GTOX
–
a multipurpose oxide^{+} database

GTT Users Meeting, 28.06.2017 Herzogenrath

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[1]GTT-Technologies, [2]IEK2-FZ Jülich

Contents of presentation

- A bit of history
- Components, Phases → the Slag Atlas
- G-modelling
- Going down to the binary element systems Me-O
- Addition of P_2O_5 and SO_3
- Fields of Application
- Conclusions and future developments

HotVeGas project

Phase I	**September 2007 – August 2011**
Phase II	**September 2011 – August 2015**
Phase III	**January 2016 – December 2019**

Partners:

- ***IEK-2, FZ Jülich***
- ***Bergakademie Freiberg***
- ***TU München***
- ***GTT-Technologies***

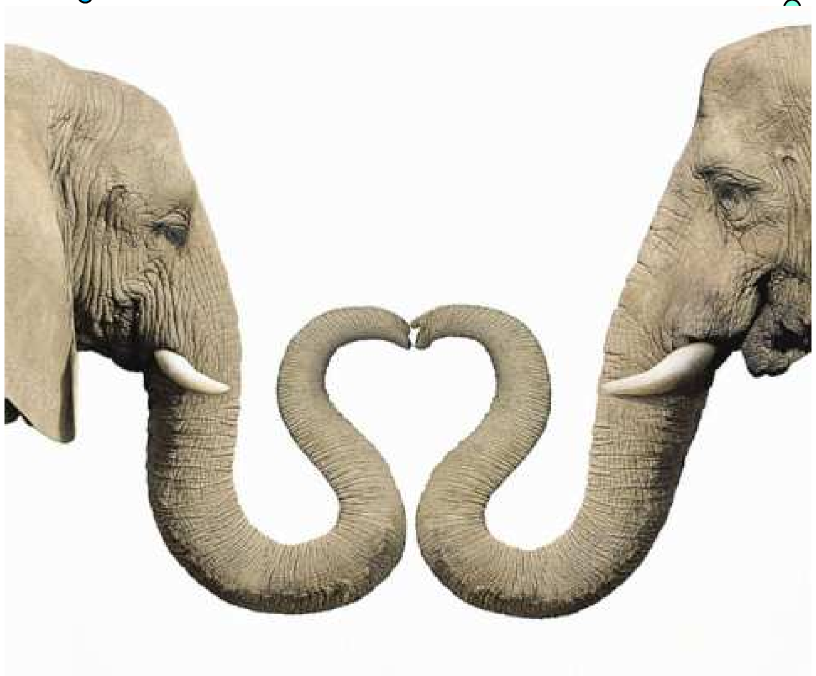
A bit of history-Elephant's wedding

GTT-Technologies

Al_2O_3-K_2O-Na_2O-SiO_2

Al_2O_3-CaO-FeO-Fe_2O_3-MgO-SiO_2

JÜLICH FORSCHUNGSZENTRUM



GTT-TECHNOLOGIES

The present state of GTOX database

GTT-Technologies

The GTOX database contains the assessment of the Al_2O_3-Al_2S_3-CaF_2-CaO-CaS-$CaSO_4$-CrO-Cr_2O_3-CrS-FeO-Fe_2O_3-FeS-K_2O-K_2S-K_2SO_4-Na_2O-Na_2S-Na_2SO_4-MgO-MgS-$MgSO_4$-MnO-Mn_2O_3-MnS-P_2O_5-SiO_2-TiO_2-ZnO system

Contents	*Slagatlas, Year*					
	2.0 2010	3.0 2011	9.0 2014	10.0 2015	11.0 2015	12.0 2017
Binary systems	24	26	89	109	116	130
Ternary systems	11	34	75	80	97	110
Quaternaries	-	5	6	6	6	7
Slag components	48	50	113	132	151	166
Components	9	9	19	25	27	28
Solid solution phases	32	41	68	75	85	104
Stoichiometric phases	112	145	291	339	543	661
Total pages	157	281	648	706	850	920

G-modelling

Modelling

Stoichiometric compounds

$(Me1O)_x(Me2O)_y$

$$G_m = \sum({}^0G_{MeO_x}) + a + b \cdot T$$

Solid solution phases

$(A,B,C)_x(D)_y$

$$G_m = y_A^I y_D^{II}\, {}^\circ G_{A:D} + y_B^I y_D^{II}\, {}^\circ G_{B:D} + y_C^I y_D^{II}\, {}^\circ G_{C:D} + RT(y_A^I \ln y_A^I + y_B^I \ln y_B^I + y_C^I \ln y_C^I) + RT y_D^{II} \ln y_D^{II} + G_m^{ex}$$

Liquid phase (slag)

$$G_m = \sum x_i\, {}^\circ G_i + RT \sum x_i \ln_i + \sum_{i<j}\sum x_i x_j \sum_{v=0} L_{ij}^{(v)} (x_i - x_j)^v$$

Slag in GTOX database

The associate species were described in the same way in similar systems in order to provide a handle for the use in multi-component systems. The composition of the associate species are as introduced by Spear taking two moles of cations per associate.

	System	Associate species
Me-O	*Cr-O*	*Cr, Cr_2O_2, Cr_2O_3, Cr_3O_4*
	Fe-O	*Fe, Fe_2O_2, Fe_2O_3, Fe_3O_4*
	Mn-O	*Mn, Mn_2O_2, Mn_2O_3, Mn_3O_4*
$CaO-Me_2O_3$	*$CaO-Al_2O_3$*	*$CaAl_2O_4$*
	$CaO-Cr_2O_3$	*$CaCr_2O_4$*
	$CaO-Fe_2O_3$	*$CaFe_2O_4$*
	$CaO-Mn_2O_3$	*$CaMn_2O_4$*
$CrO-Me_2O_3$	*$CrO-Al_2O_3$*	*$CrAl_2O_4$*
	$CrO-Fe_2O_3$	*$CrFe_2O_4$*
	$CrO-Mn_2O_3$	*$CrMn_2O_4$*
	$MgO-Mn_2O_3$	*$MgMn_2O_4$*
$FeO-Me_2O_3$	*$FeO-Al_2O_3$*	*$FeAl_2O_4$*
	$FeO-Cr_2O_3$	*$FeCr_2O_4$*
	$FeO-Mn_2O_3$	*$FeMn_2O_4$*

