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Coupling Gibbs Energy and Viscosity Modelling

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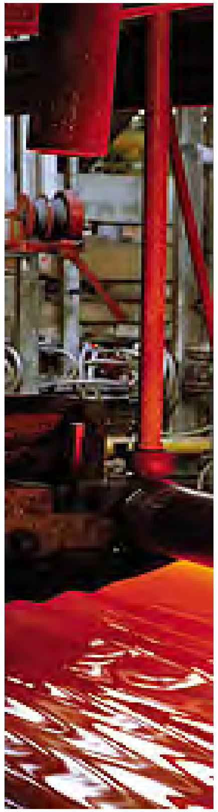
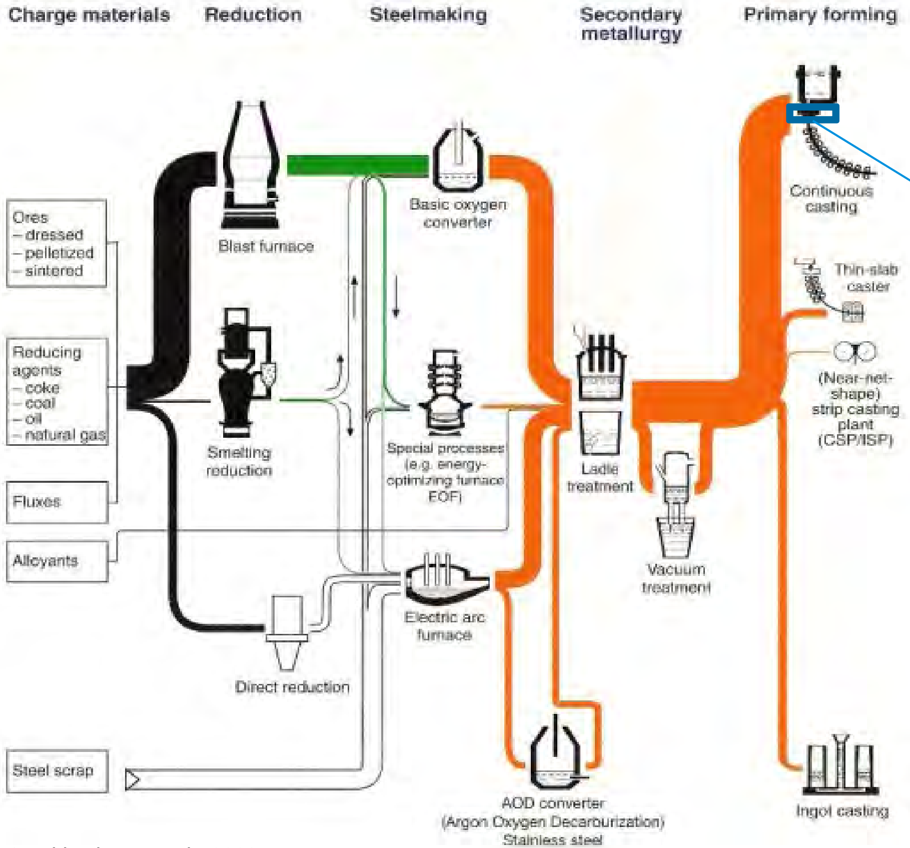
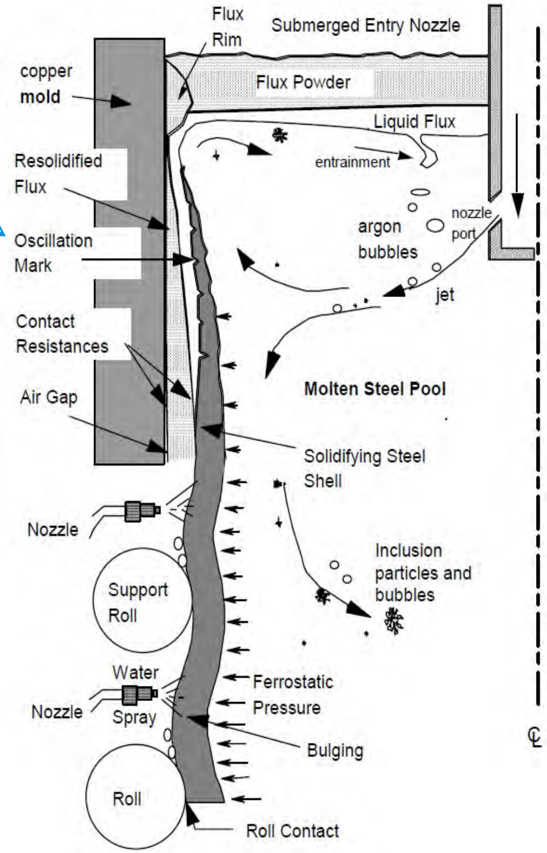
Introduction & Motivation



www.siemens.com/gl



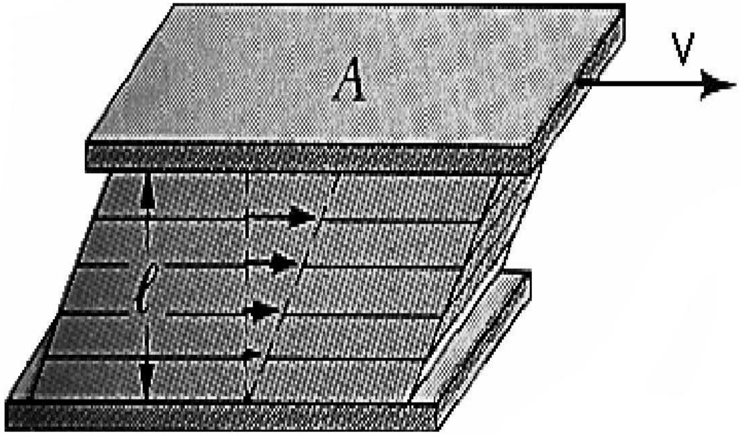
Steel institute VDEh, 2008



O.Yu, M. Dekker, New York, 2001, pp. 499-540.

- Measurement of viscosity is of significant importance, however, it can not supply all data encountered in related industries.
- **Modelling of viscosity** is a promising approach to solve this problem.

Definition of Viscosity



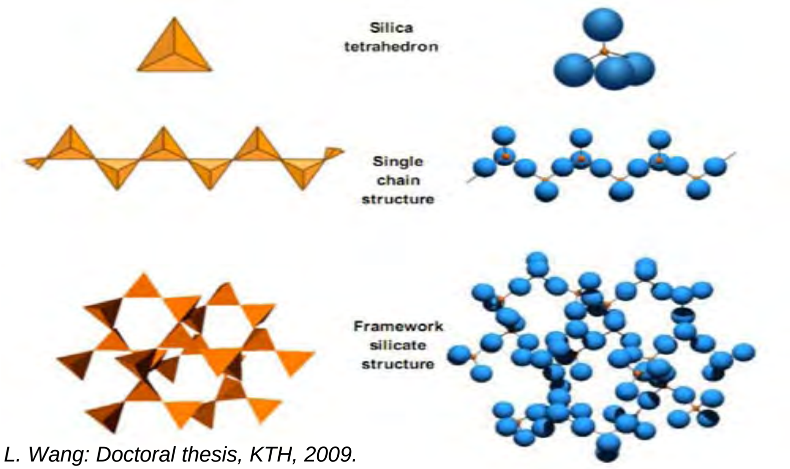
L. Forsbacka: Doctoral thesis, TKK, 2007.

$$\tau = \frac{F}{A} = \eta \cdot \frac{dv}{d\ell}$$

η: **dynamic viscosity**, **Pa·s**

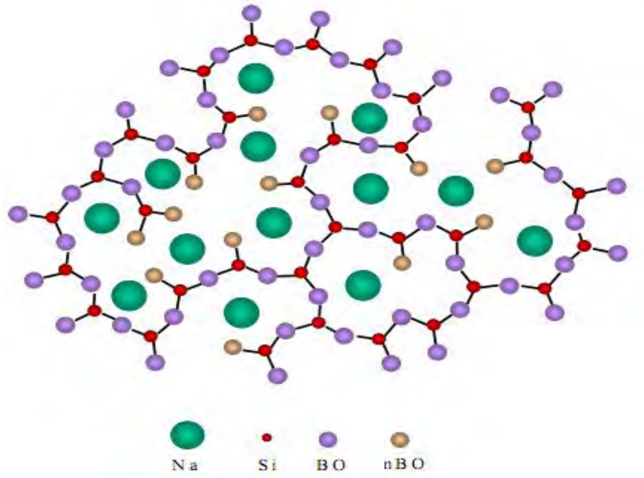
- Viscosity: **internal fluid friction**
- The fluid is sandwiched between two suspending parallel plates in a liquid.
- The viscosity is described by the **shear stress** that suppresses the relative movement of the two suspending parallel plates.

