Thermodynamic Databases and Their Applications for Sulfur Control in Steelmaking

Youn-Bae Kang[1)] and Arthur D. Pelton[2)]

1) Graduate Institute of Ferrous Technology (GIFT), Pohang University of Science and Technology (POSTECH), Rep. of Korea

2) Centre for Research in Computational Thermochemistry (CRCT), Dept. de Genie Chimique, Ecole Polytechnique de Montreal, Canada

FactSage™

Solution Databases :

FToxid	**- oxide database for slags, glasses, ceramics, refractories**
FSstel	**- steel database**
FTlite	**- light metal database (formerly FSlite)**
Ftsalt	**- salt database**
FThall	**- Hall alumium database**
FThelg	**- aqueous (Helgeson) database**
Ftmisc	**- miscealleneous database for sulfides, alloys, etc.**
Ftpulp	**- pulp and paper database (and corrosion and combustion)**
Fscopp	**- copper alloy database**
Fslead	**- lead alloy database**
FSupsi	**- ultrapure silicon database**
SGnobl	**- noble metal database (formerly FSnobl)**
SGnucl	**- nuclear database**
SGTE(2007)	**- alloy database (formerly SGTE (2004))**
SGsold	**- solders database**
BINARY(2004)	**- free alloy database**
OLI-Systems	**- aqueous databases**
TDNucl	**- Thermodata nuclear database**

Thermodynamic model for oxide

Molten Oxide

$CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}FeO\text{-}Fe_2O_3\text{-}MgO\text{-}MnO\text{-}Mn_2O_3\text{-}CrO\text{-}Cr_2O_3\text{-}TiO_2\text{-}Ti_2O_3\text{-}CoO\text{-}NiO\text{-}...$

+ oxysulfide + oxyfluoride

Capacity: SO_4, PO_4, H_2O, F, Cl, C, N, ...

Solids (solutions/stoichiometric compounds)

Spinel: $MgAl_2O_4$, Fe_3O_4, $MgCr_2O_4$, $FeAl_2O_4$, etc.

$[Mg^{2+},Fe^{2+},Cr^{2+},Ni^{2+},Mn^{2+},Co^{2+},Al^{3+},Fe^{3+},Cr^{3+},Zn^{2+},Co^{3+}]^T$

$(Mg^{2+},Fe^{2+},Ni^{2+},Mn^{2+},Mn^{3+},Mn^{4+},Co^{2+},Al^{3+},Fe^{3+},Cr^{3+},Zn^{2+},Co^{3+},Va)_2{}^OO_4$

Olivine: Mg_2SiO_4, Fe_2SiO_4, Mn_2SiO_4, etc.

$[Mg^{2+},Ca^{2+},Fe^{2+},Mn^{2+},Ni^{2+},Co^{2+}]^{M2}$

$(Mg^{2+},Ca^{2+},Fe^{2+},Mn^{2+},Ni^{2+},Co^{2+})^{M1}SiO_4$

Monoxide: periclase, wustite, etc.

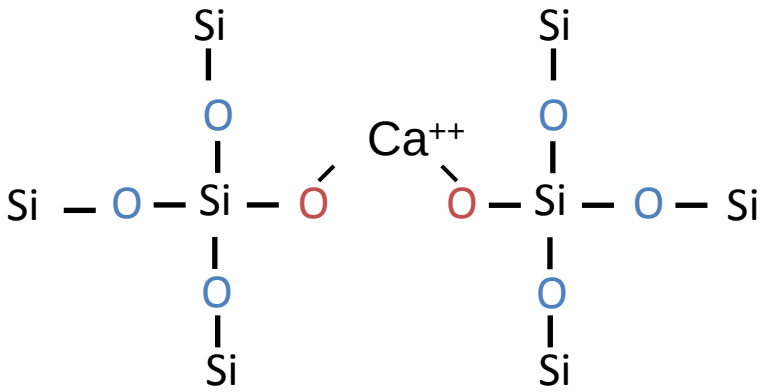
$CaO\text{-}MgO\text{-}FeO\text{-}MnO\text{-}CoO\text{-}NiO\text{-}Al_2O_3\text{-}Fe_2O_3\text{-}Mn_2O_3\text{-}Cr_2O_3\text{-}...$