System

System

Al_2O_3– K

Al_2O_3– Na

Fe_2O_3– K

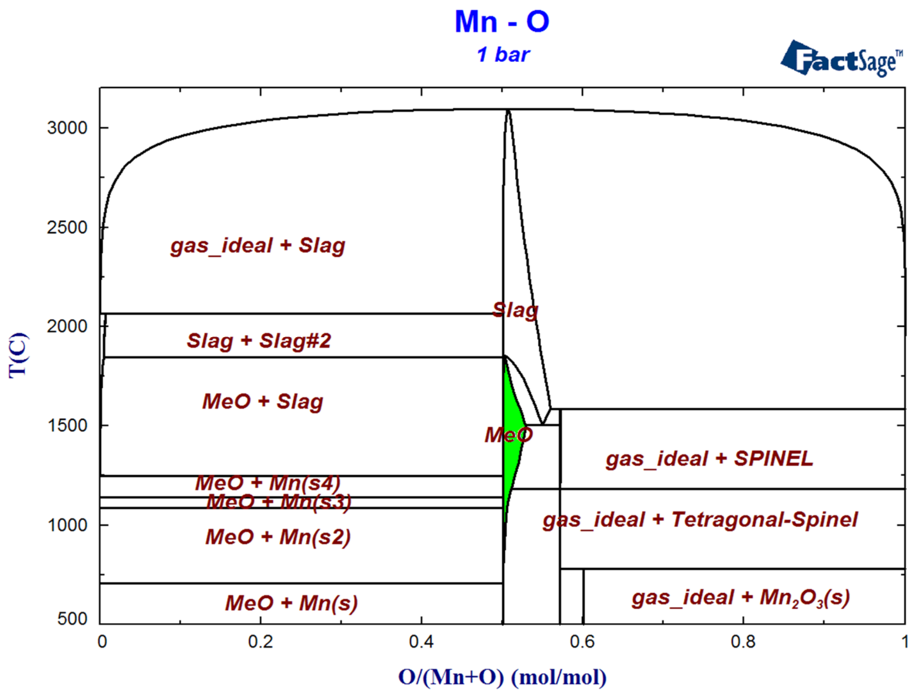
Fe_2O_3– Na

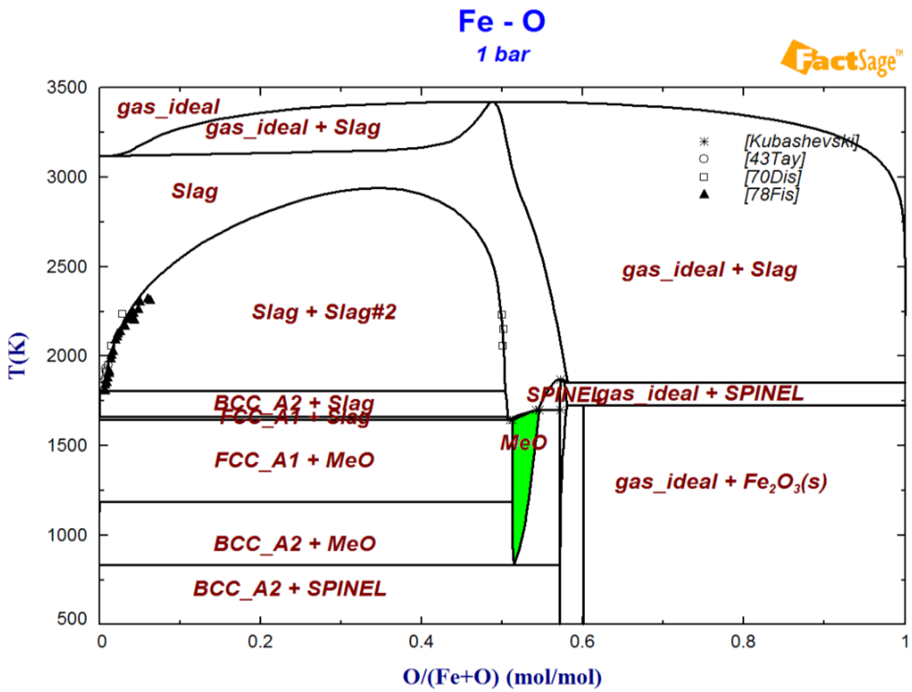
$MgO-MnO-SiO_2$

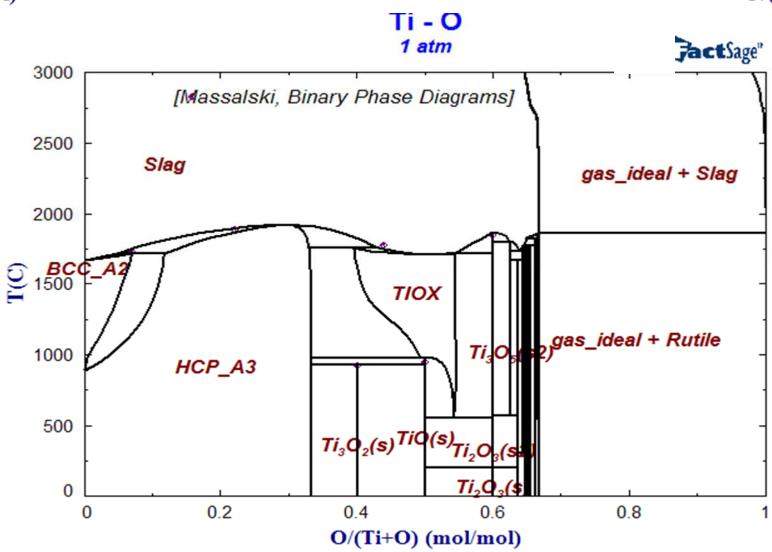
1:1

In total 166 associate species

Binary Fe-O and Mn-O systems

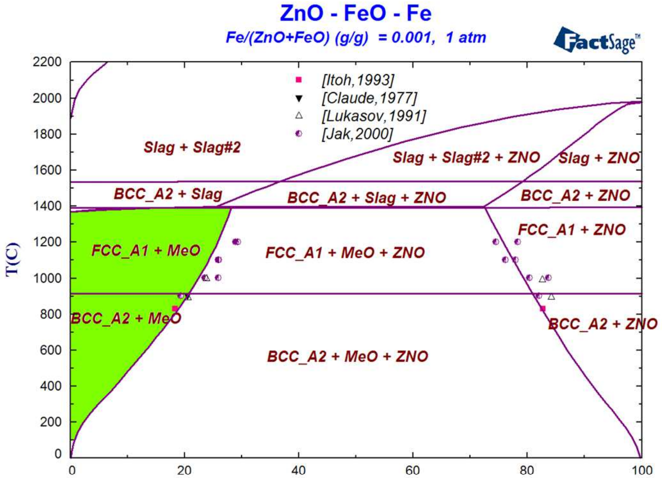


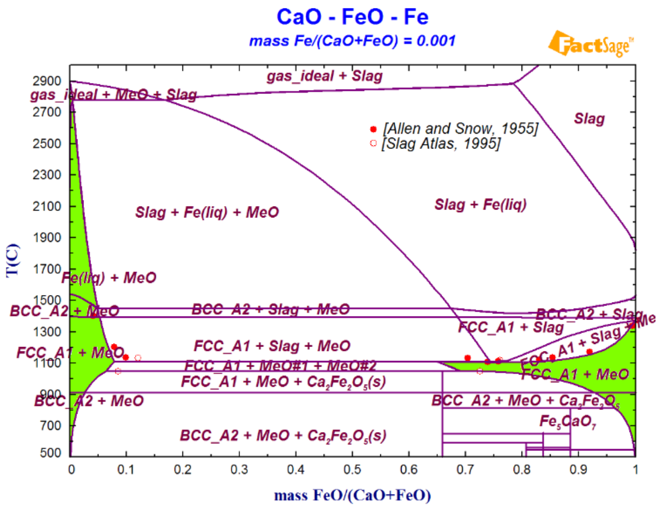


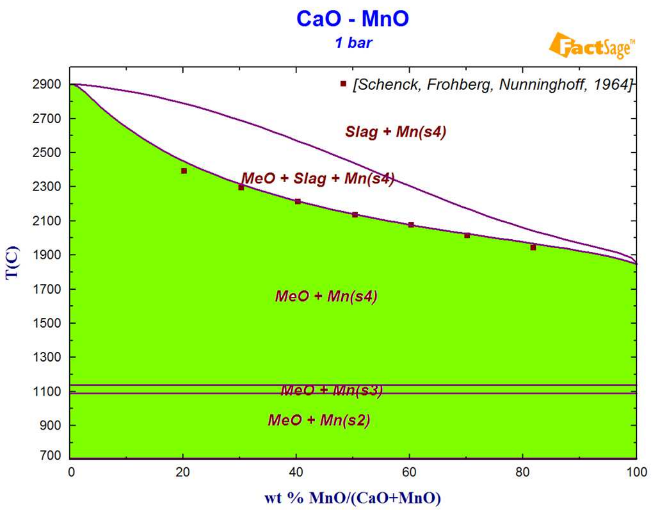


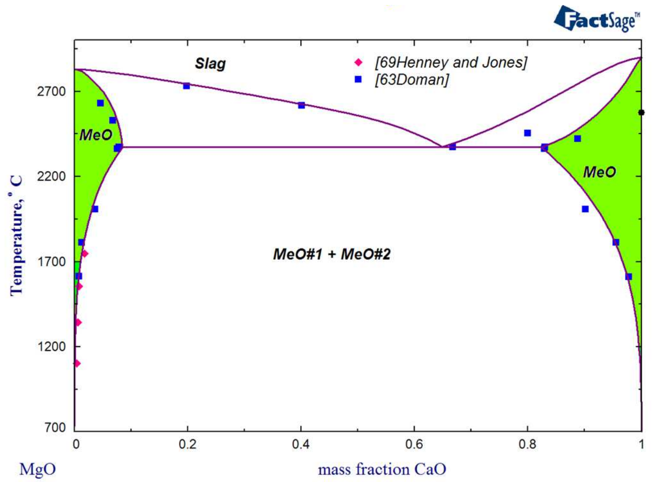
Description of the phase MeO

MeO - $(Al^{+3},\underline{Ca}^{+2},Cr^{+3},\underline{Mn}^{+2},Mn^{+3},\underline{Fe}^{+2},Fe^{+3},\underline{Mg}^{+2},Na^{+1},Zn^{+2},Va)(O^{-2})$



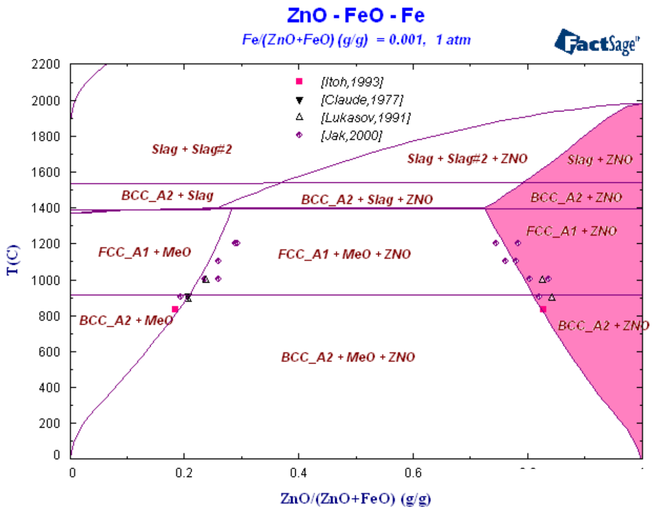


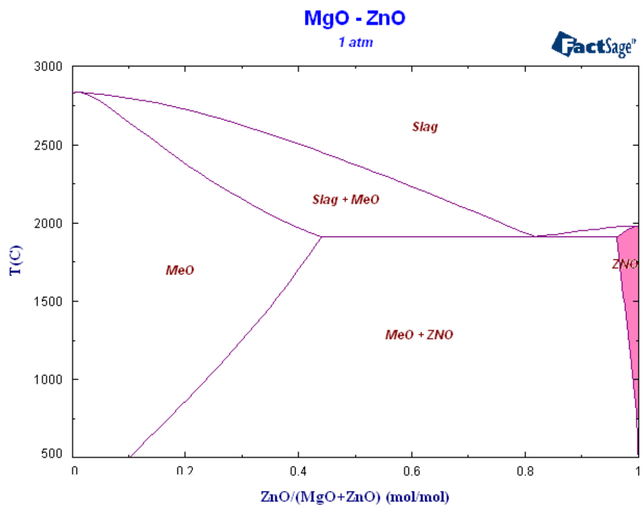


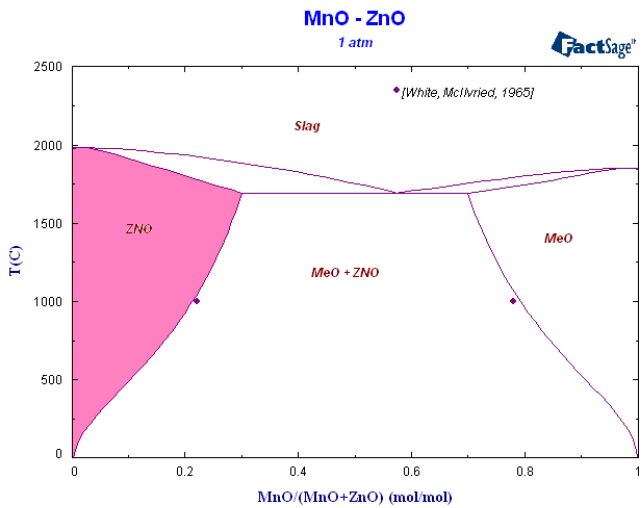


Description of the phase Zincite

Zincite - $(Ca^{+2},Cr^{+3},Mn^{+2},Mn^{+3},Fe^{+2},Fe^{+3},Mg^{+2},\underline{Zn}^{+2},Va)(O^{-2})$

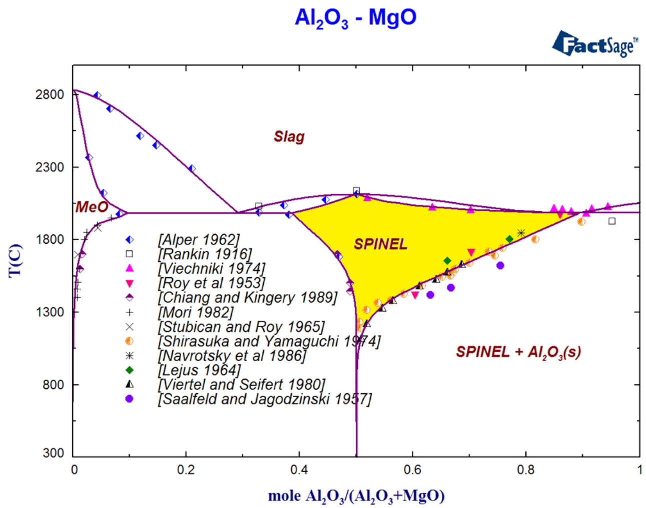


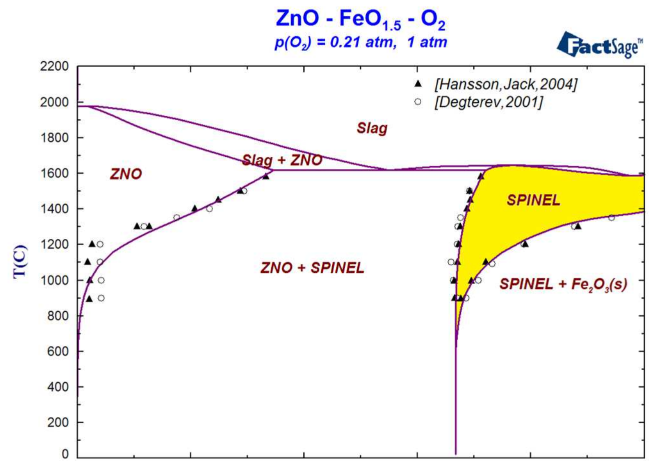


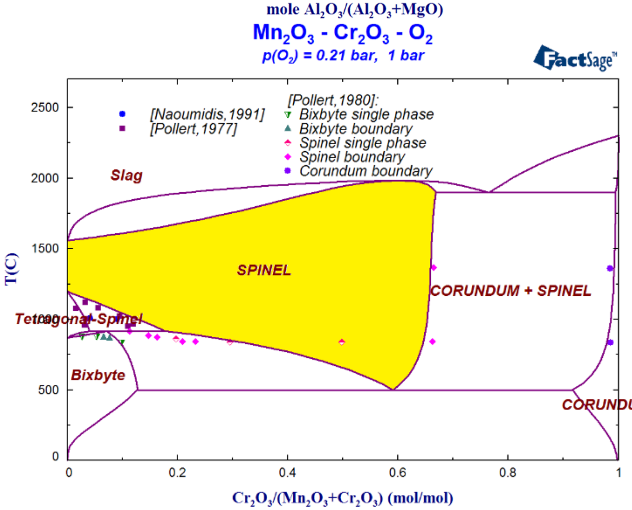


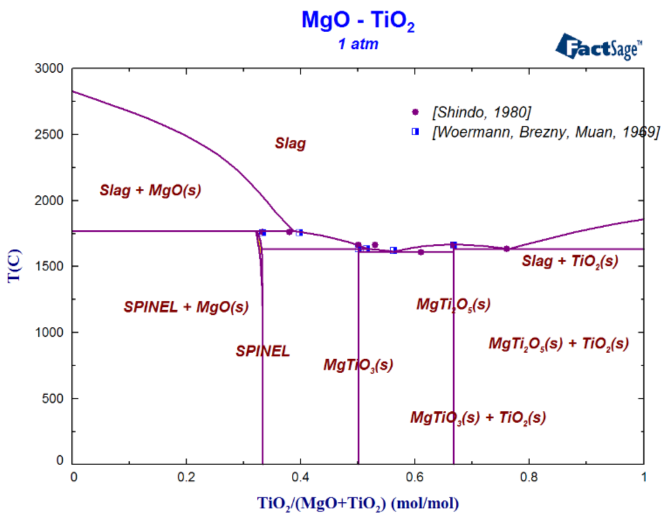
Description of the phase Spinel

Spinel ***(Al^{+3},Cr^{+2},Cr^{+3},Fe^{+2},Fe^{+3},Mg^{+2}, Ti^{+4}, Mn^{+2},Zn^{+2})(Al^{+3},Ca^{+2},Cr^{+3},Fe^{+2},Fe^{+3},Mg^{+2}, Mn^{+2},Mn^{+3},Mn^{+4},Va)$_2$ (Cr^{+2}, Fe^{+2}, Mg^{+2},Va)$_2$(O^{-2})$_4$***