Structure of Slag



L. Wang: Doctoral thesis, KTH, 2009.

Fig. 1

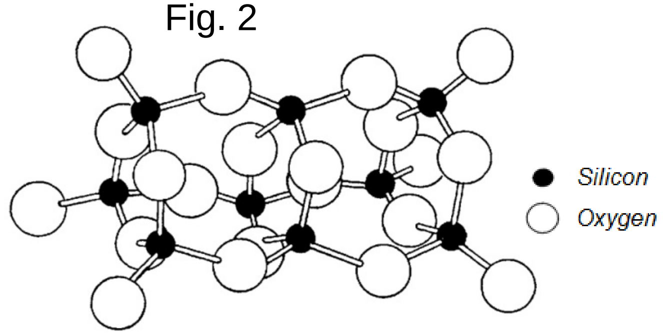


B.E. Warren, J. Biscoe: J. Amer. Ceram. Soc., Vol. 21, 1938, pp. 259-265.

Fig. 2

Slag can be treated as **an oxide mixture**.
They are categorized as three groups:

- **network formers** (e.g. SiO_2)
- **network modifiers** (e.g. CaO, Na_2O)
- **amphoterics** (e.g. Al_2O_3).



J.O'M. Bockris, etc.: Trans. Faraday Soc., Vol. 51, 1955, pp.1734-1748.

Fig. 3: $[Si_9O_{21}]^{6-}$

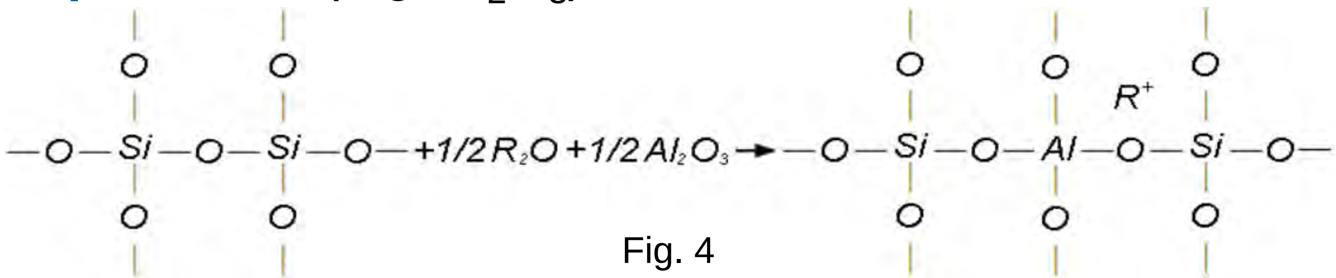
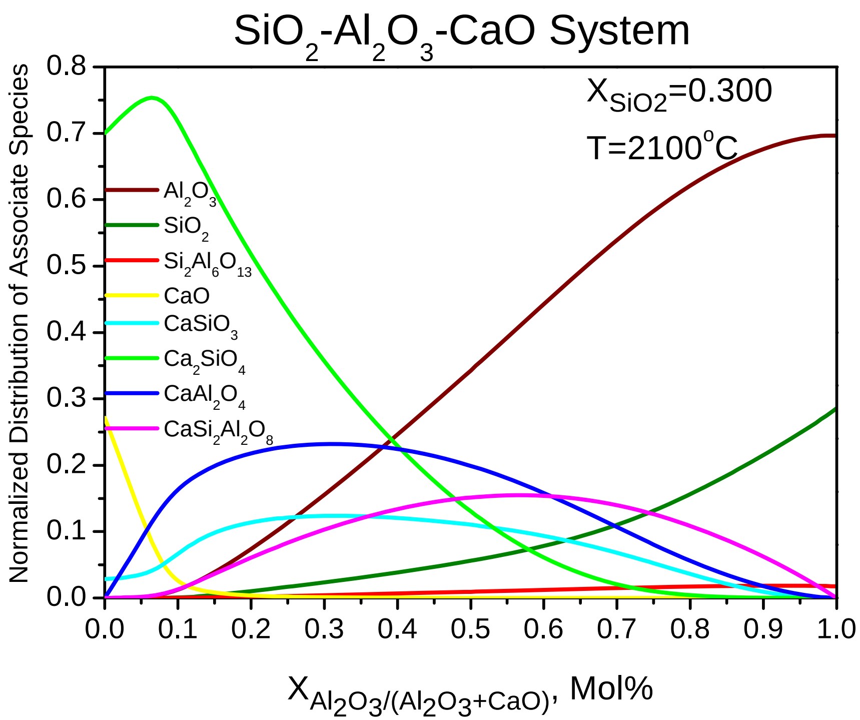


Fig. 4

Viscosity Model I

System	Associate Species
SiO_2	Si_2O_4
Al_2O_3	Al_2O_3
CaO	Ca_2O_2
MgO	Mg_2O_2
SiO_2-Al_2O_3	$Si_2Al_6O_{13}$
SiO_2-CaO	$CaSiO_3$ and Ca_2SiO_4
SiO_2-MgO	$SiMgO_3$ and $Si_2Mg_4O_8$
Al_2O_3-CaO	$CaAl_2O_4$
Al_2O_3-MgO	$Al_4Mg_2O_8$
SiO_2-Al_2O_3-CaO	$Ca_2Si_4Al_4O_{16}$
SiO_2-Al_2O_3-MgO	$Si_5Al_4Mg_2O_{18}$
SiO_2-CaO-MgO	--
Al_2O_3-CaO-MgO	--
SiO_2-Al_2O_3-CaO-MgO	--



- **Associate species model** is employed to predict the **slag structure**, which can be presented by the relative concentrations of each **associate species**.

Viscosity Model II

$$G = \sum_i X_i \cdot G_i^o + R \cdot T \cdot \sum_i X_i \cdot \ln X_i + G^{ex}$$

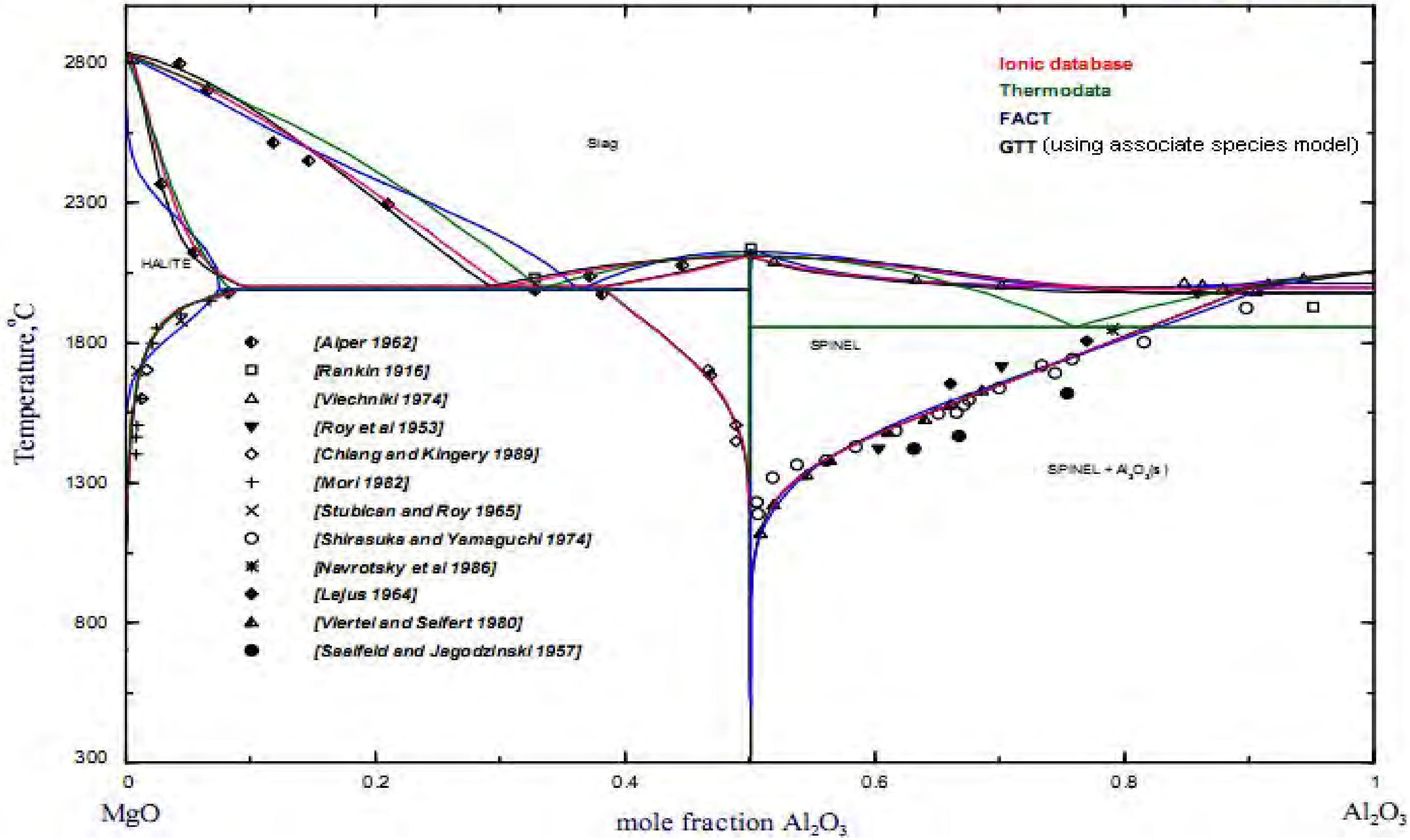
where: subscript i represents i-th associate species in solution; X_i is the mole fraction; G_i^o is the Gibbs energy of the pure i-th associate species; G^{ex} is the excess Gibbs energy to summarize all other contributions to the Gibbs energy except for the entropy contribution.