Melilite, Ca_2SiO_4, Perovskite, Corundum, Pyroxene, etc. + Pure Compounds

$CaO\text{-}SiO_2$ binary molten slag

$(Ca\text{-}O^{2-}\text{-}Na) + (Si\text{-}O^{\circ}\text{-}Si) = 2(Ca\text{-}O^{-}\text{-}Si)$ Δg

- Free oxygen
- Non-bridging oxygen
- **Bridging oxygen**



Thermodynamic model for liquid oxide - Slag

Quasichemical Model (pair approximation)

$(A\text{-}A)_{pair} + (B\text{-}B)_{pair} = 2(A\text{-}B)_{pair}$; w_{QM}

A and B are distributed non-randomly on lattice sites

The pairs are distributed randomly over "pair sites"

$ZX_A = 2\,n_{AA} + n_{AB}$, $ZX_B = 2\,n_{BB} + n_{AB}$

Z = coordination number

n_{ij} = moles of pairs, X_{ij} = pair fraction = $n_{ij}/(n_{AA} + n_{BB} + n_{AB})$

$$\Delta S^{config} = -R\left(X_{AA}\ln\left(X_{AA}/X_A^2\right) + X_{BB}\ln\left(X_{BB}/X_B^2\right) + X_{AB}\ln\left(X_{AB}/2X_AX_B\right)\right)$$

$$-R\left(X_A\ln X_A + X_B\ln X_B\right)$$

This expression for ΔS^{config} is:

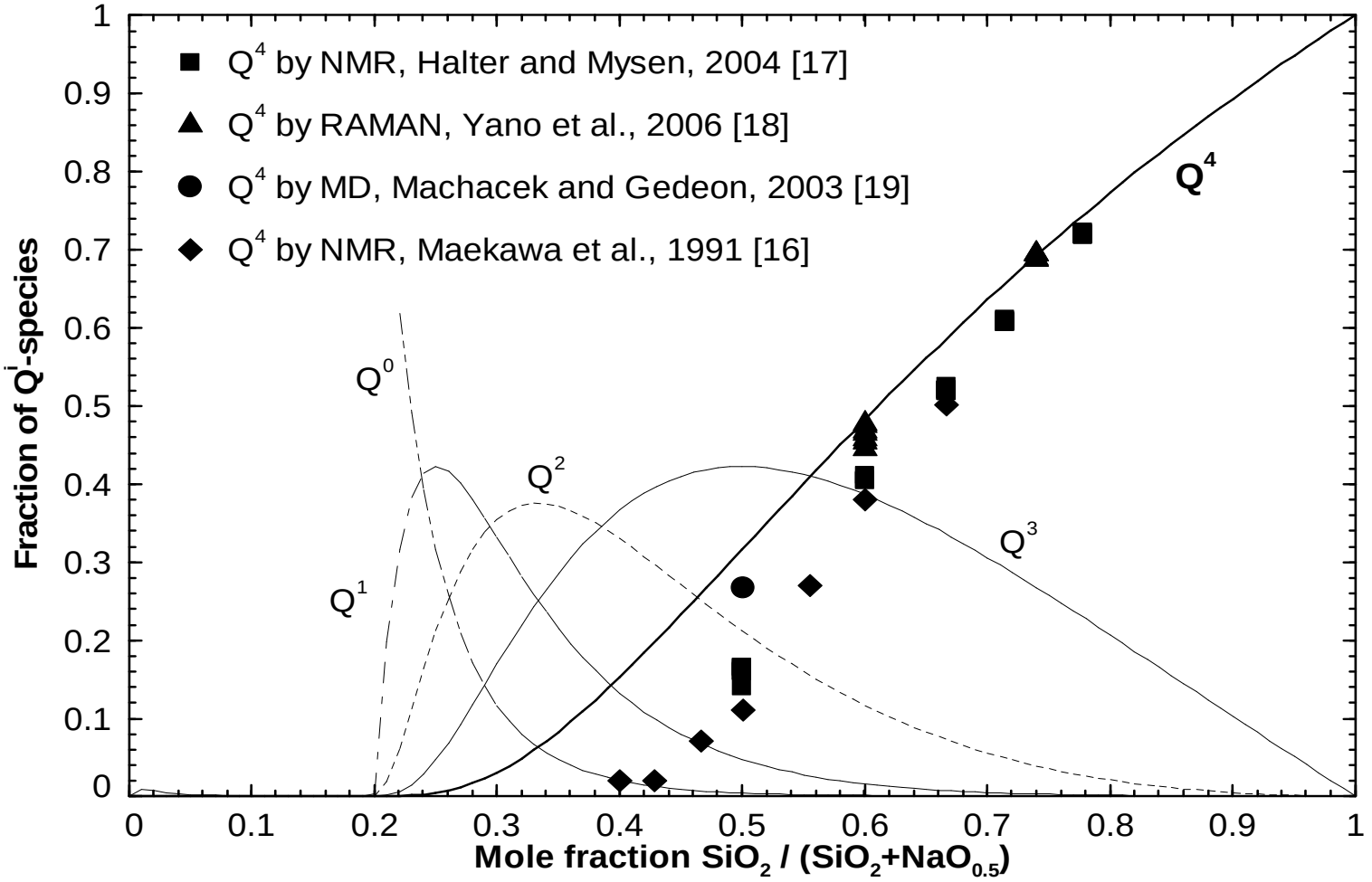
- **mathematically exact in one dimension (Z = 2)**
- **approximate in three dimensions**