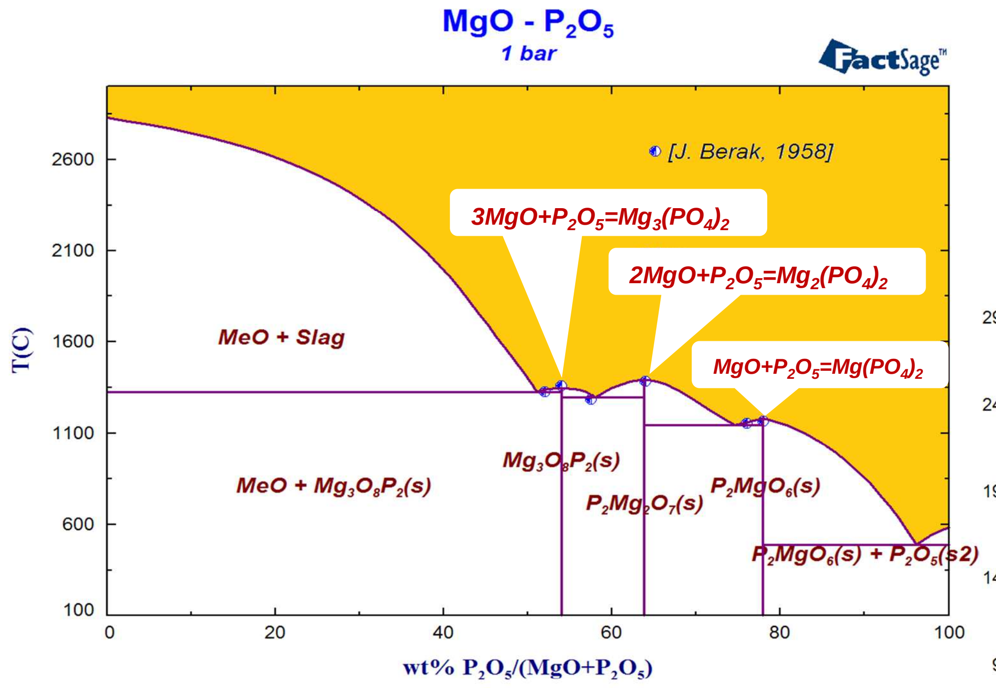


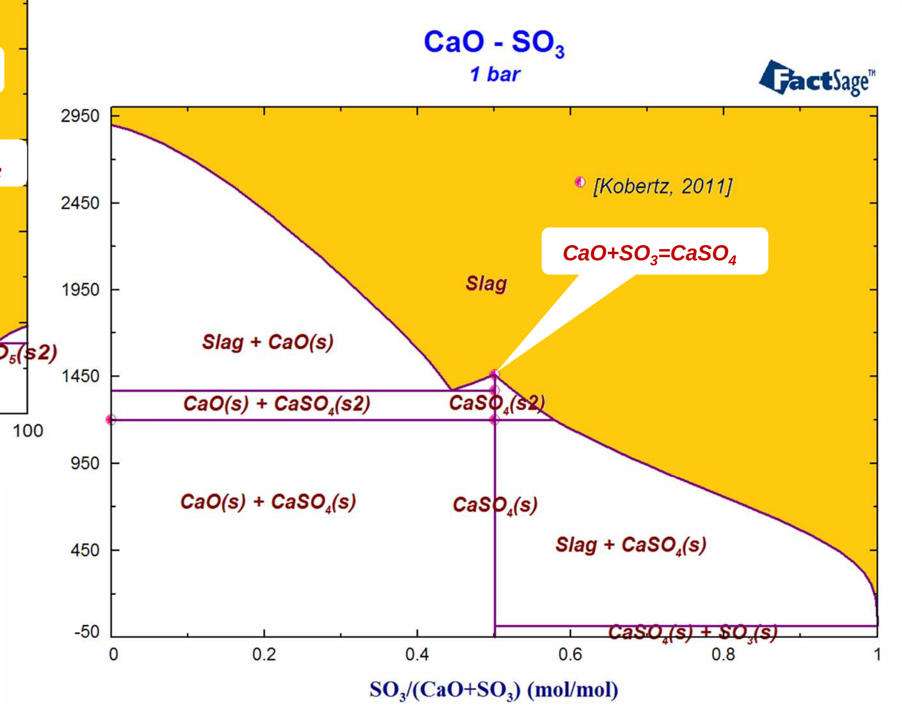




Inclusion of P_2O_5 and SO_3

Phosphates and Sulphates are double oxides

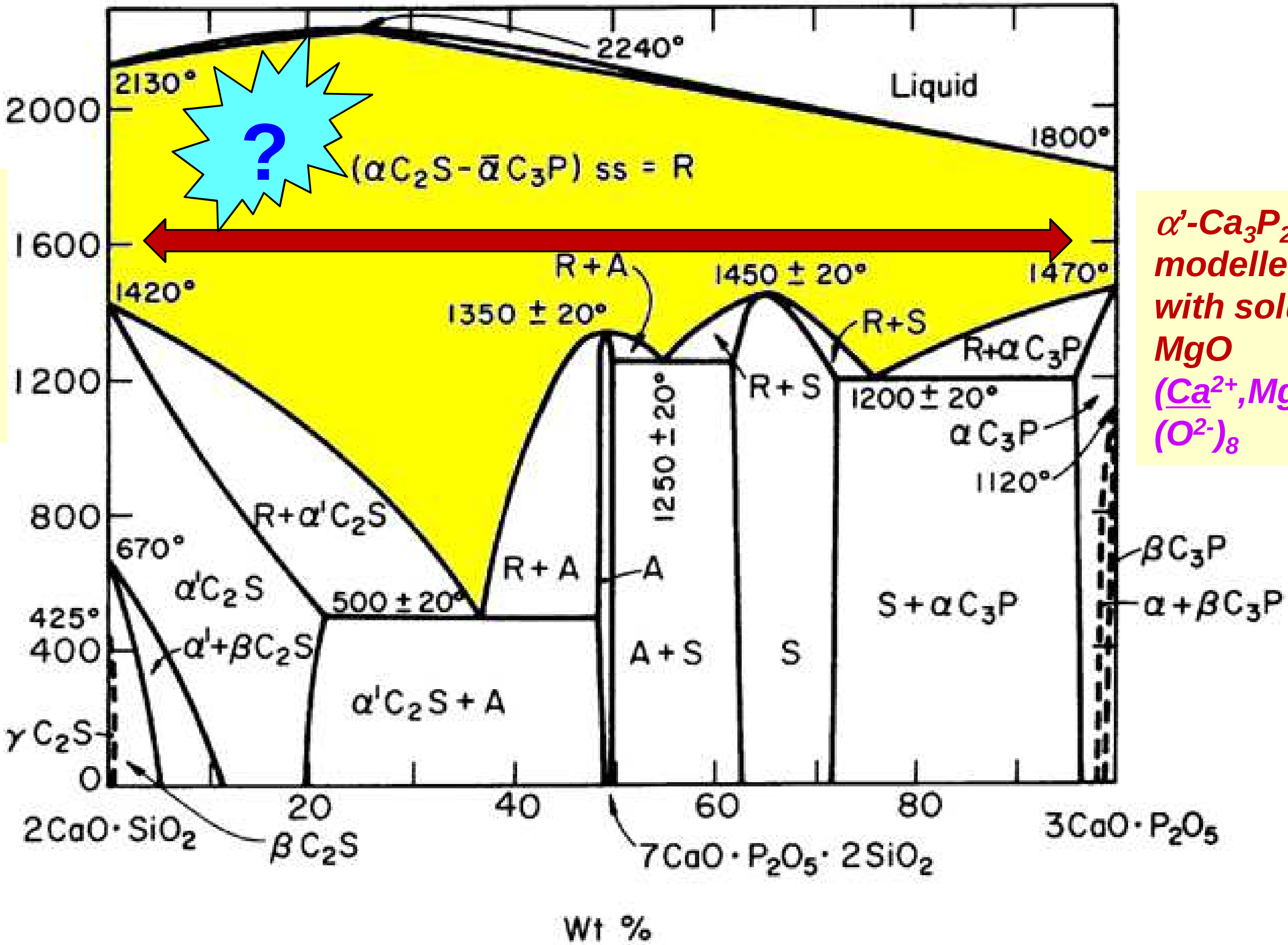




Isopleth section Ca_2SiO_4-$Ca_3P_2O_8$

α-Ca_2SiO_4, modelled before with solubility for CrO and MgO

$(\underline{Ca}^{2+},Cr^{2+},Mg^{2+})_2(Si^{4+})(O^{2-})_4$



α'-$Ca_3P_2O_8$ modelled before with solubility for MgO

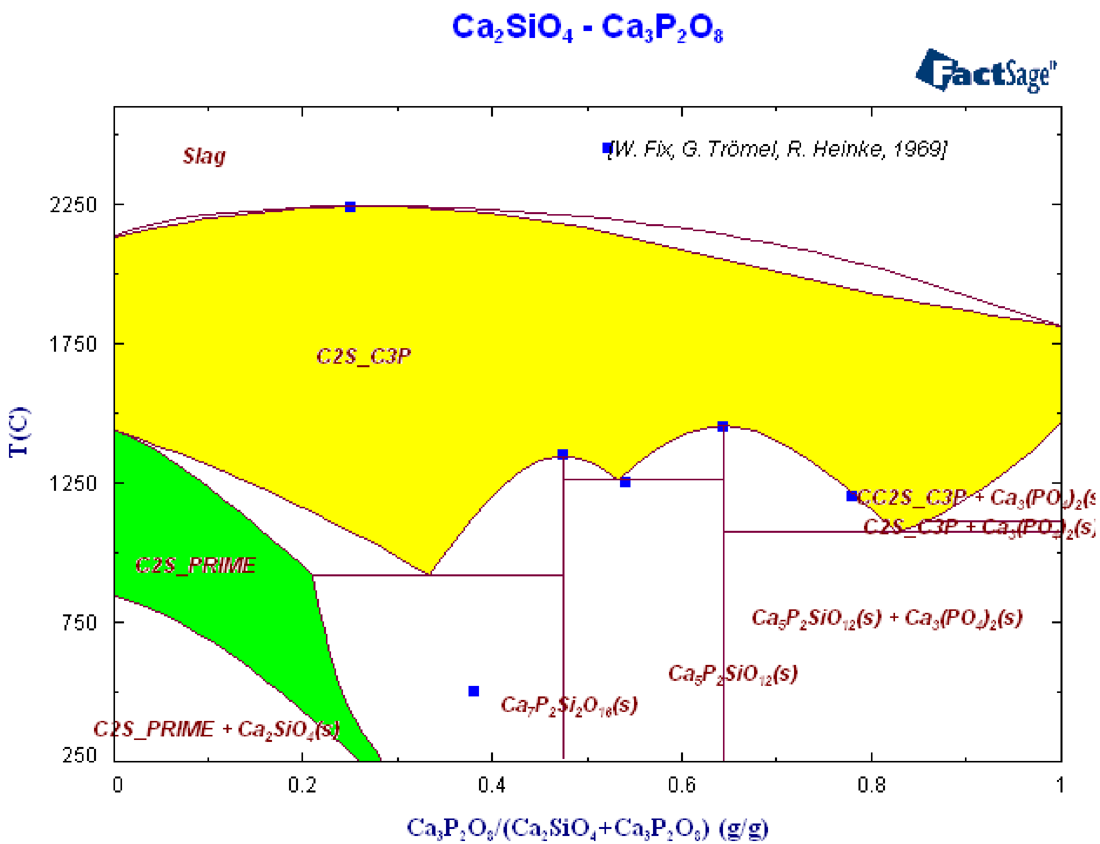
$(\underline{Ca}^{2+},Mg^{2+})_3(P^{5+})_2(O^{2-})_8$