Redlich-Kister Polynomial Relationship

+

Associated Solution Theory

Viscosity Model III



K. Hack, T. Jantzen: 12th Annual Workshop, GTT, Herzogenrath, 2010.

Viscosity Model IV

- **Arrhenius model (modified)**

$$\ln \eta = \sum_{i=1}^{N} X_i \cdot \ln \eta_i = X_{SiO_2} \cdot \ln \eta_{SiO_2} + \sum_{i=1}^{N-1} X_i \cdot (A_i + \frac{B_i}{T})$$

$$\ln \eta_{SiO_2} = [A_{SiO_2,\,small} + A_{SiO_2,\,intermediate} \cdot (X_{SiO_2})^{m} + A_{SiO_2,\,large} \cdot (X_{SiO_2})^{n}]$$

$$+ \frac{[B_{SiO_2,\,small} + B_{SiO_2,\,intermediate} \cdot (X_{SiO_2})^{m} + B_{SiO_2,\,large} \cdot (X_{SiO_2})^{n}]}{T}$$

where: X_i is the molar fraction of structural unit i; A_i and B_i are fitting parameters of structural unit i.

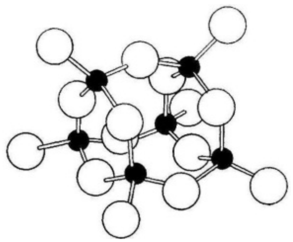


Fig. 1

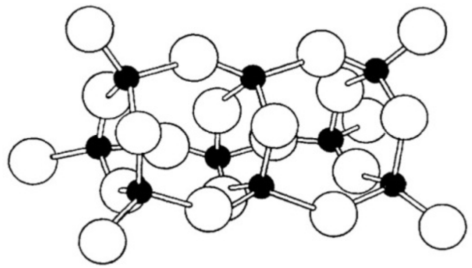
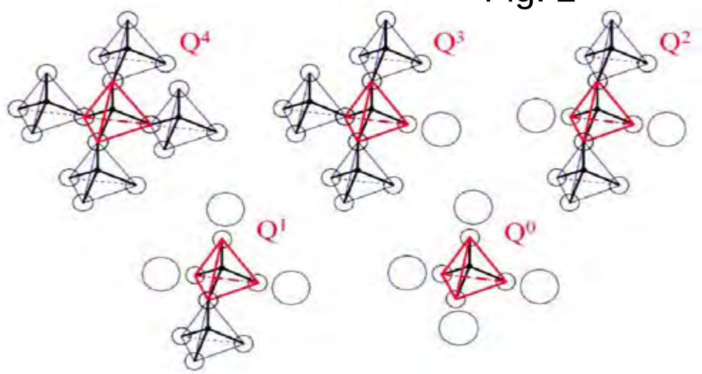


Fig. 2

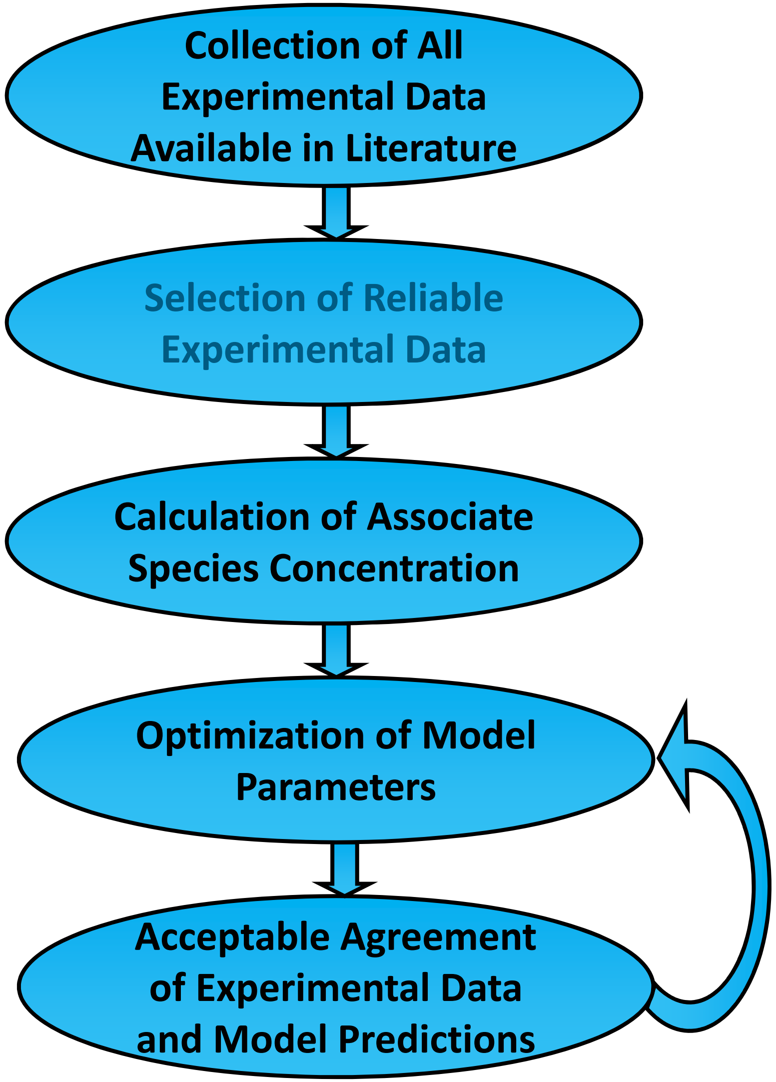


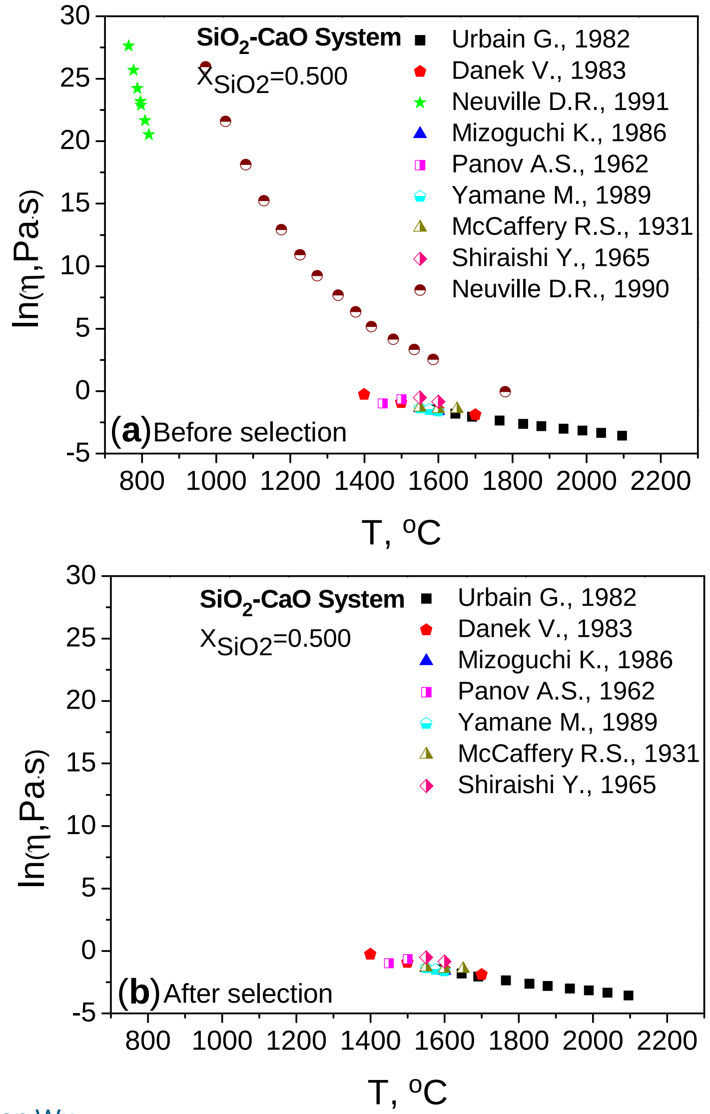
T. Nentwig: Doctoral thesis, RWTH Aachen, 2011.