$$\Delta H = \left(X_{AB}/2\right)\omega_{QM}$$

$$"K" = X_{AB}^2/\left(X_{AA}X_{BB}\right) = 4\exp\left(-\omega_{QM}/RT\right)$$

Thermodynamic model for oxide

Grundy et al. (2008), Int. J. Mater. Res.



Molten oxide with dissolve Sulfur

Models for Sulfide Capacity in Slags

$$C_S = (\text{mass pct. S})_{slag} \left(\frac{pO_2}{pS_2} \right)^{\frac{1}{2}}$$

Defined by Fincham and Richardson (1954)

Previously, sulfide capacity of slags have been calculated using

- ❑ Optical bascity (Sosinsky and Sommerville)
- ❑ KTH capacity model (Nzotta and Seetharaman)
- ❑ IRSID cell model (Lehmann and Gaye)
- ❑ Reddy-Blander-Pelton capacity model

- function of composition, defined only for calculating C_S itself
- requires many empirical parameters
- S is one of model species in a large slag database, can be extended to high sulfur content
- requires no model parameters, but limited to dilute region, non-acidic slags

Present Thermodynamic Models for Sulfur Dissolved in Slags

The present thermodynamic model is developed using the Modified Quasichemical Model in the Quadruplet Approximation.

1.taking into account dissolution mechanism of sulfur.
2.for describing solution behavior of sulfur, not just for calculating capacities.
3.in consistent with already well developed **FactSage** molten oxide thermodynamic database.
4.for calculating not only solubility in dilute region but also for calculating phase diagrams (solubility limit of sulfide).
5.with NO adjustable fitting parameters.

Main Reactions to Be Considered in Thermodynamic Models for Sulfur in Slag

$$\frac{1}{2}S_2(g) + (O)_{slag} = \frac{1}{2}O_2(g) + (S)_{slag}$$

In order to describe dissolution behavior of S in molten oxide, the following two reactions must be taken into account.

Ex) **S in $CaO\text{-}SiO_2$ slag**

Second Nearest Neighbor
Short-range-ordering

❑Second-Nearest-Neighbor (SNN) pair exchange reaction

(Ca-O-Ca) + (Si-O-Si) = 2(Ca-O-Si); $\Delta g_{CaSi/OS} (= \sim -60 kJ/mol)$

$O^{2-} + O^o = 2O^-$

SiO_4^{4-} anions are surrounded by two Ca^{2+} cations.

❑Reciprocal exchange reaction among liquid components

$2CaO(liq) + SiS_2(liq) = 2CaS(liq) + SiO_2(liq)$; $\Delta g^{exchange}_{CaSiOS} (= \sim -400 kJ/mol)$

