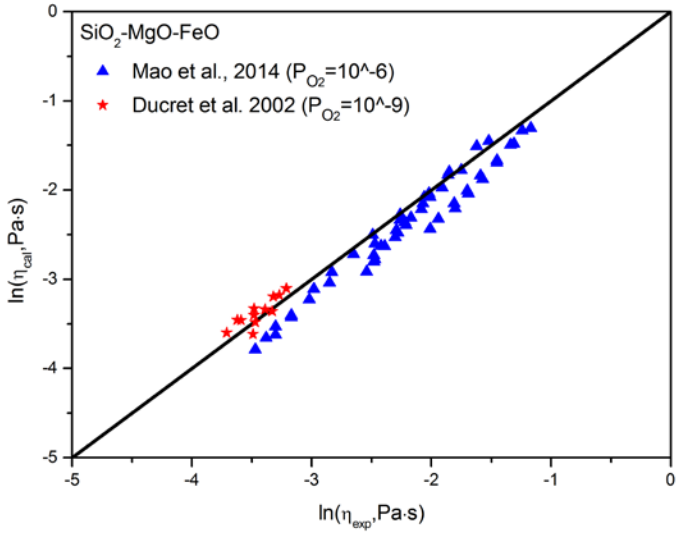
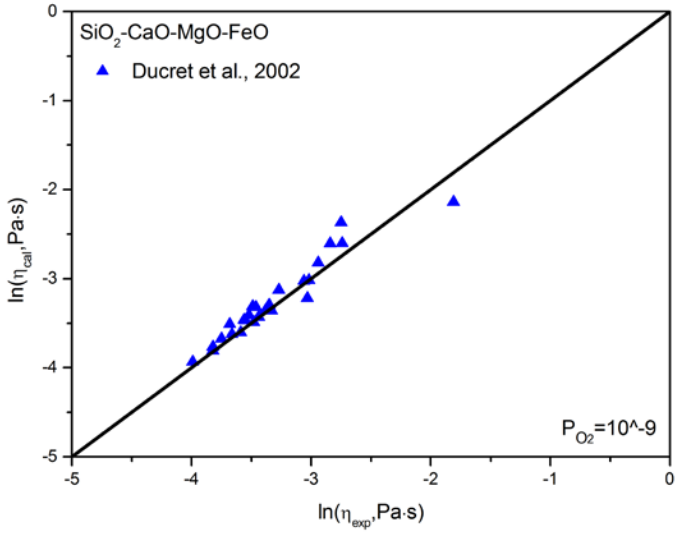
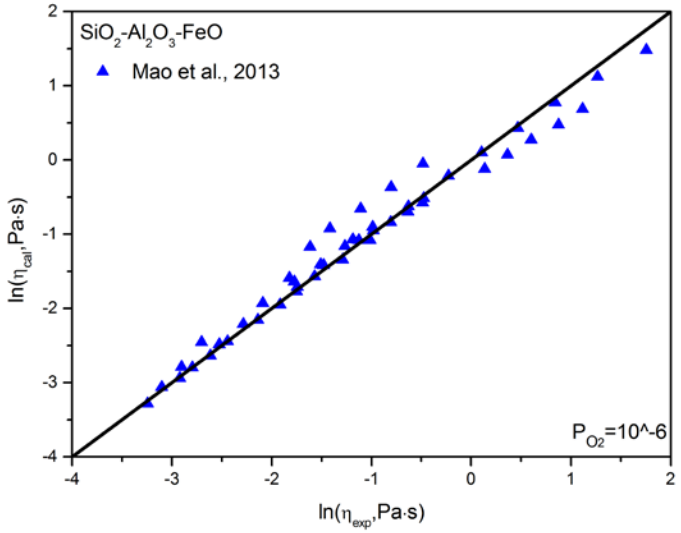


First result (known P_{O_2})