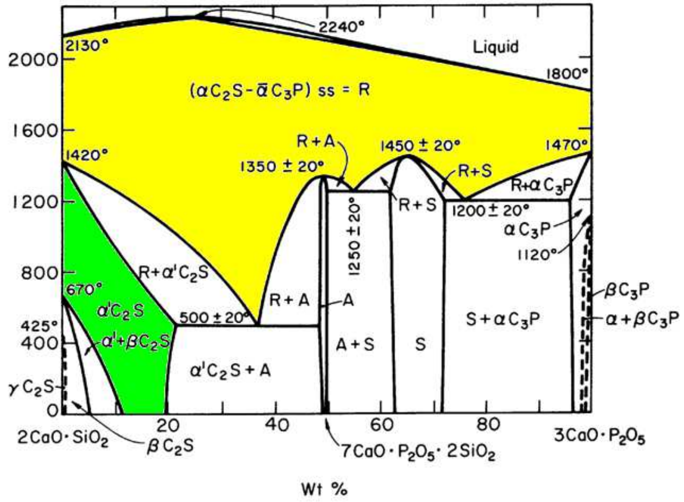
W. Fix, H. Heymann, and R. Heinke, J. Am. Ceram. Soc., 52 [6] 346-347 (1969).

Isopleth section Ca_2SiO_4-$Ca_3P_2O_8$

The following description was suggested for the phase

C2S-C3P : $(Ca^{2+},Cr^{2+},Mg^{2+})_3(Ca^{2+},Va)_1(P^{5+},Si^{4+})_2\,(O^{2-})_8$





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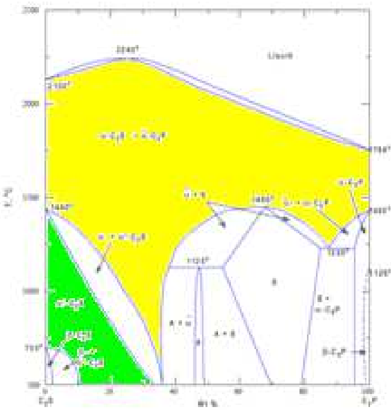
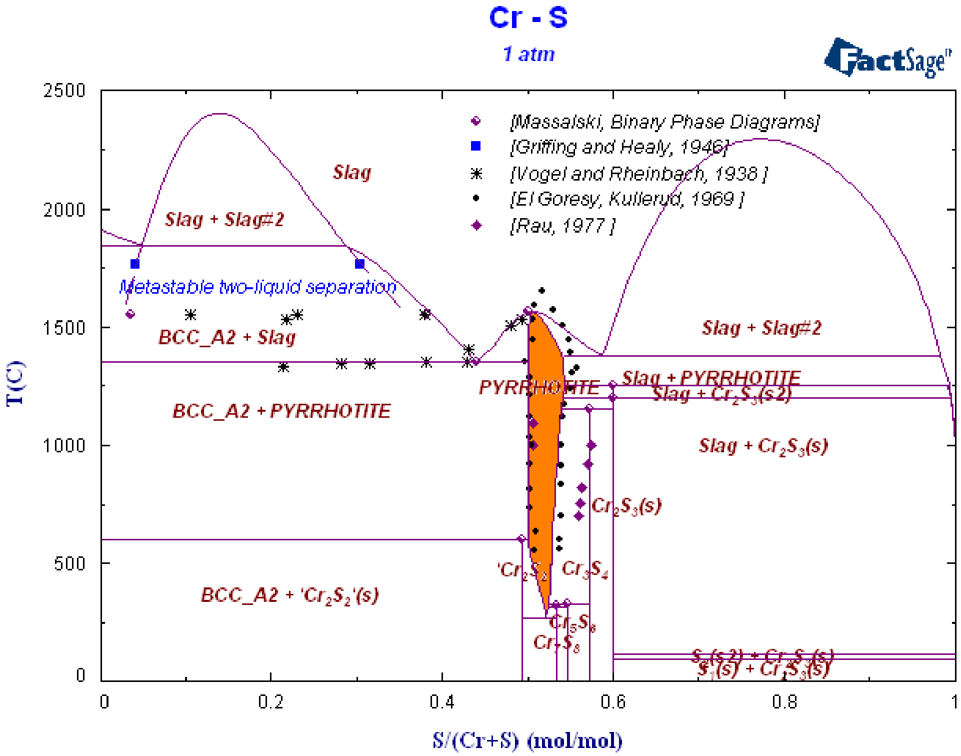
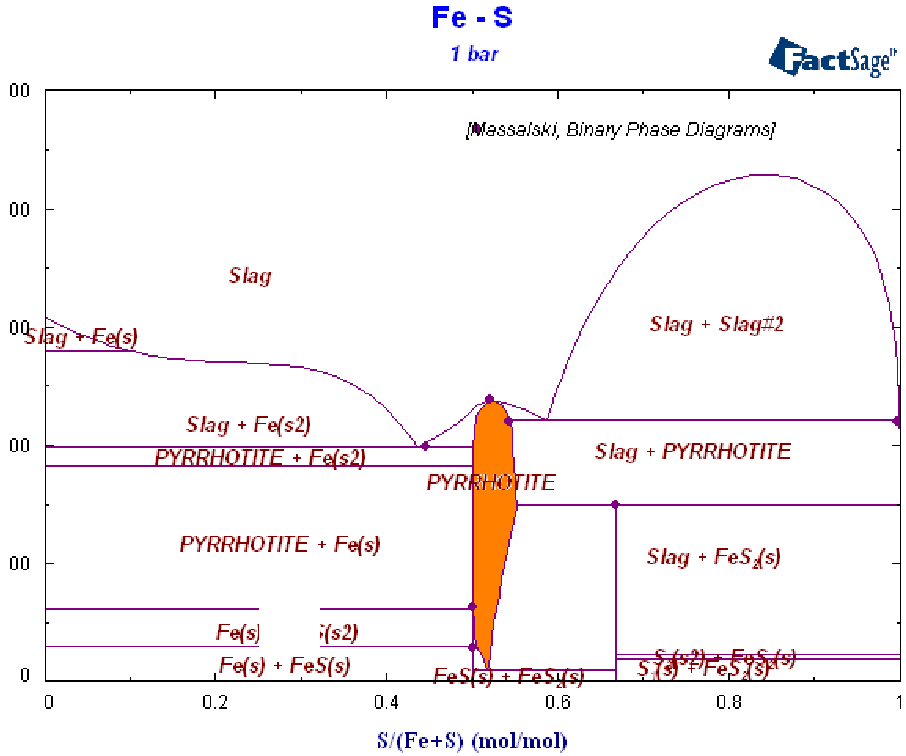


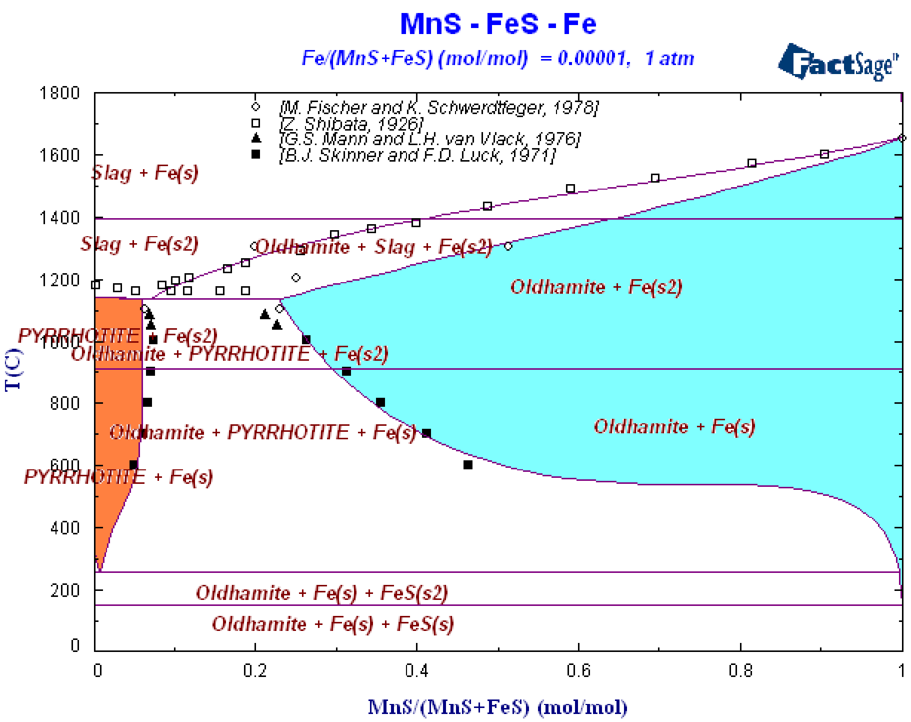
R. W. Nurse, J. H. Welch, W. H. Gutt, J. Chem. Soc.,1077-1083 (1959).