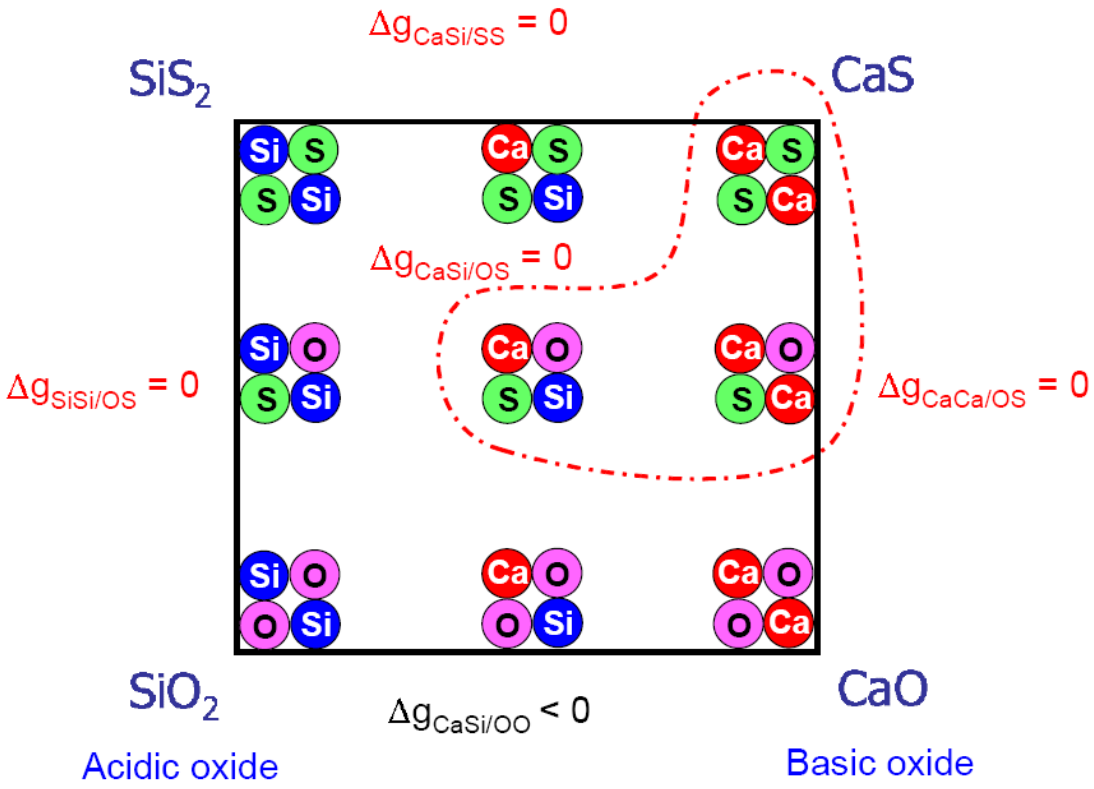
S in the slag exist mostly as CaS, not SiS_2.

First Nearest Neighbor
Short-range-ordering

In order to take into account the two reactions simultaneously,

- Slags are assumed to have cationic and anionic sublattices,
- All possible quadruplets are considered.