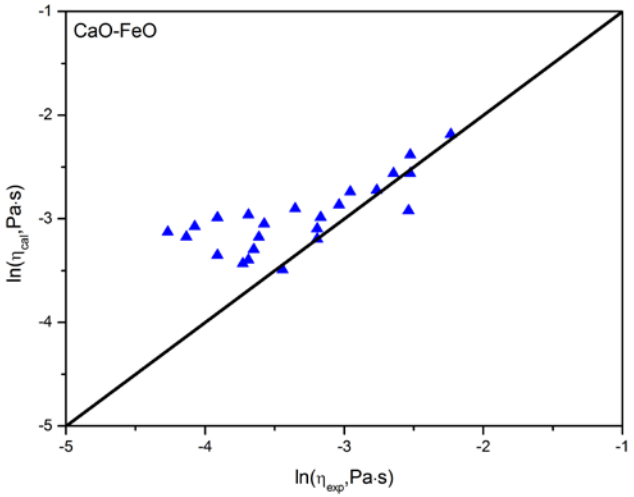


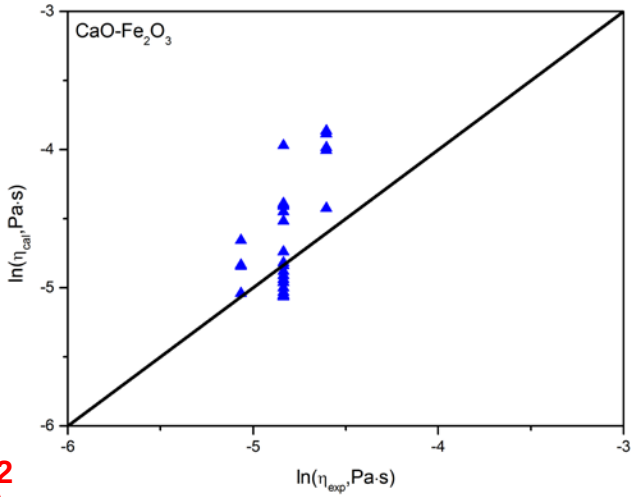




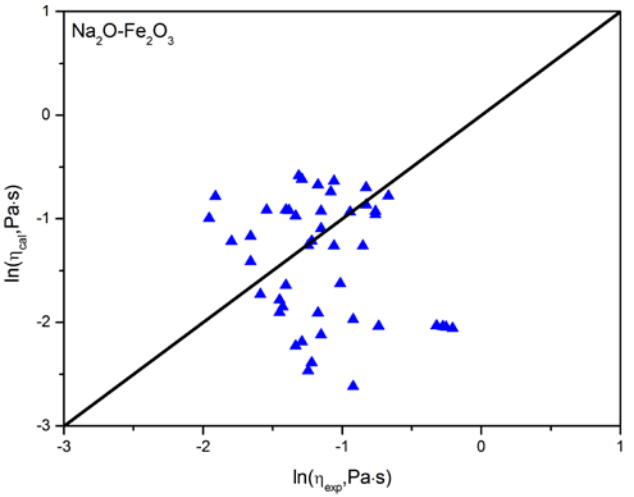
First result (unknown P_{O_2})

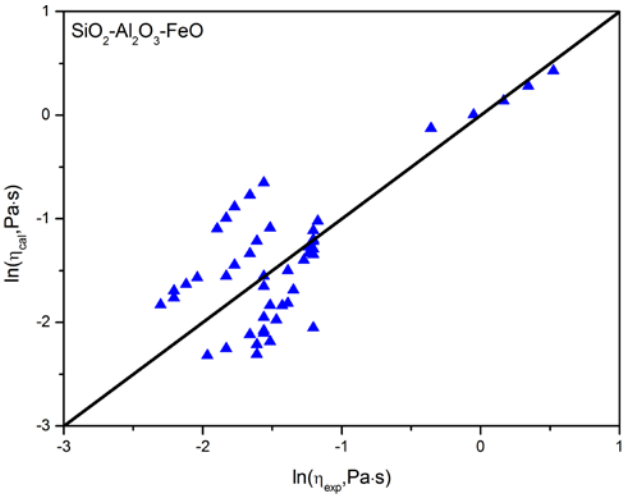
The source of the experimental data: SciGlass database