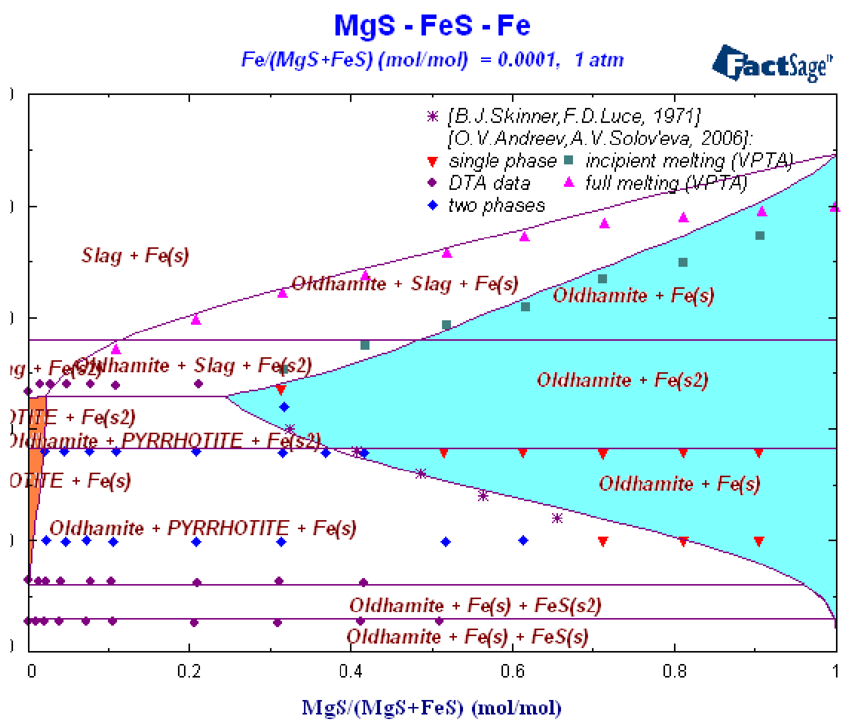
Binary Cr-S and Fe-S phase diagrams



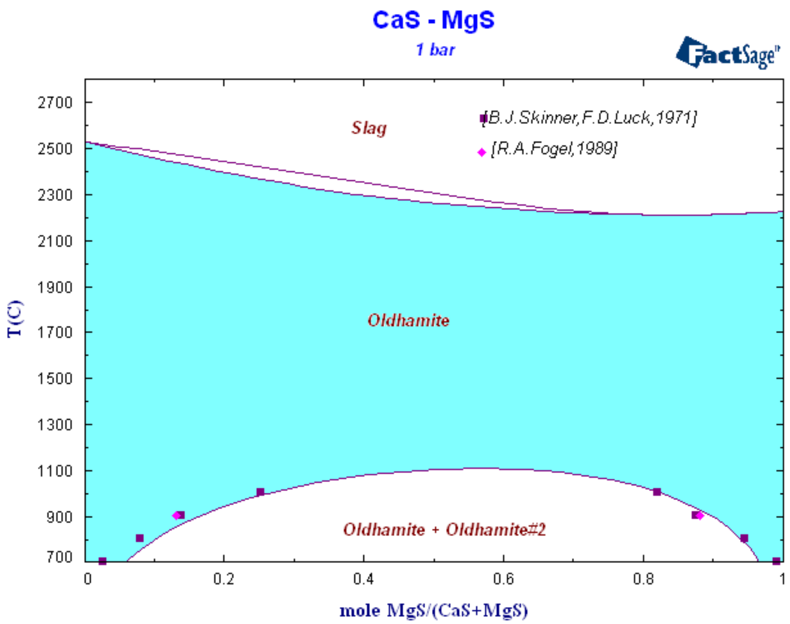


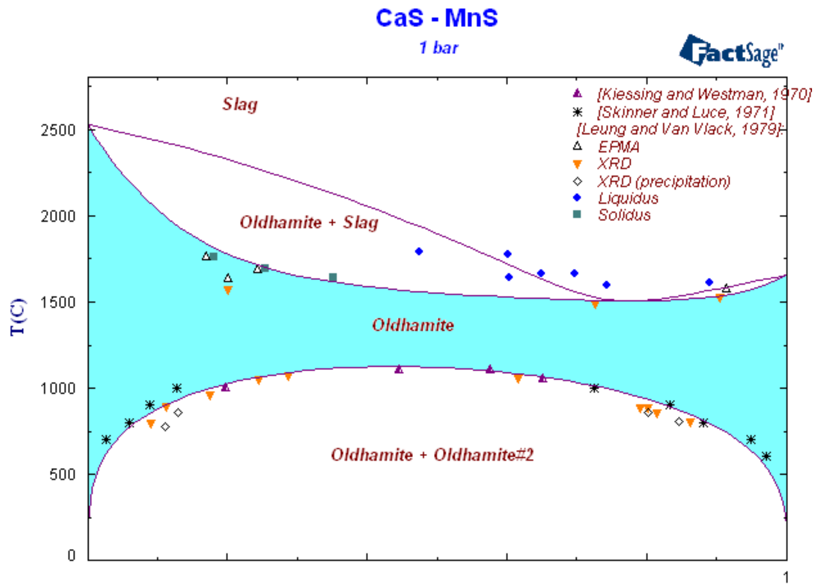
FeS-MgS and FeS-MnS phase diagrams

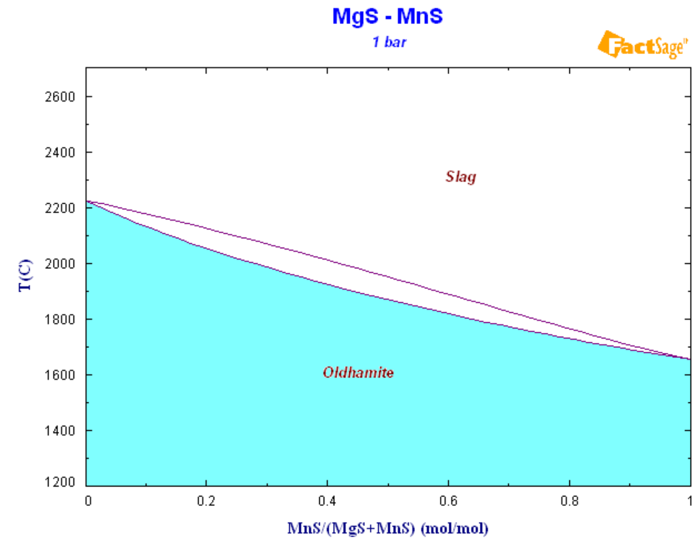




Quasi-binaries with Oldhamite

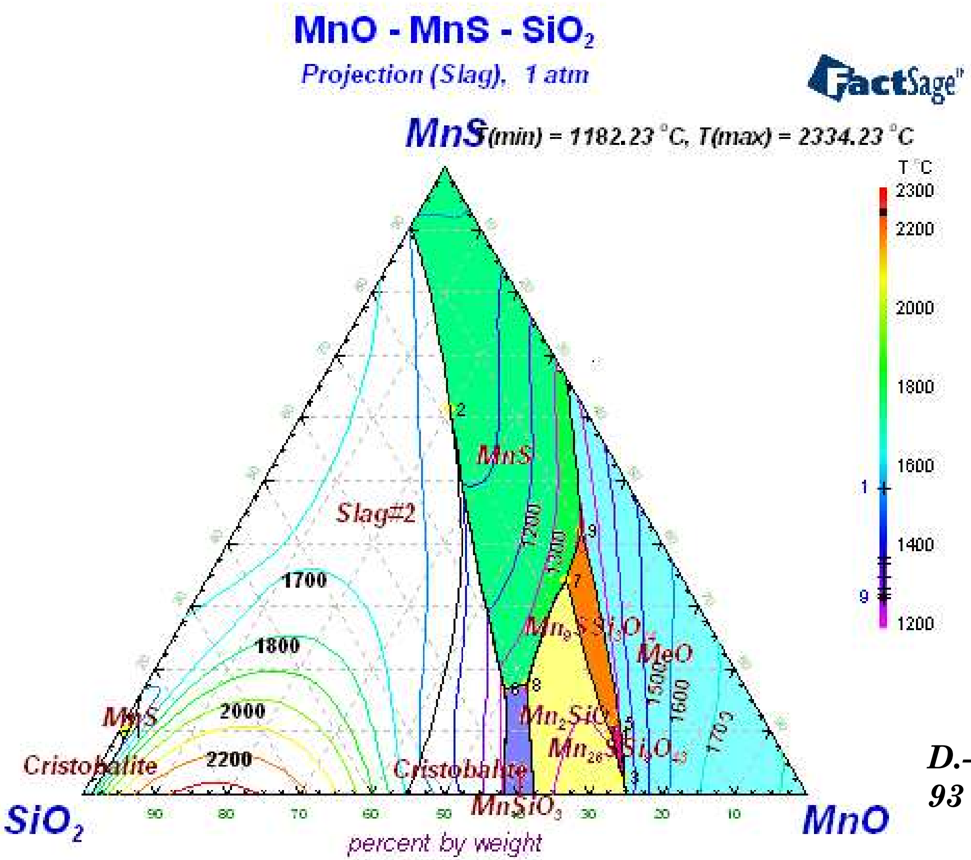


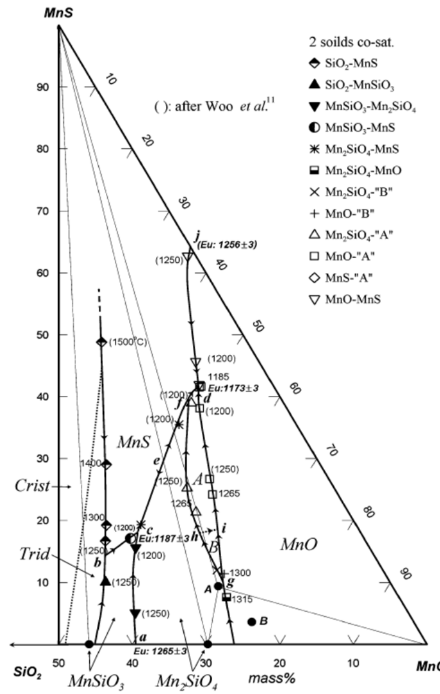




Sulfide	Pearson Symbol	Space group	Struktur-bericht	Prototype
CaS	cF8	$Fm\bar{3}m$	B1	NaCl
MgS	cF8	$Fm\bar{3}m$	B1	NaCl
MnS	cF8	$Fm\bar{3}m$	B1	NaCl

Liquidus surface in $MnO-MnS-SiO_2$



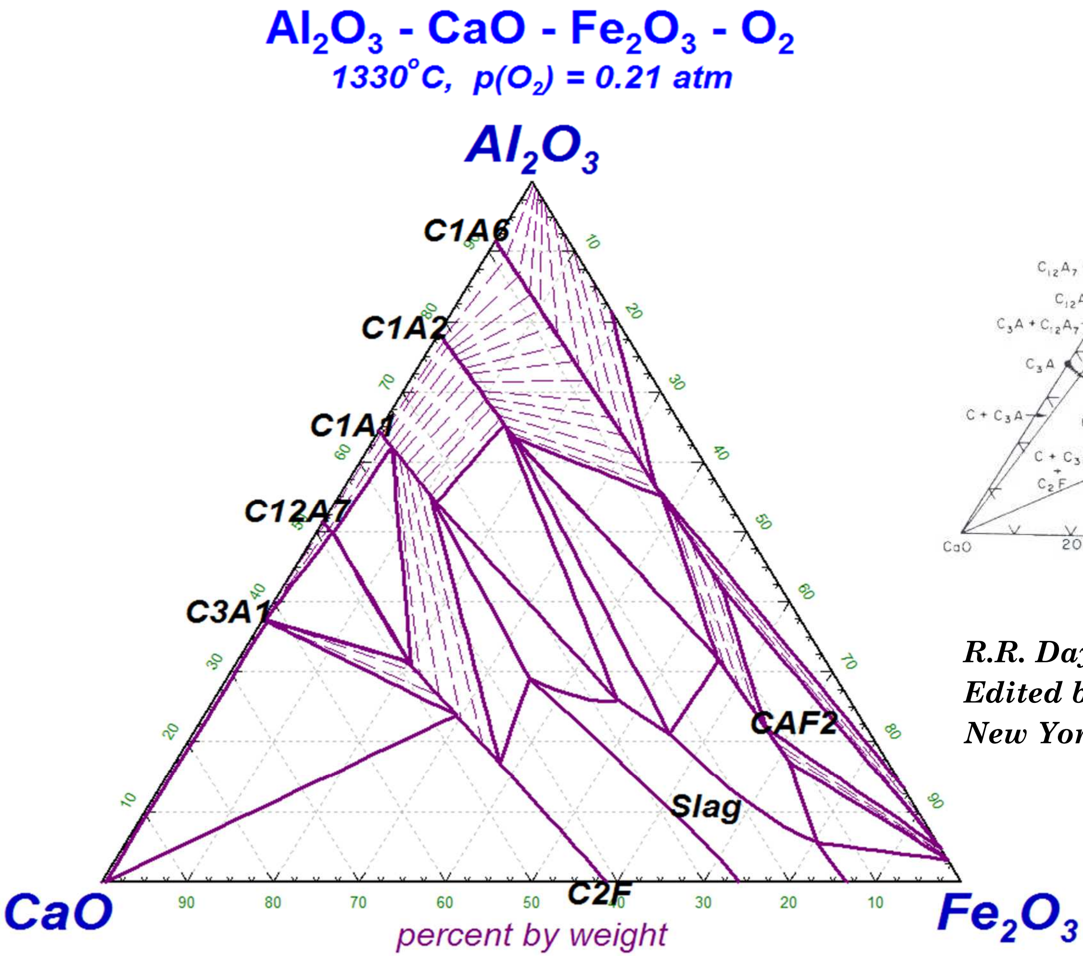


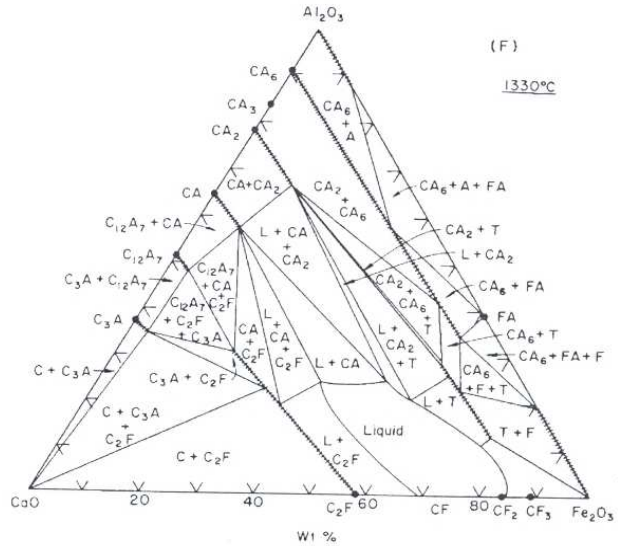
D.-H. Woo and H.-G. Lee, J. Am. Ceram. Soc., 93 [7], (2010), pp. 2008-2106.