Fig. 3

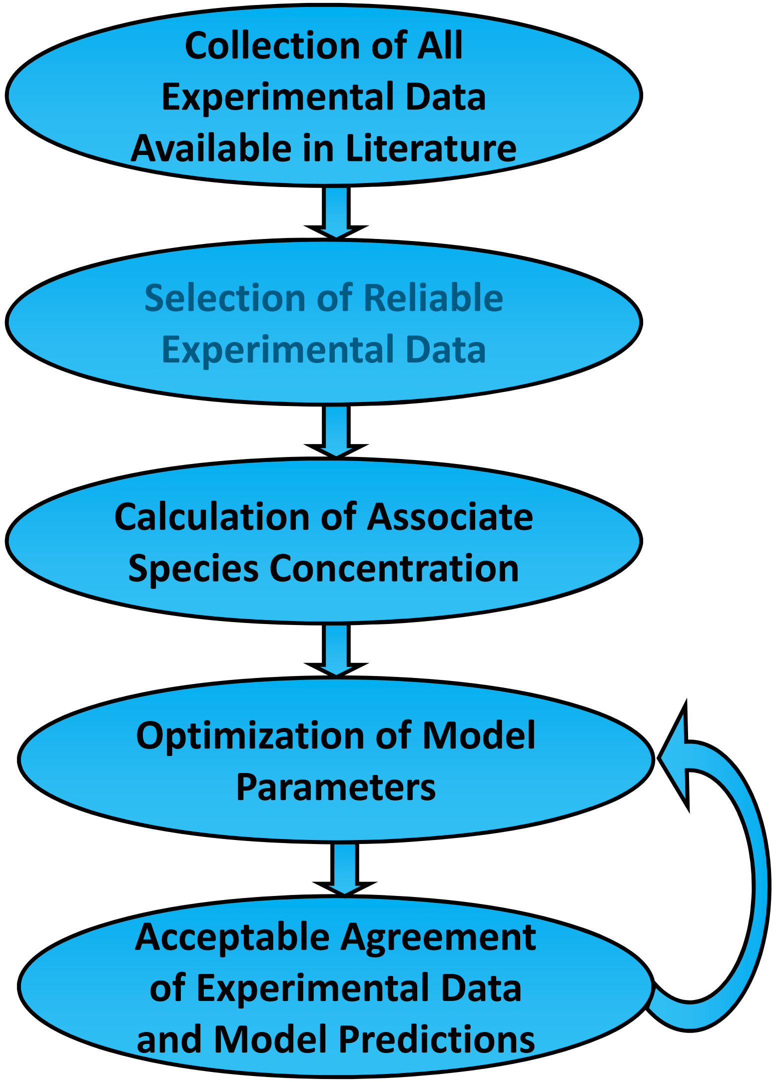
Q_n-groups	Associate species		
	SiO_2-Al_2O_3	SiO_2-CaO	SiO_2-MgO
Q_0	$Al_8Si_2O_{16}$	$Ca_8Si_2O_{12}$	$Mg_8Si_2O_{12}$
Q_1	$Al_6Si_2O_{13}$	$Ca_6Si_2O_{10}$	$Mg_6Si_2O_{10}$
Q_2	$Al_4Si_2O_{10}$	$Ca_4Si_2O_8$	$Mg_4Si_2O_8$
Q_3	$Al_2Si_2O_7$	$Ca_2Si_2O_6$	$Mg_2Si_2O_6$
Q_4	Si_2O_4		

Optimization Process I



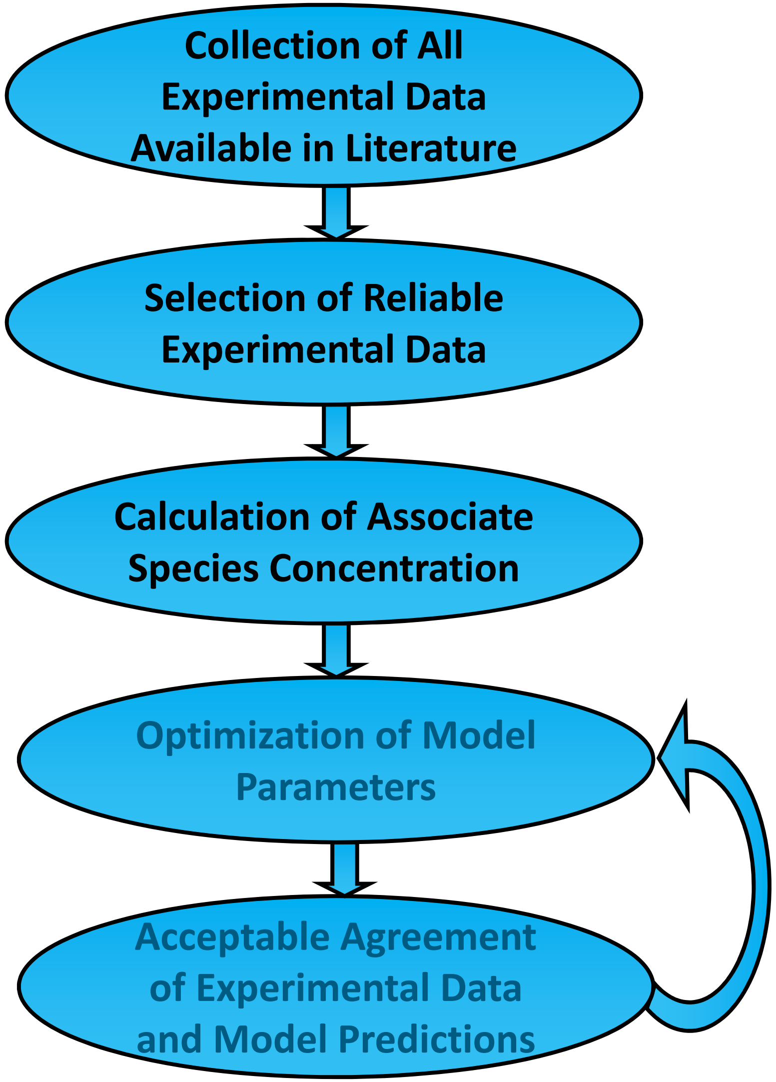


Optimization Process II



System	No. of available literature	No. of total experimental points	No. of reliable experimental points
SiO_2	19	326	239
Al_2O_3	4	58	36
CaO	--	--	--
MgO	--	--	--
SiO_2-Al_2O_3	4	109	73
SiO_2-CaO	34	518	308
SiO_2-MgO	4	73	36
Al_2O_3-CaO	22	285	136
Al_2O_3-MgO	--	--	--
CaO-MgO	--	--	--
SiO_2-Al_2O_3-CaO	82	4226	1964
SiO_2-Al_2O_3-MgO	26	1309	379
SiO_2-CaO-MgO	29	656	262
Al_2O_3-CaO-MgO	4	58	23
SiO_2-Al_2O_3-CaO-MgO	91	4913	1430

Optimization Process III



The influence of **experimental data** and **extrapolation** of other related systems on the optimization of model parameters is assumed to be **equal**. 'Ideal Point Approach' is employed to achieve this goal.