Fix the P_{O_2} (assumed)





Estimated P_{O_2}

- Dealing with unclear atmospheres as follows:

  - $Fe^{2+}/\sum Fe$
  - $Fe^{3+}/\sum Fe$

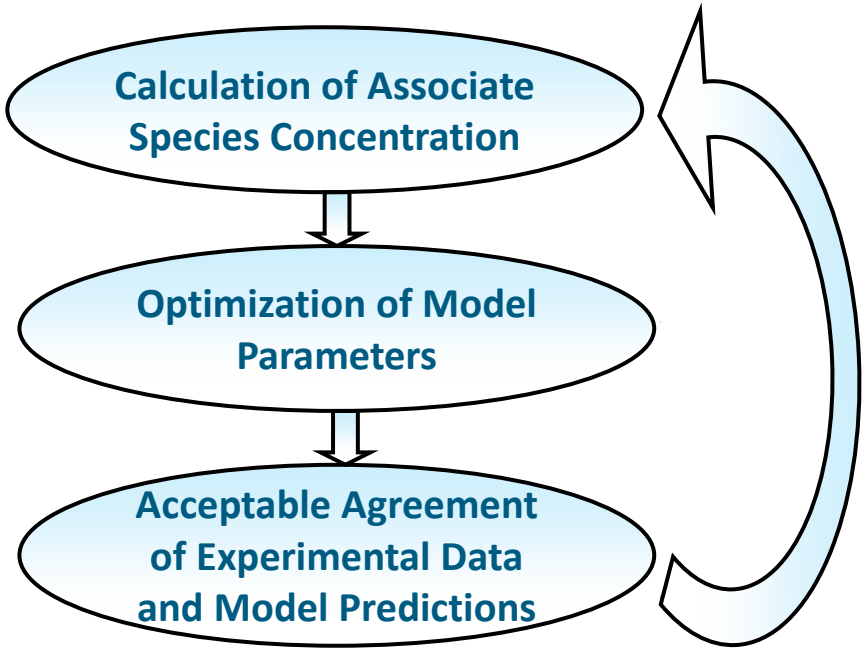
  $$= \frac{Fe^{2+} \text{ or } Fe^{3+} \text{ based associate species}}{Fe \text{ based associate species}}$$

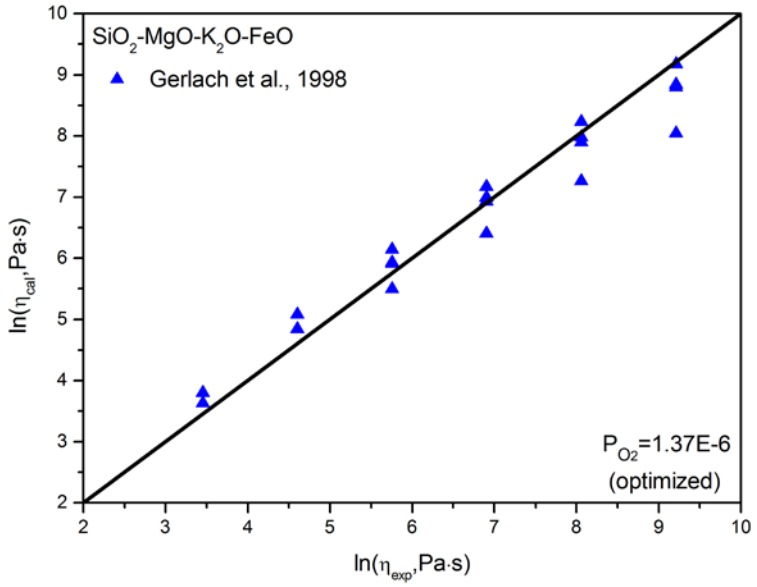
  → **P_{O_2} (Calculated)**

  - Reducing atmosphere → **P_{O_2} (10^-12~ 10^-6)**
  - Oxidizing atmosphere → **P_{O_2} (10^-6~ 0.21)**
  - Neutral atmosphere → **P_{O_2} (10^-12~ 10^-6)**