$8MnO{\cdot}MnS{\cdot}3SiO_2$	stoichiometric	modelled by GTT
$25MnO{\cdot}MnS{\cdot}9SiO_2$	stoichiometric	modelled by GTT

Fields of Application: Cement making

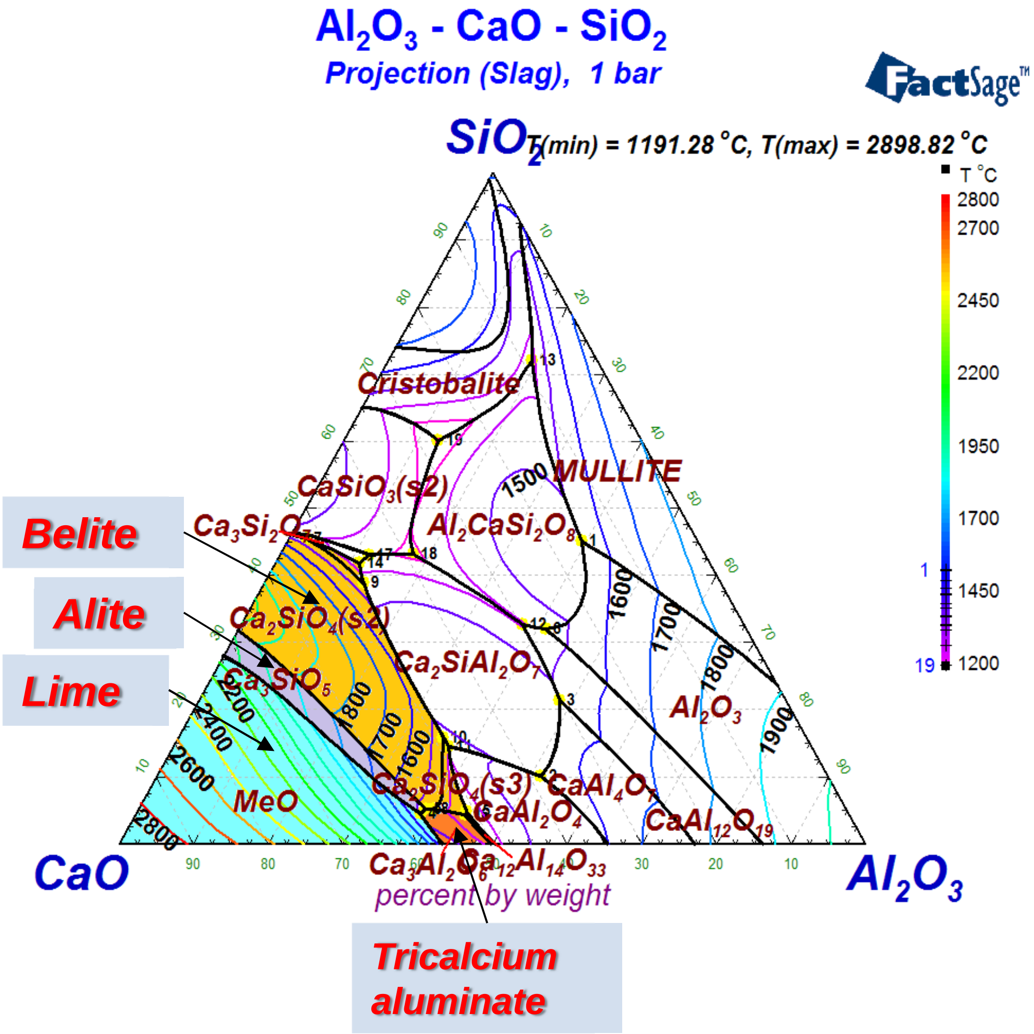
GTT-Technologies

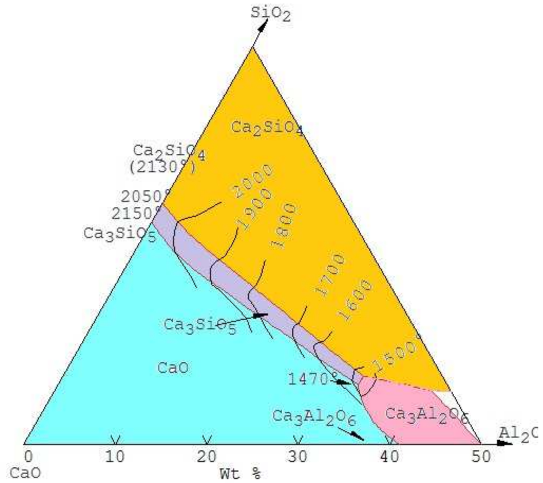




R.R. Dayal, F.P. Glasser, Sci. Ceram., Vol. 3, Edited by G.H. Stewart, Academic Press, New York, (1967), pp.191-214.

Fields of Application: Cement making





W.H. Gutt, A.D. Russel, J. Mater. Sci., 12 [9], (1977), pp.1869-1878.

K_2SO_4 also incorporated !

Fields of Application: Slagging and Fouling

Composition of hard coal ashes

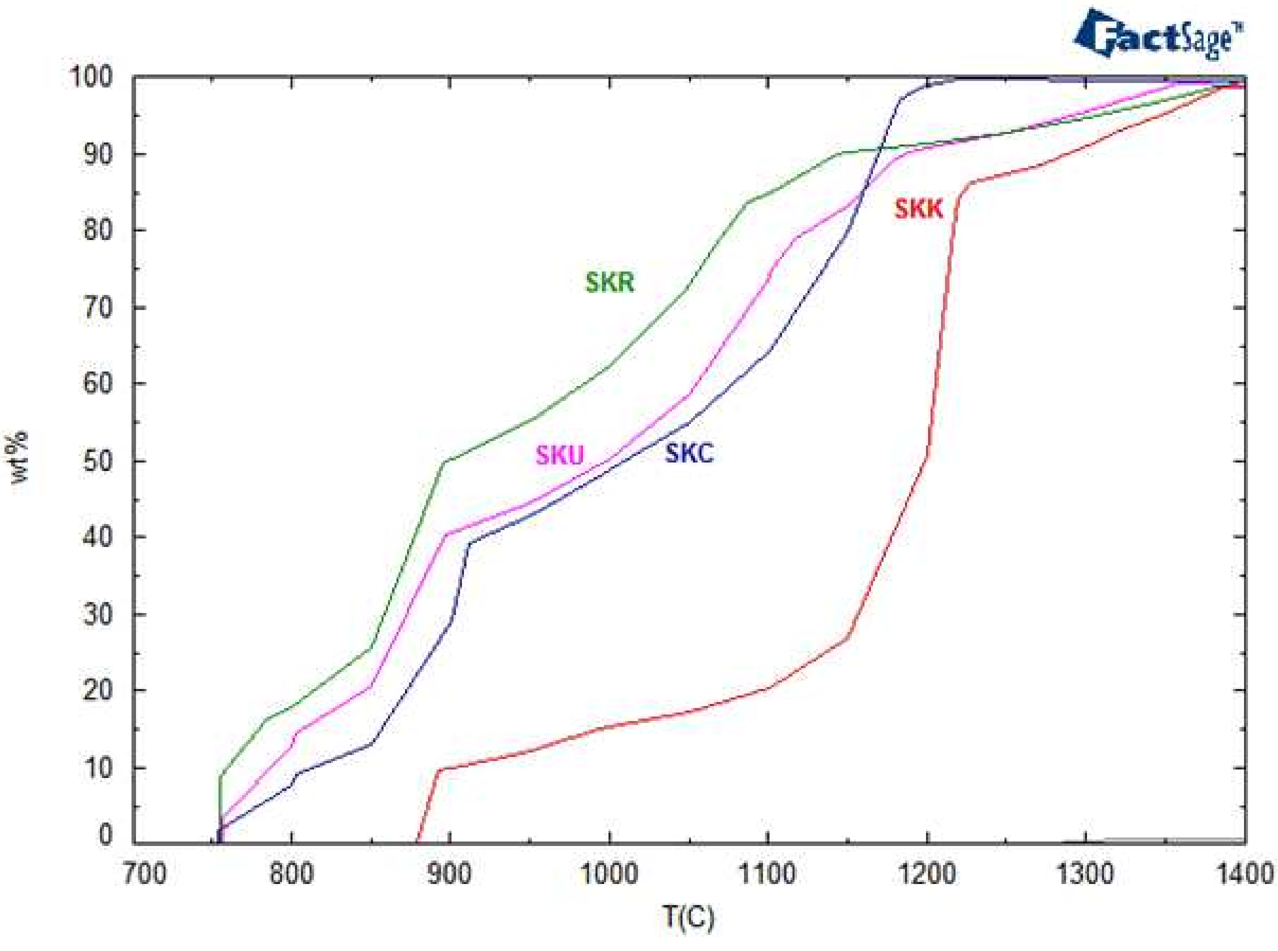
		Columbia	South Afr.	Russia	USA
Component	Unit	SKC	SKK	SKR	SKU
Al2O3	%	14.6	25.9	22.1	20.6
CaO	%	2.1	7.1	4.9	3.7
Fe2O3	%	15.5	15.4	6.8	14.6
K2O	%	1.4	0.7	2.9	2.4
MgO	%	1.1	0.1	0.2	0.9
Na2O	%	1.8	0.2	1.3	0.7
P2O5	%	0.1	1.5	0.5	0.2
SiO2	%	60.7	45.4	57.1	52.6
SO3	%	1.9	2.5	3.2	3.0
TiO2	%	0.8	1.4	0.9	1.1