Example: $(Ca^{2+},Si^{4+})(O^{2-},S^{2-})$



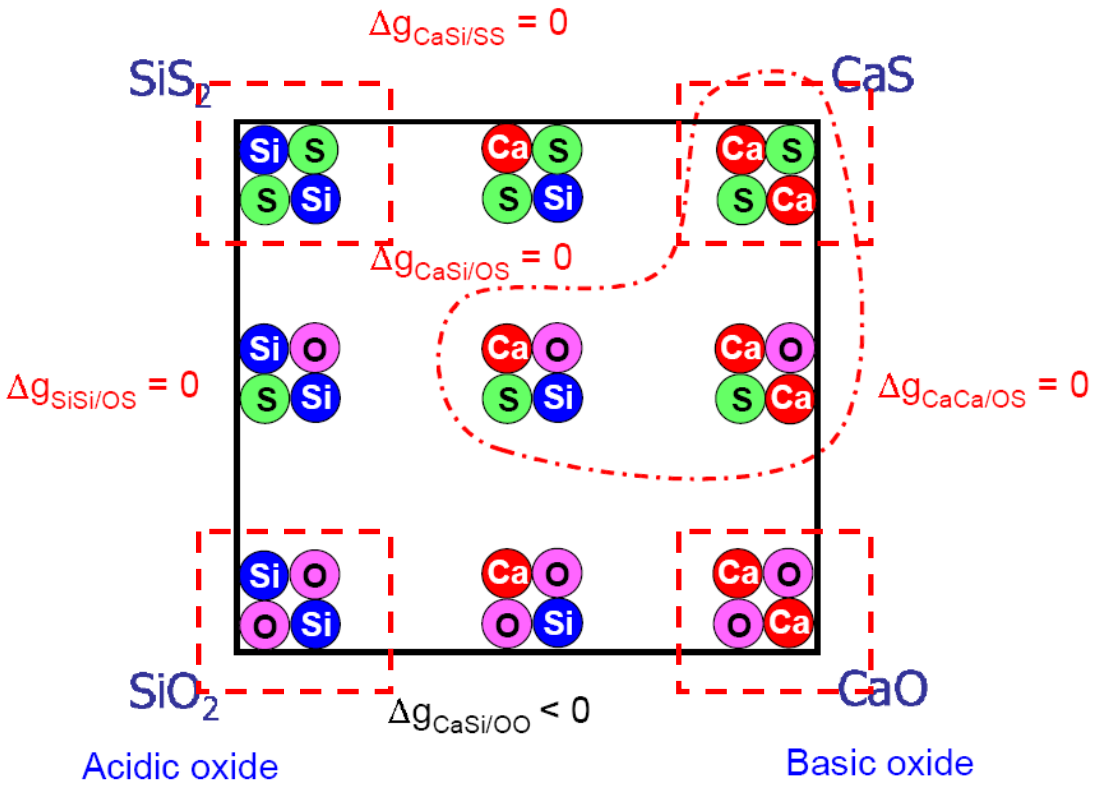
Gibbs energy of each Quadruplets

- $g_{CaCa/OO}$, $g_{CaCa/SS}$, $g_{SiSi/OO}$, $g_{SiSi/SS}$ are taken from literature (Gibbs energies of pure oxides and sulfides).
- $\Delta g_{CaSi/OO}$ is taken from existing thermodynamic database (**FactSage** database).
- $\Delta g_{CaSi/SS}$, $\Delta g_{CaCa/OS}$, and $\Delta g_{SiSi/OS}$ are set to zero (i.e. treated as ideal solutions).
- $g_{CaSi/OS}$ is the average of $g_{CaSi/OO}$, $g_{CaSi/SS}$, $g_{CaCa/OS}$ and $g_{SiSi/OS}$.

In order to take into account the two reactions simultaneously,

- Slags are assumed to have cationic and anionic sublattices,
- All possible quadruplets are considered.