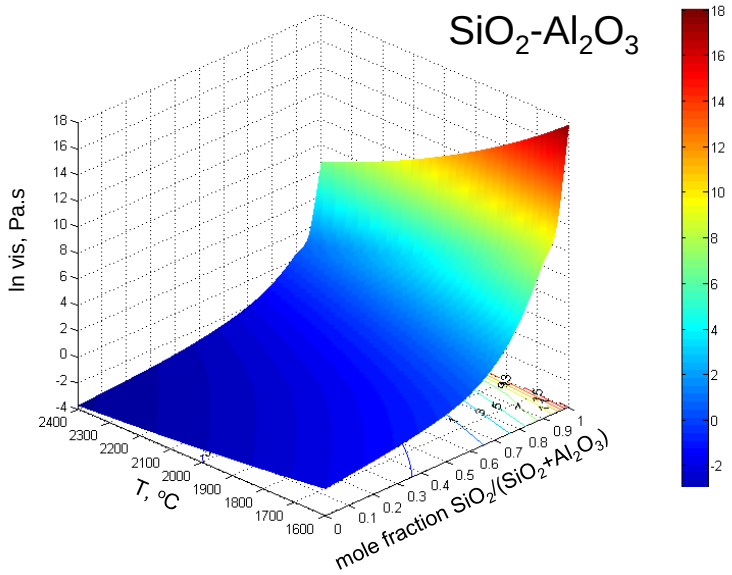
Treating P_{O_2} as a variable

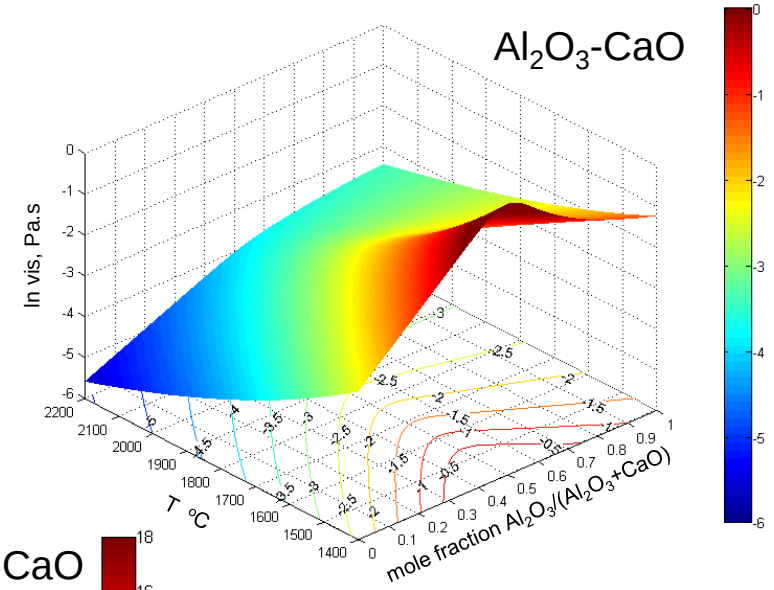
Modified optimization process

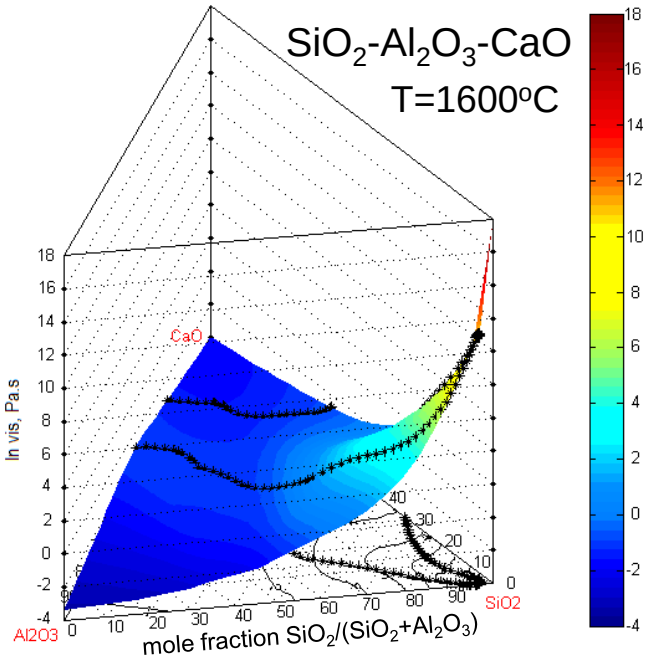




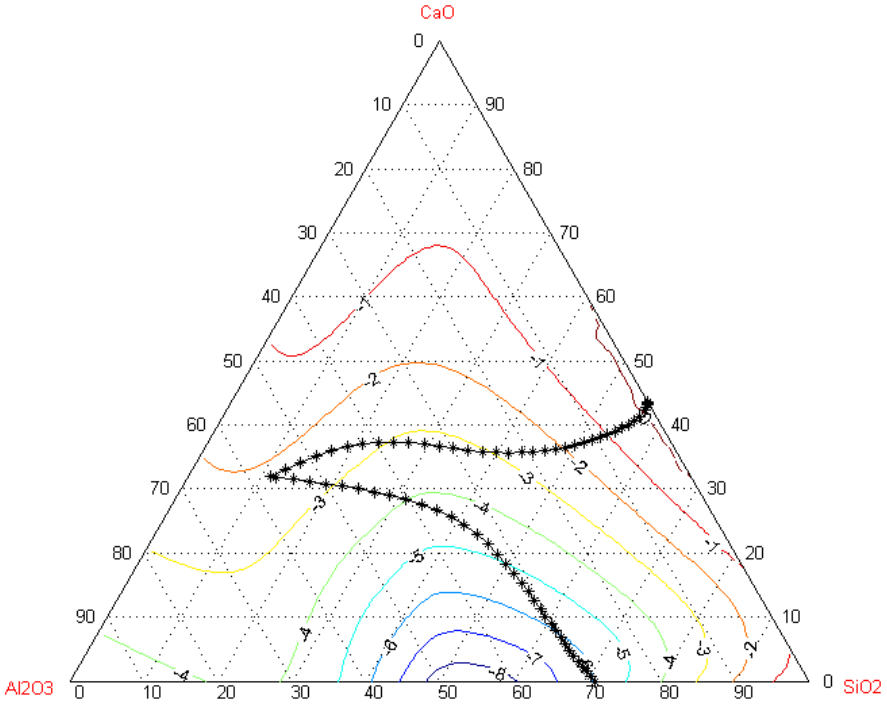
Viscosity surface I





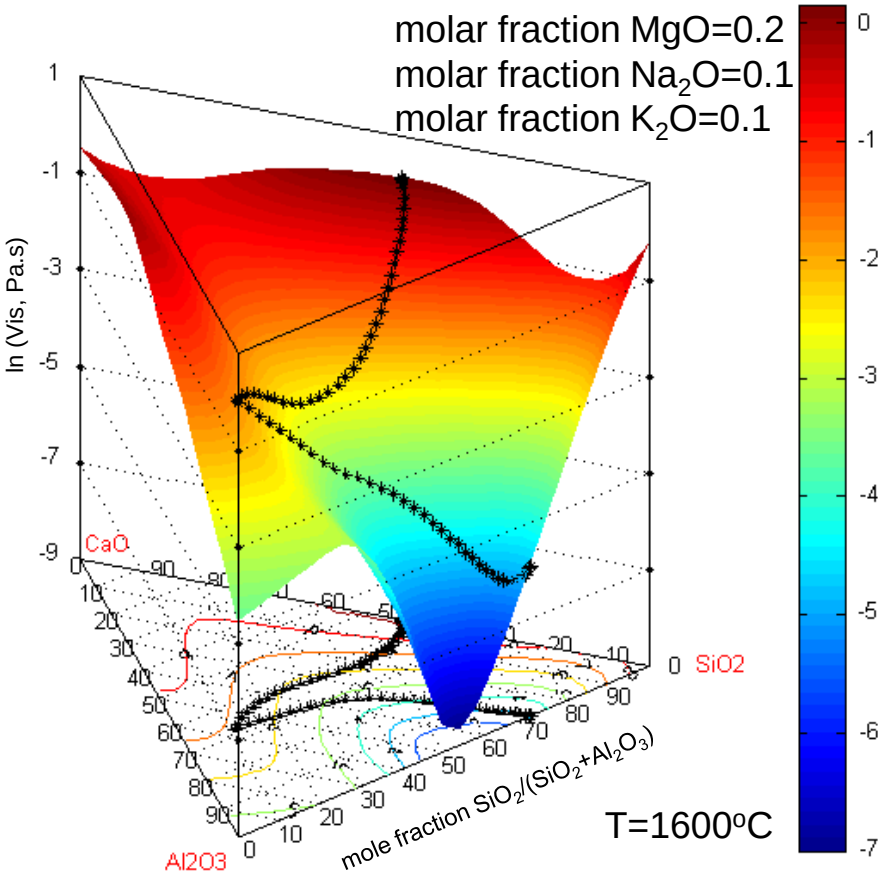


Viscosity surface II



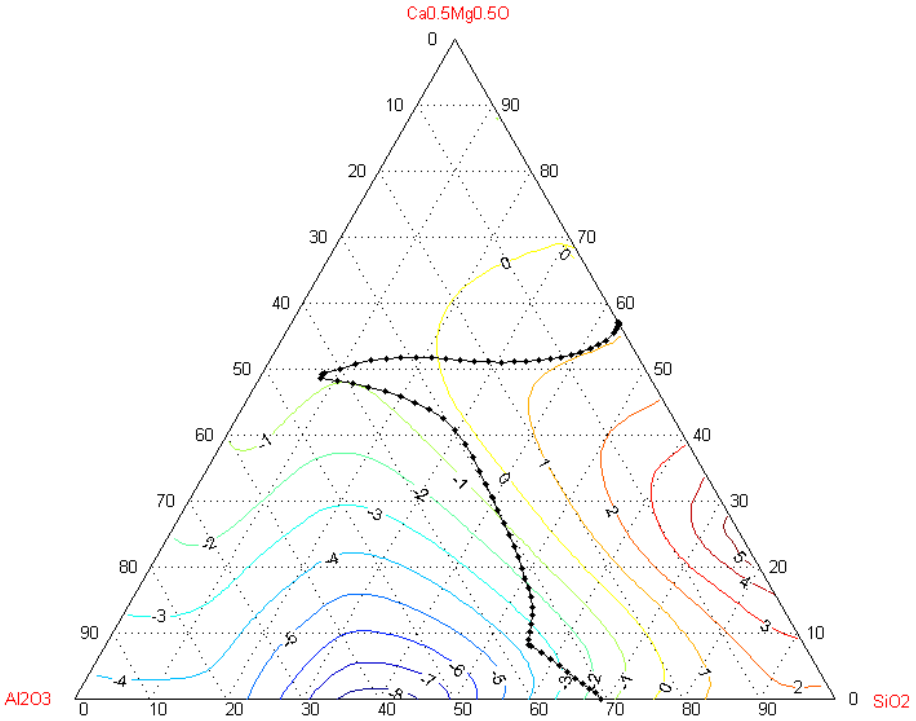