Ideal Point Approach

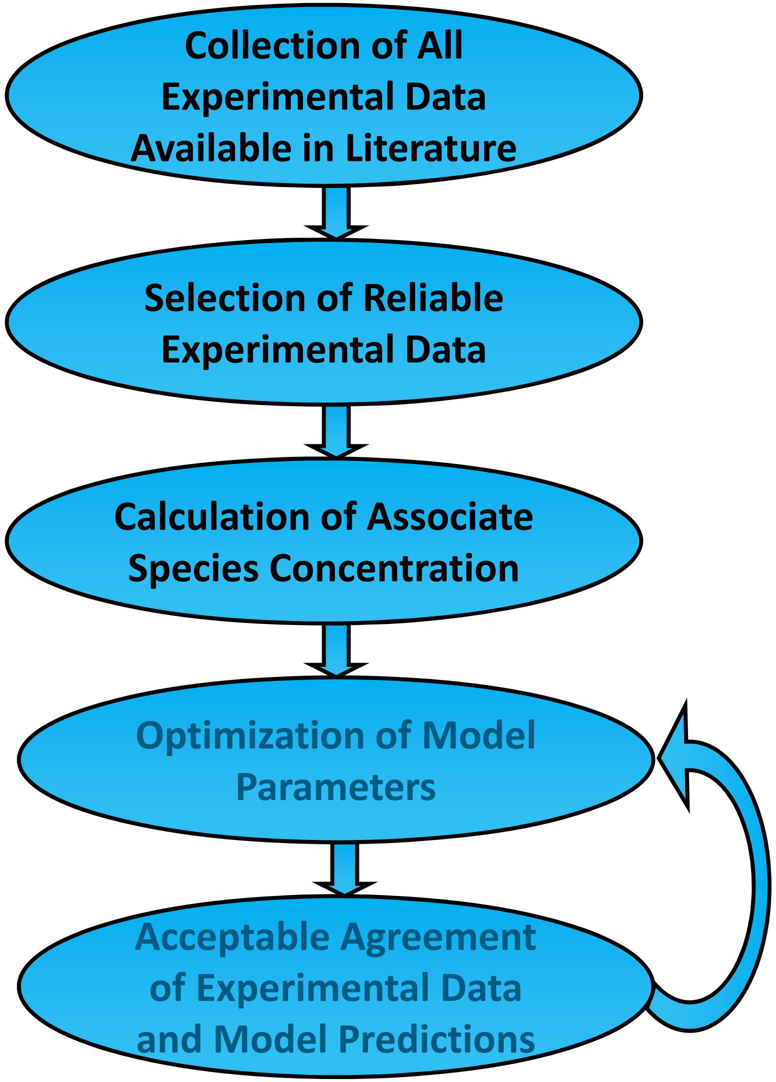
- Ideal points f_i^0:

$$f_i^0 = \frac{1}{N} \cdot \sum_{j=1}^{N} \left| \ln \eta_{j,cal} - \ln \eta_{j,exp} \right|$$

- Evaluation function f(x):

$$f(x) = \sqrt{\sum_{i=1}^{N} (f_i(x) - f_i^0)^2}$$

Optimization Process IV



Associate species	Arrhenius model parameters			
	A_i	B_i	m	n
$SiO_{2,large}$	0.093421	17.4248	--	44
$SiO_{2,intermediate}$	9.015518	29.64266	3	--
$SiO_{2,small}$	-11.1009	24.04727	--	--
Al_2O_3	-8.34598	12.24506	--	--
CaO	-2.86872	6.34E-07	--	--
MgO	-8.52174	10.69859	--	--
$Si_2Al_6O_{13}$	-36.5656	50.60674	--	--
$CaSiO_3$	-12.5291	19.71572	--	--
Ca_2SiO_4	-9.21692	13.32073	--	--
$SiMgO_3$	-15.2726	26.24836	--	--
$SiMg_2O_4$	-8.04222	10.4456	--	--
$CaAl_2O_4$	-19.4109	35.71868	--	--
Al_2MgO_4	-5.52128	10.91831	--	--
$CaSi_2Al_2O_8$	-15.4246	40.86163	--	--
$Si_5Al_4Mg_2O_{18}$	-24.138	56.37161	--	--

SiO2

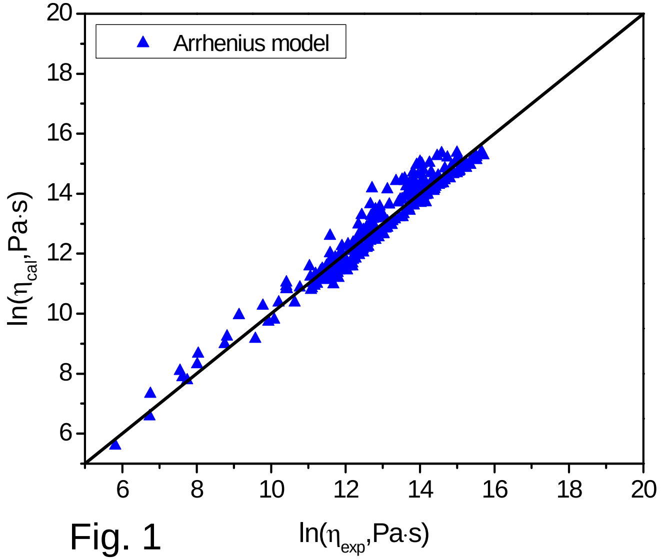


Fig. 1

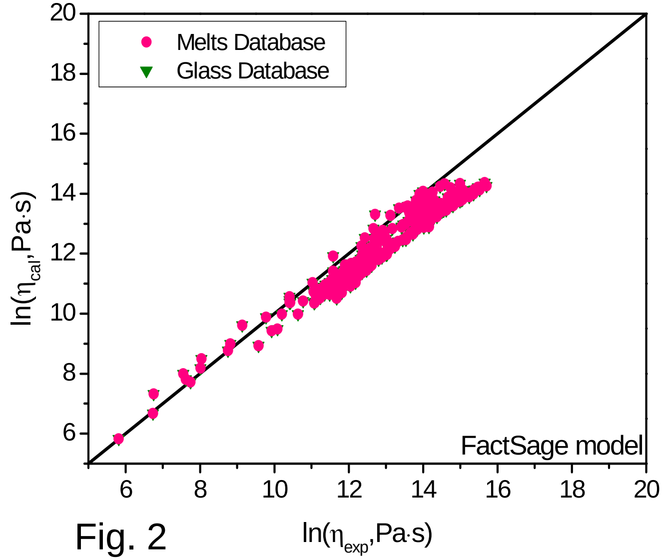


Fig. 2

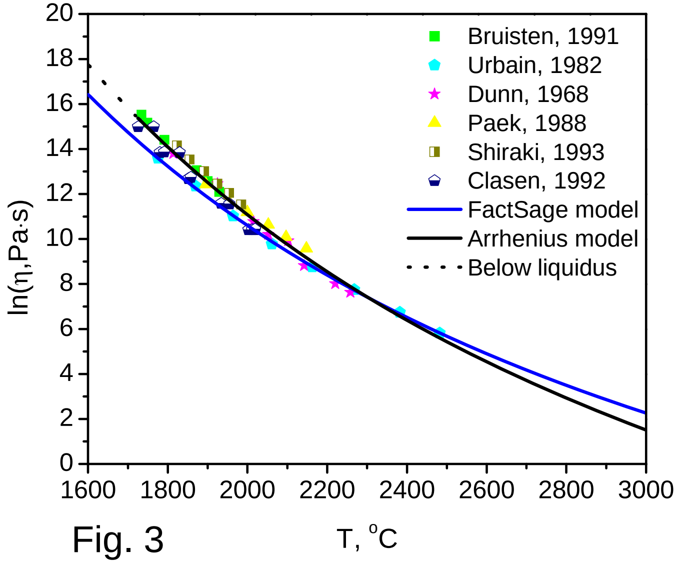
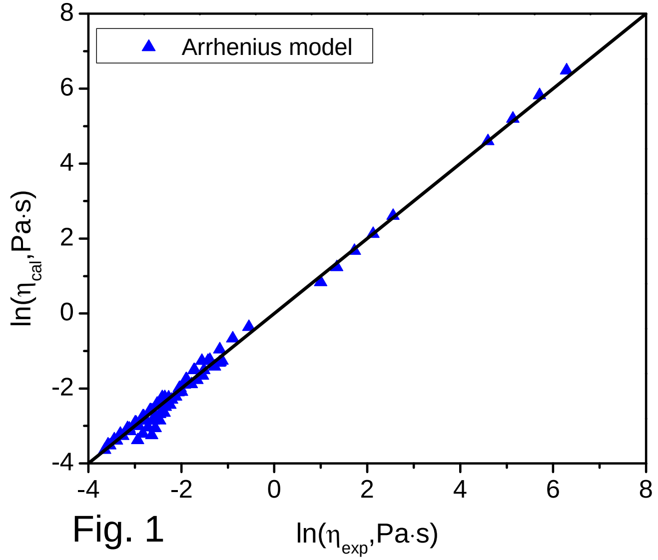