Example: $(Ca^{2+},Si^{4+})(O^{2-},S^{2-})$



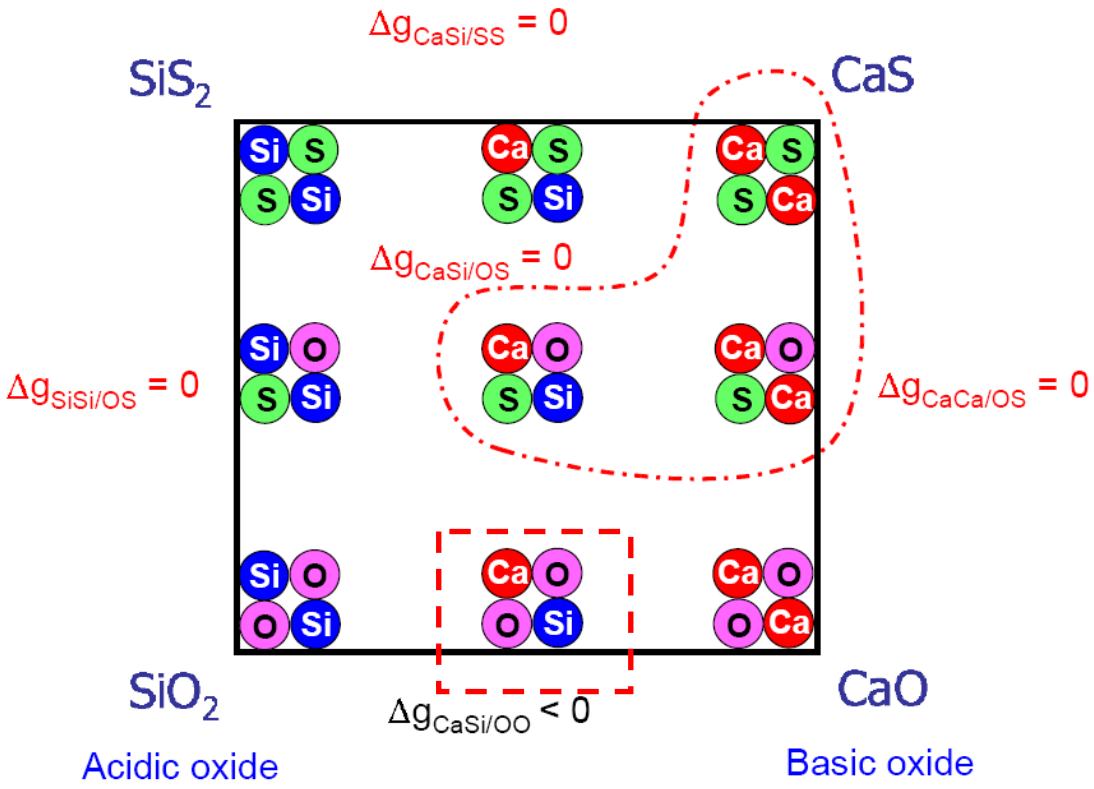
Gibbs energy of each Quadruplets

- $g_{CaCa/OO}$, $g_{CaCa/SS}$, $g_{SiSi/OO}$, $g_{SiSi/SS}$ are taken from literature (Gibbs energies of pure oxides and sulfides).
- $\Delta g_{CaSi/OO}$ is taken from existing thermodynamic database (**FactSage** database).
- $\Delta g_{CaSi/SS}$, $\Delta g_{CaCa/OS}$, and $\Delta g_{SiSi/OS}$ are set to zero (i.e. treated as ideal solutions).
- $g_{CaSi/OS}$ is the average of $g_{CaSi/OO}$, $g_{CaSi/SS}$, $g_{CaCa/OS}$ and $g_{SiSi/OS}$.

In order to take into account the two reactions simultaneously,

- Slags are assumed to have cationic and anionic sublattices,
- All possible quadruplets are considered.