Inclusion of TiO_2 → See T. Jantzen

Fields of Application: Slagging and Fouling

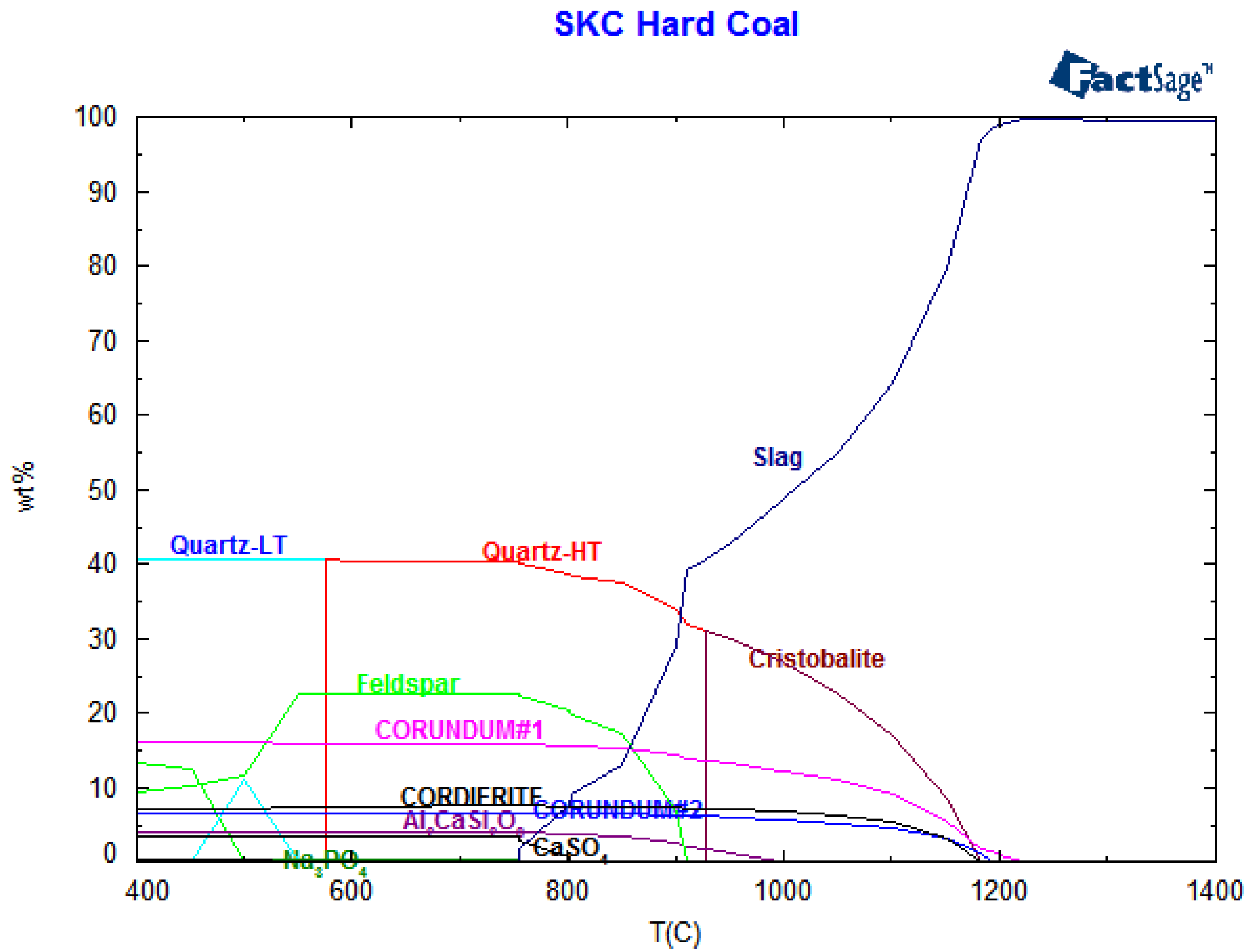
GTT-Technologies

VerSi project: Melting behaviour of different Hard Coals



Fields of Application: Slagging and Fouling

VerSi project: Melting behaviour of hard coal SKC



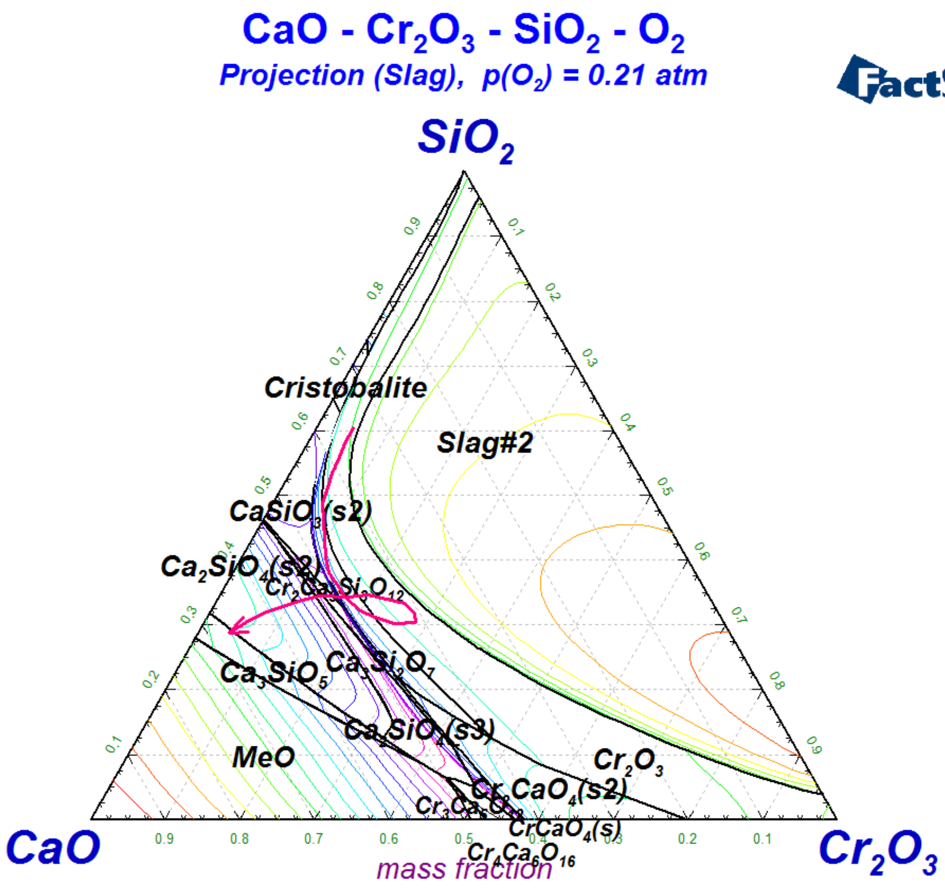
Fields of Application: Stainless steel-making

Low C in steel:

$$2\,Cr + 3\,CO(g) = 3\,C + Cr_2O_3$$

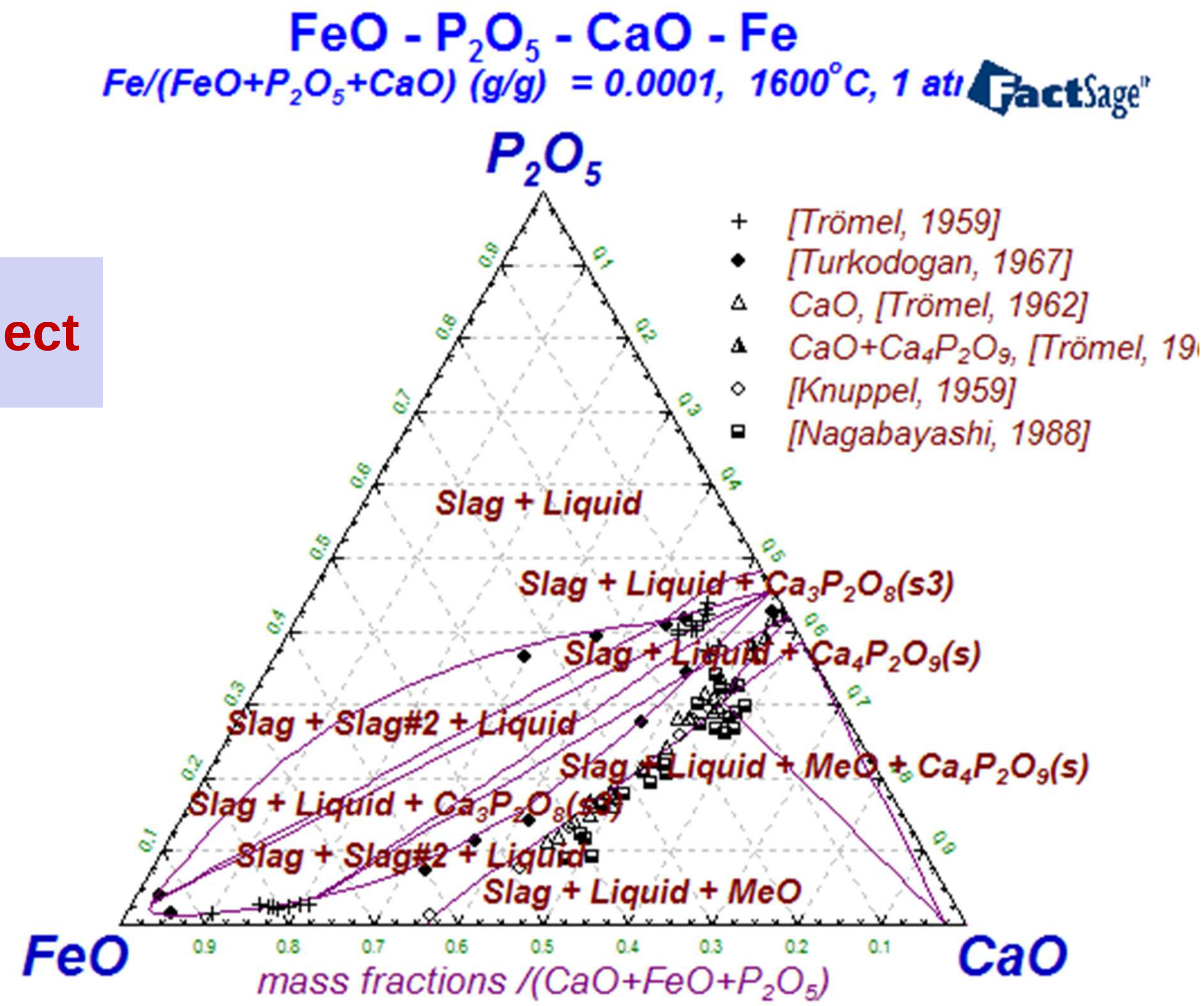
Law of Mass Action:

$$\log a_C = 1/3 \log K(T) + 2/3 \log a_{Cr} - 1/3 \log a_{Cr2O3} + \log P_{CO}$$



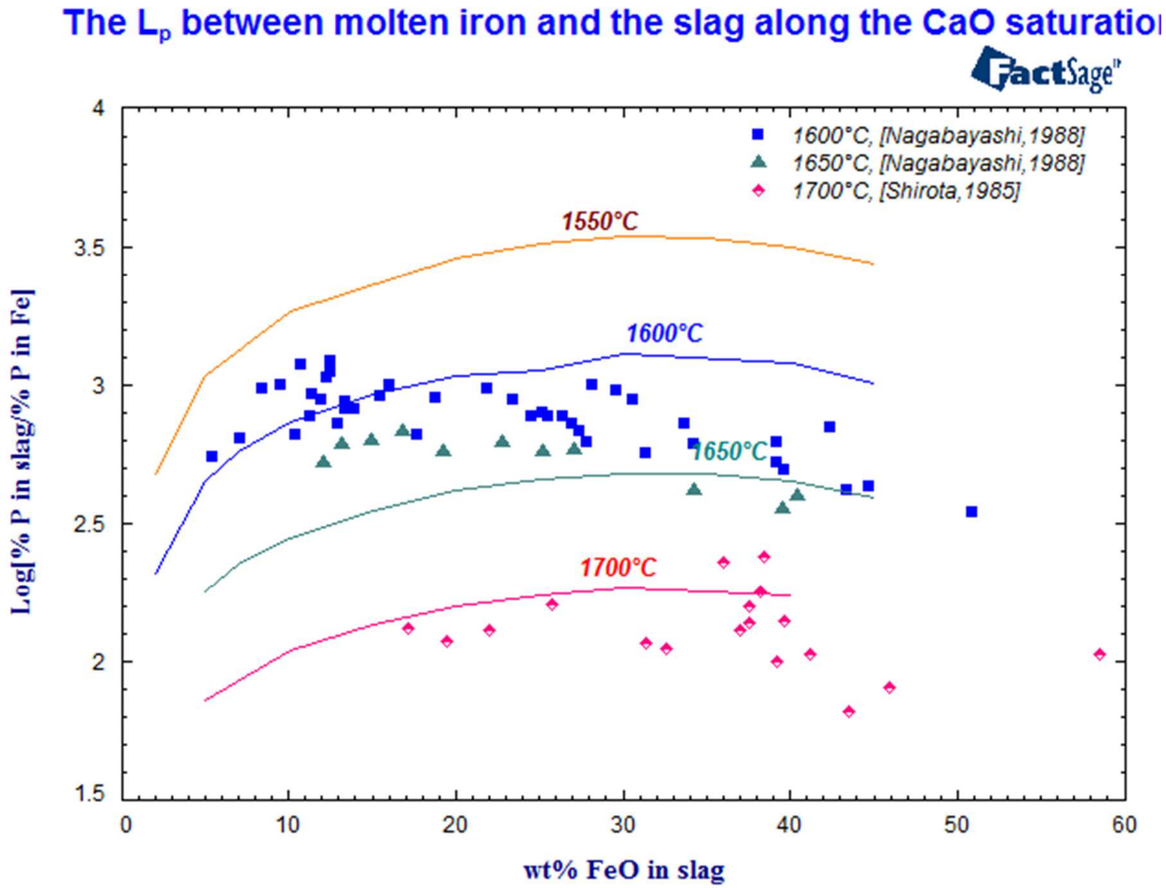
Fields of Application: Steel dephosphorisation