SiO_2-Al_2O_3-CaO-MgO-Na_2O-K_2O

molar fraction MgO=0.2
molar fraction Na_2O=0.1
molar fraction K_2O=0.1



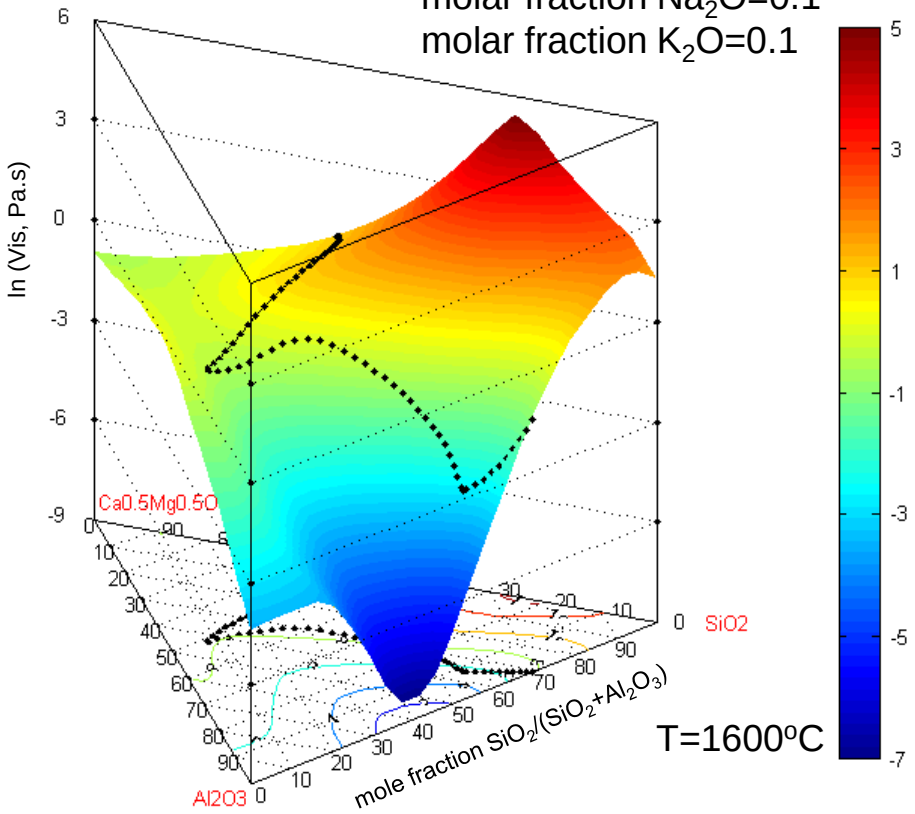
T=1600°C

Viscosity surface III



SiO_2-Al_2O_3-CaO-MgO-Na_2O-K_2O

molar ratio CaO/MgO=1
molar fraction Na_2O=0.1
molar fraction K_2O=0.1



T=1600ºC

Conclusions:

- The current structurally-based viscosity model is capable of predicting the viscosity for the fully liquid system SiO_2-Al_2O_3-CaO-MgO-Na_2O-K_2O-FeO-Fe_2O_3 and its subsystems;
- The partial pressure of oxygen is taken into account for the viscosity modelling of FeO/Fe_2O_3 containing system.

Outlook:

- Further analyzing available experimental data for FeO/Fe_2O_3 containing systems;
- Further optimizing the model parameters of the FeO/Fe_2O_3 containing systems;
- Considering the potential polymerization of Fe^{3+}-based quasi-tetrahedron structure units;
- Extending the current viscosity model from the fully liquid to the mixture of liquid and solid.

JÜLICH
FORSCHUNGSZENTRUM

Thank you very much for your attention!