Fig. 3

SiO_2-Al_2O_3



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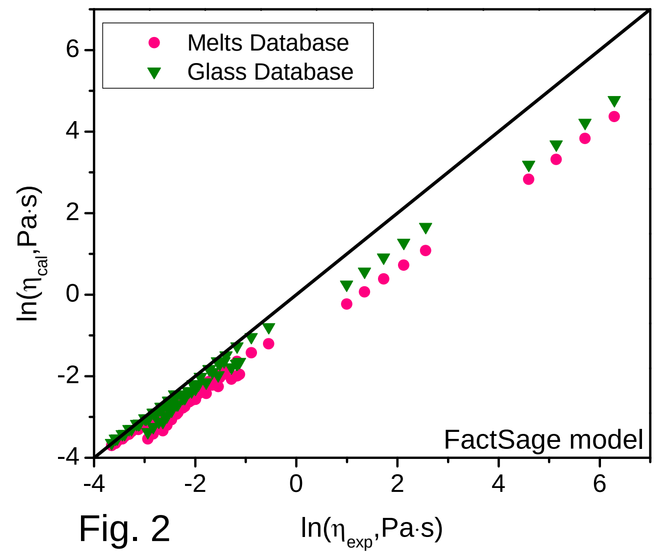


Fig. 2

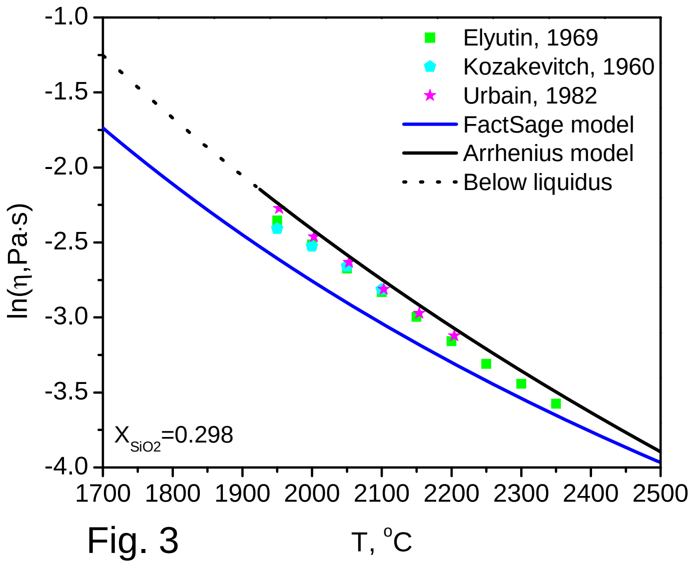


Fig. 3

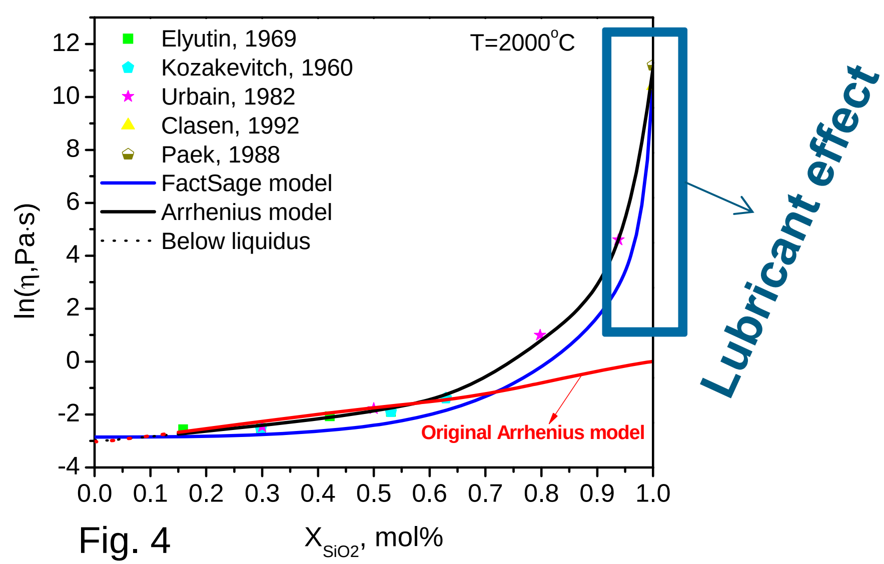


Fig. 4

Al_2O_3-CaO

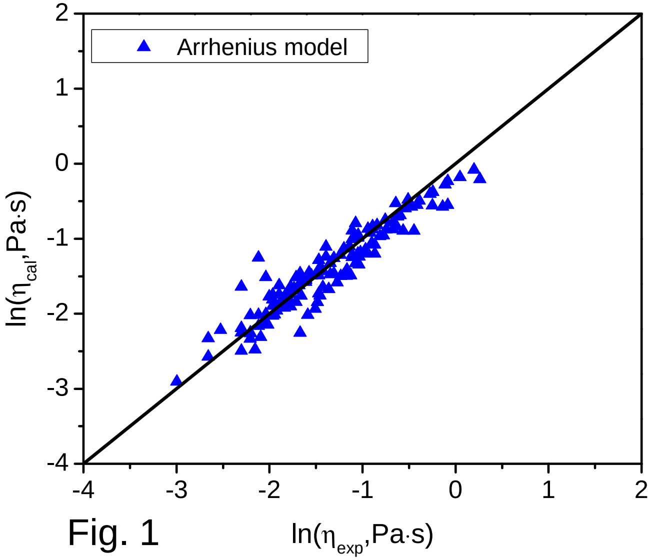


Fig. 1

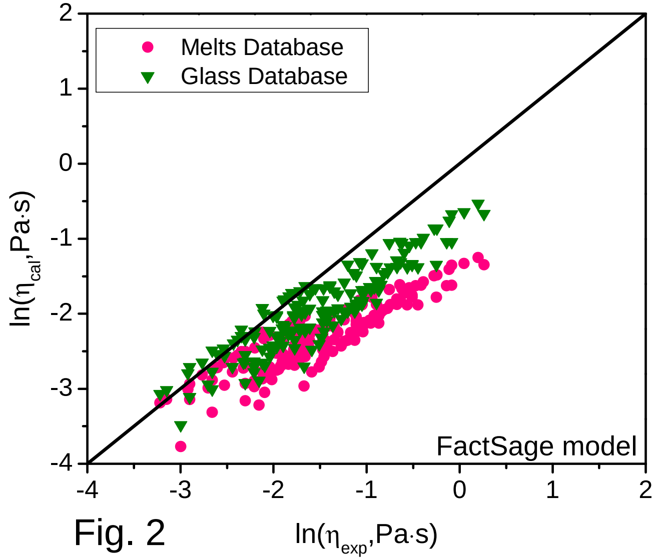
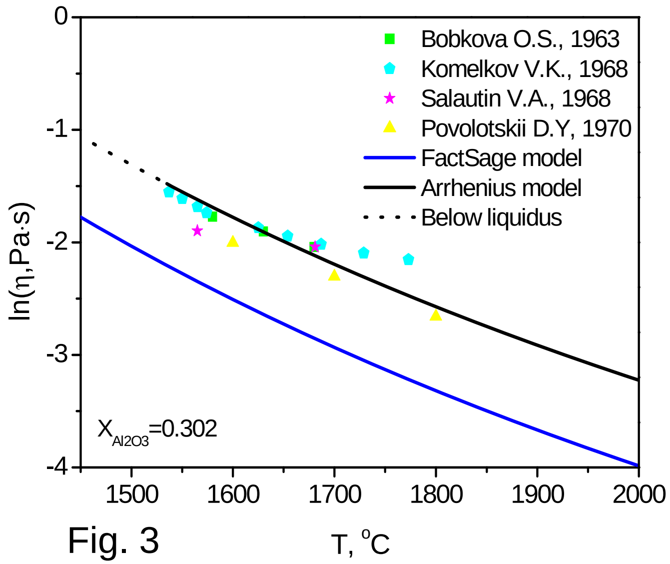


Fig. 2



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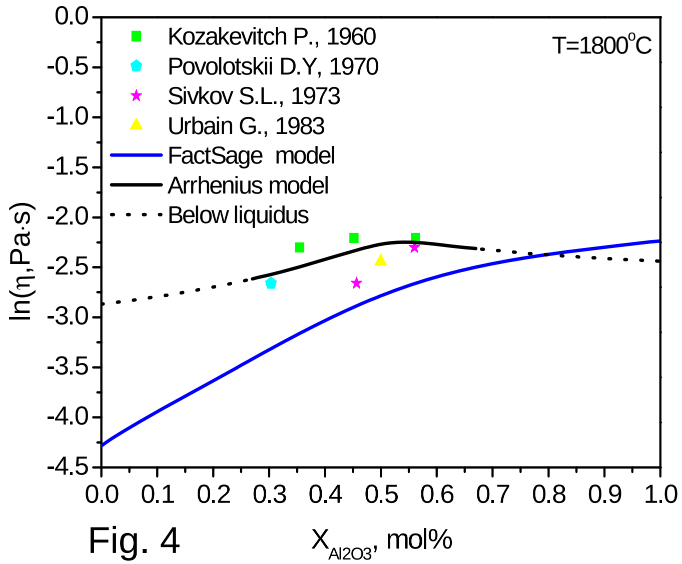