BofDePhos project



Fields of Application: Steel dephosphorisation

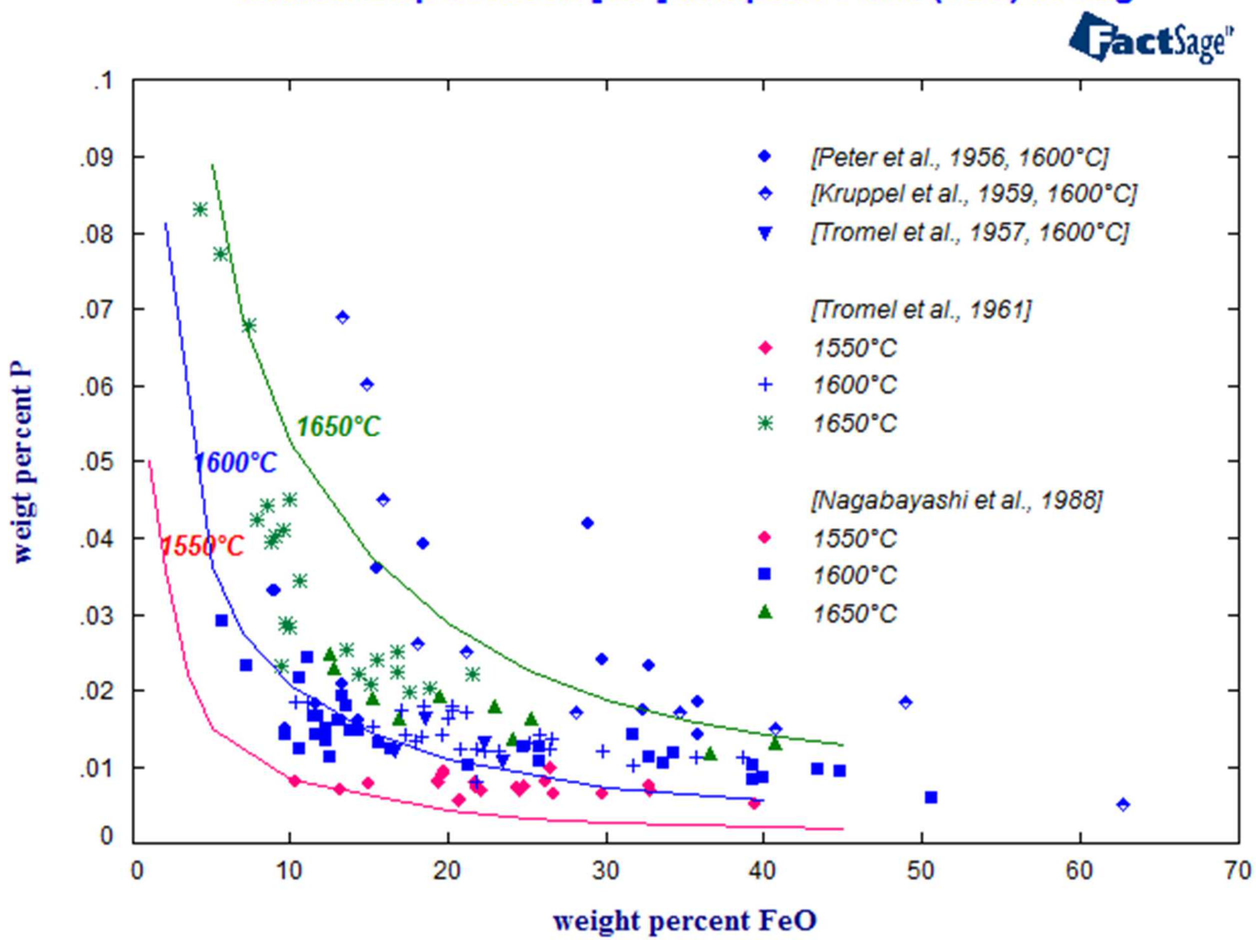
BofDePhos project



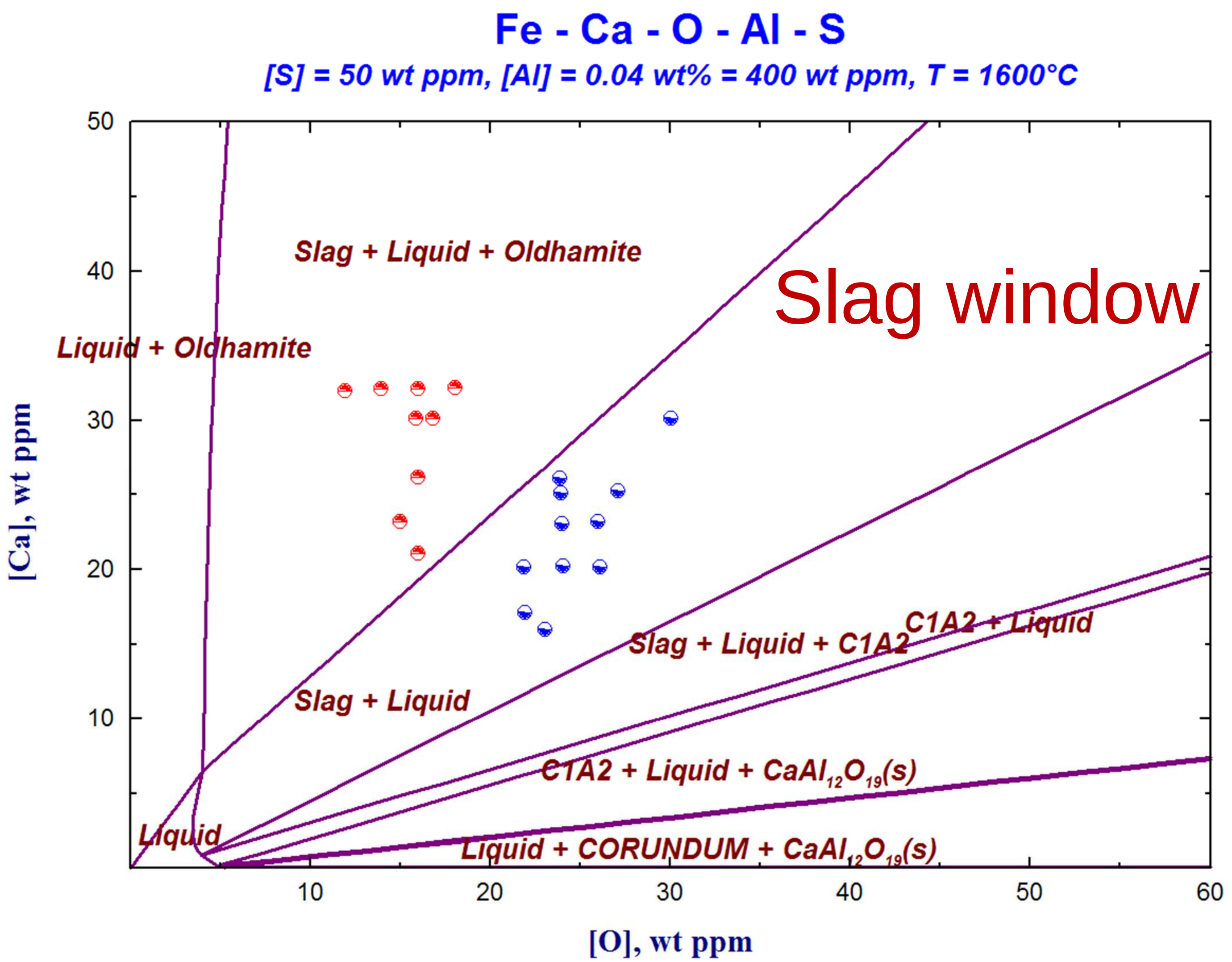
Fields of Application: Steel dephosphorisation

BofDePhos project

Relationship between [%P] in liquid Fe and (FeO) in slag



Fields of Application: Avoiding nozzle clogging

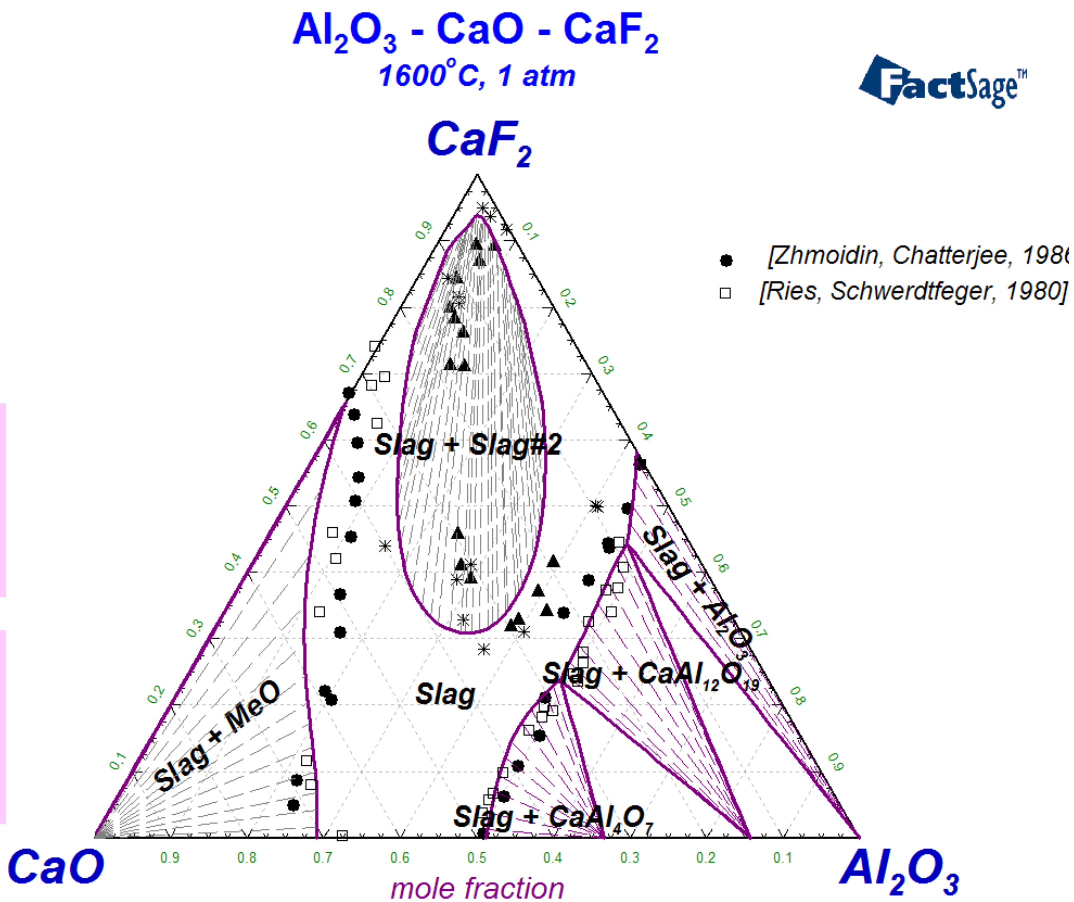


Fields of Application: Slag fluxing

CaF_2

Addition of CaF_2 (Fluorspar) decreases melting temp. of slag.

Fluorspar furthermore decreases viscosity of the slags.



Conclusions

- GTOX now covers 28 components in 104 sol. + 661 comp. phases
- The liquid phase was evaluated using the associate species model (X_j liq. constituents → x_i liquid species)
- Solids have been treated either as stoichiometric (X, G=G(T) only) or with a multi-sublattice approach (Y, $G=G(T,y_j^i)$).
- Fields of application ranging from coal combustion and gasification over cement making and metallurgy to special cases such as recycling of spent car catalysists
- Direct link to modelling of slag viscosities available

Future Developments

- Inclusion of Cu into oxide database → together with Me-S database start into a Cu-metallurgy database
- DüSol-project → production of fertilizers using solar energy
- Adding salts such as alkali-sulphates to oxide database → more practical relevance for bio-mass combustion applications

Thanks for your attention