Fig. 4

SiO_2-Al_2O_3-CaO

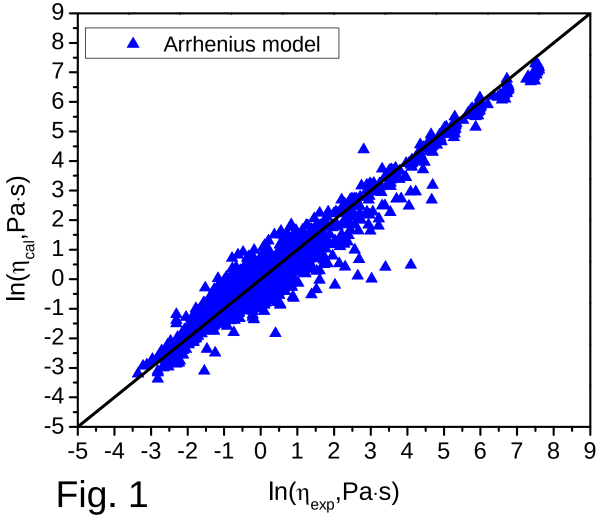


Fig. 1

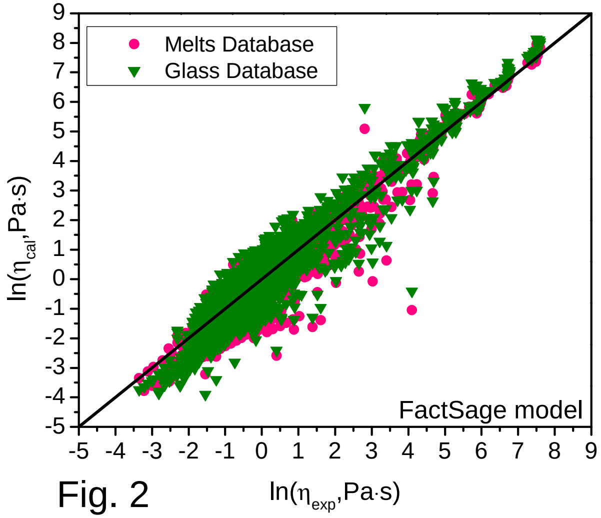
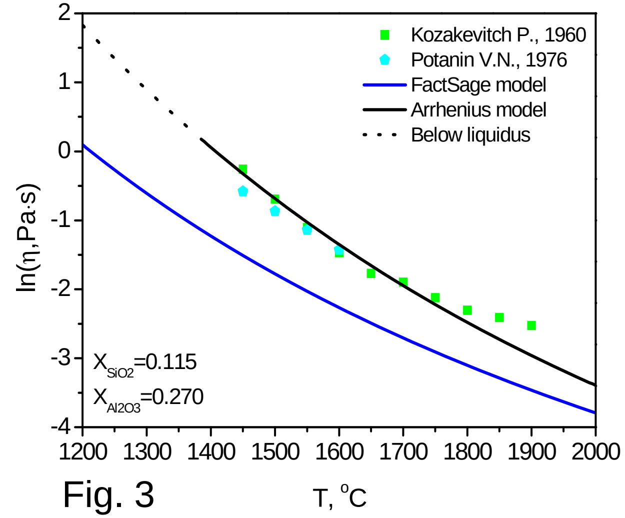


Fig. 2



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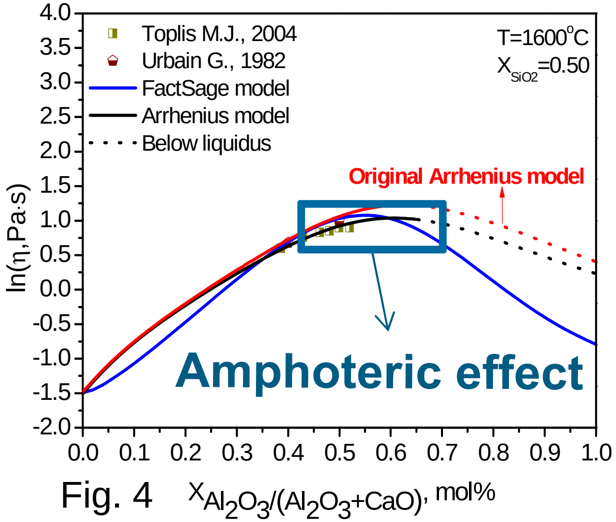


Fig. 4

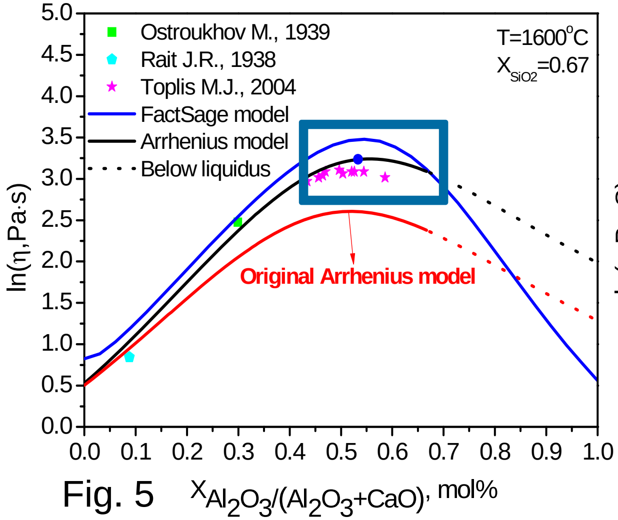


Fig. 5

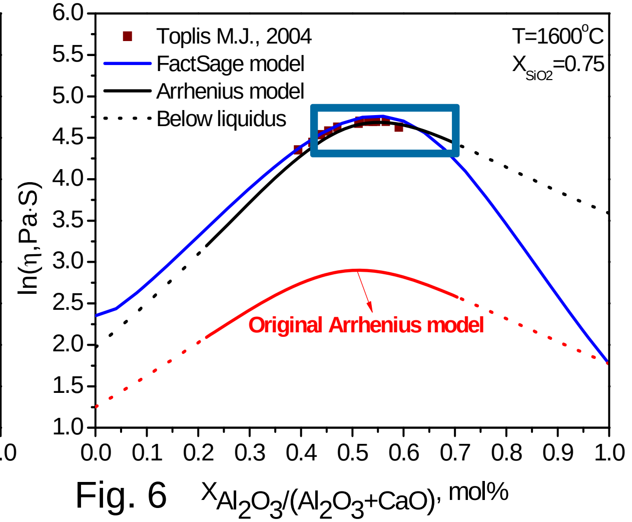


Fig. 6

Al_2O_3-CaO-MgO

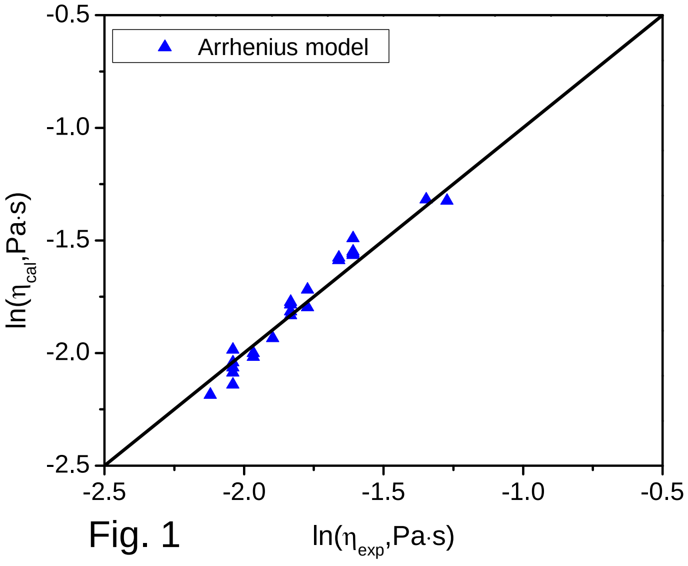


Fig. 1

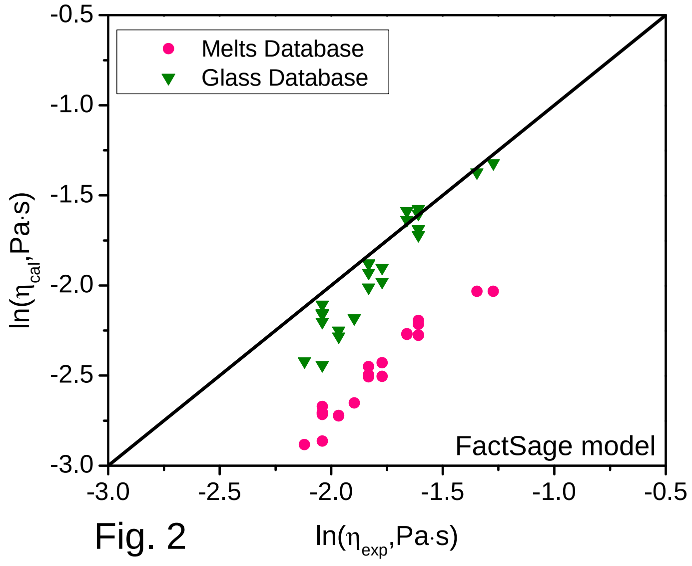


Fig. 2

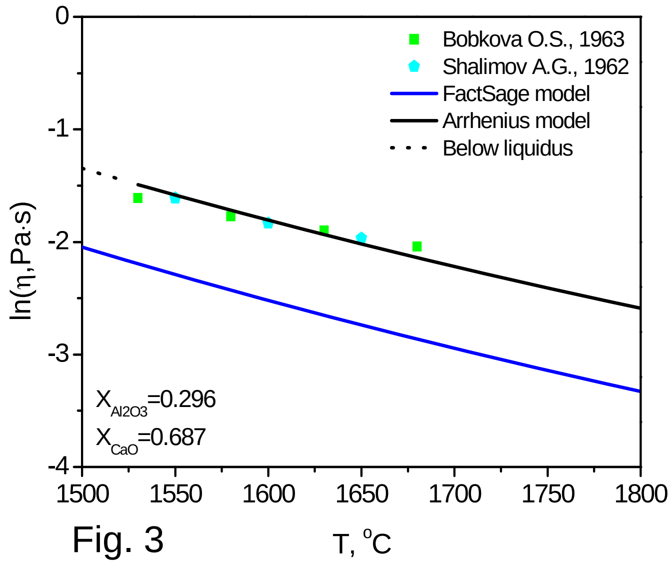


Fig. 3

SiO_2-Al_2O_3-CaO-MgO

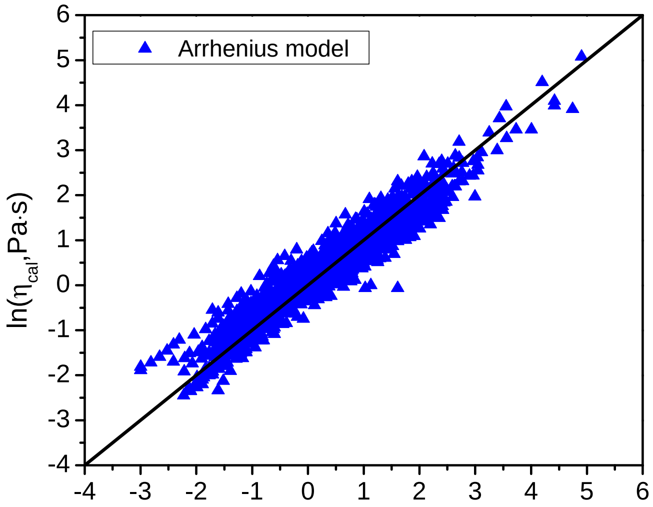


Fig. 1

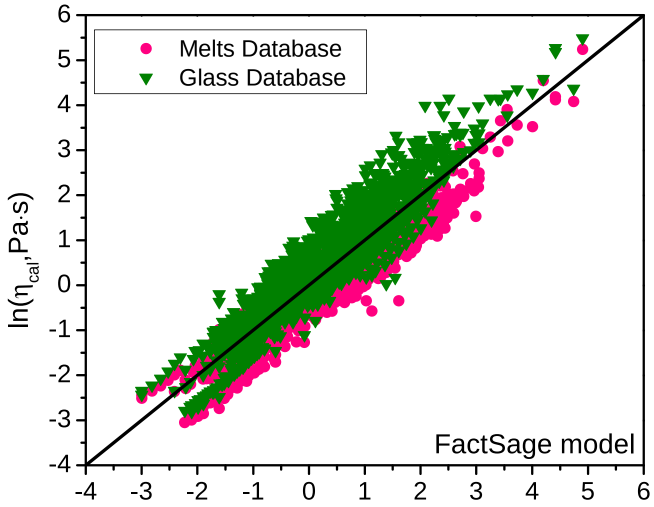
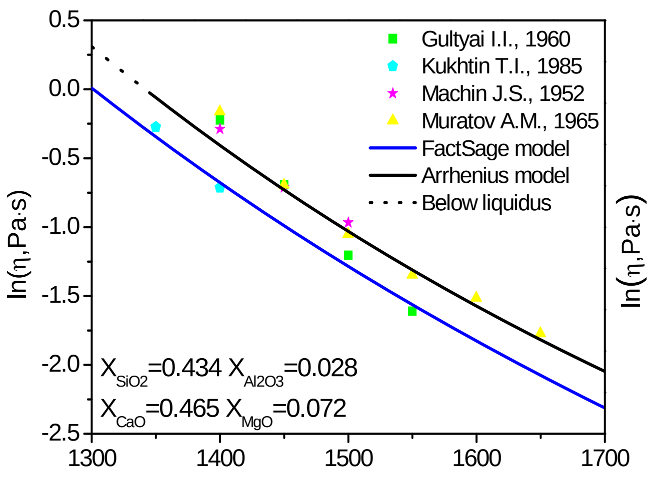


Fig. 2



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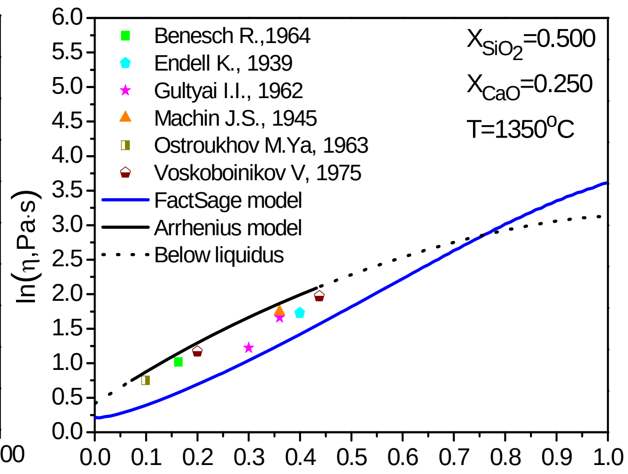

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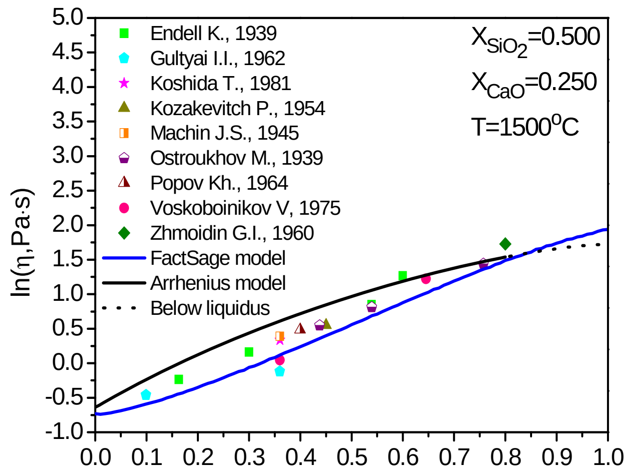

Fig. 5

Conclusion & Outlook

Conclusions:

- A new **structurally-based viscosity model** has been developed, for fully liquid system SiO_2-Al_2O_3-CaO-MgO and its subsystems.
- A good agreement between experimental data and model predictions within experimental error has been achieved, by using only **one set of model parameters**.

Outlook:

- Re-optimizing the model parameters of the system SiO_2-Al_2O_3-Na_2O-K_2O (developed by my previous colleague: Thomas Nentwig)
- Combining these two systems to develop the model parameters of the system SiO_2-Al_2O_3-CaO-MgO-Na_2O-K_2O.
- Introducing new components like FeO/Fe_2O_3 and P_2O_5 to form a higher system.
- Measuring viscosity in unknown region to validate the present model.

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Thank you for your attention!