Example: $(Ca^{2+},Si^{4+})(O^{2-},S^{2-})$



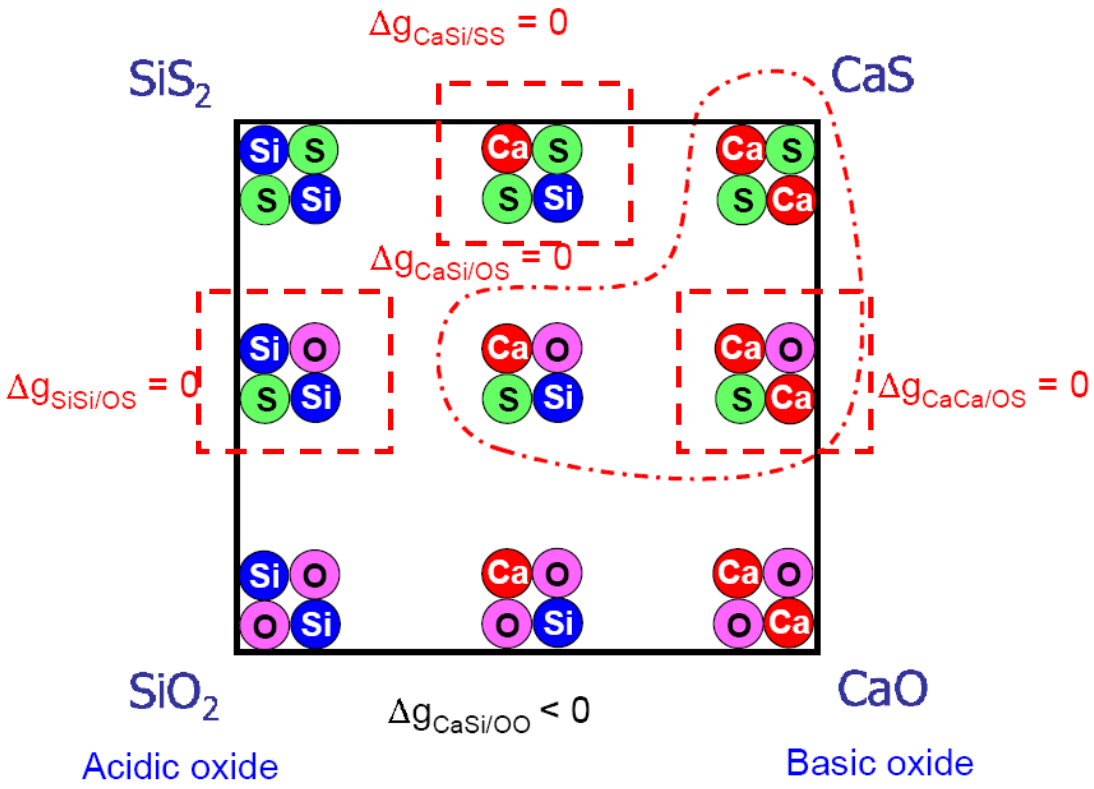
Gibbs energy of each Quadruplets

- $g_{CaCa/OO}$, $g_{CaCa/SS}$, $g_{SiSi/OO}$, $g_{SiSi/SS}$ are taken from literature (Gibbs energies of pure oxides and sulfides).
- $\Delta g_{CaSi/OO}$ is taken from existing thermodynamic database (**FactSage** database).
- $\Delta g_{CaSi/SS}$, $\Delta g_{CaCa/OS}$, and $\Delta g_{SiSi/OS}$ are set to zero (i.e. treated as ideal solutions).
- $g_{CaSi/OS}$ is the average of $g_{CaSi/OO}$, $g_{CaSi/SS}$, $g_{CaCa/OS}$ and $g_{SiSi/OS}$.

In order to take into account the two reactions simultaneously,

- Slags are assumed to have cationic and anionic sublattices,
- All possible quadruplets are considered.

Example: $(Ca^{2+},Si^{4+})(O^{2-},S^{2-})$



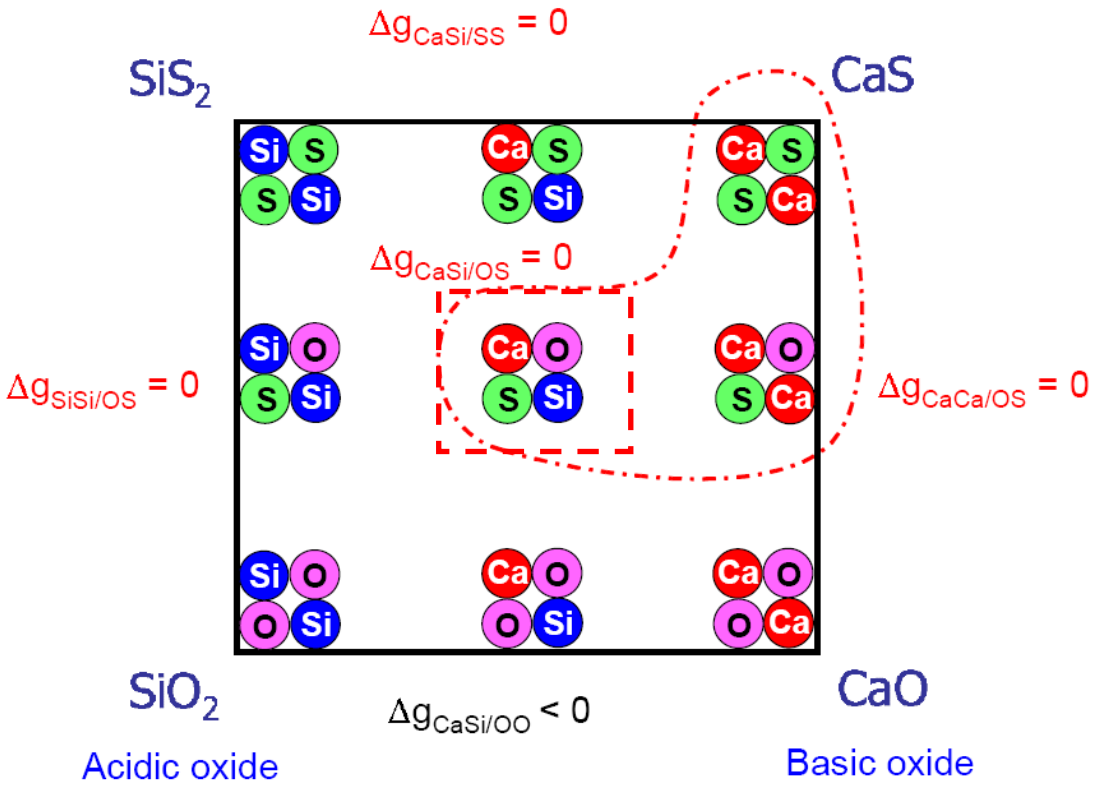
Gibbs energy of each Quadruplets

- $g_{CaCa/OO}$, $g_{CaCa/SS}$, $g_{SiSi/OO}$, $g_{SiSi/SS}$ are taken from literature (Gibbs energies of pure oxides and sulfides).
- $\Delta g_{CaSi/OO}$ is taken from existing thermodynamic database (**FactSage** database).
- $\Delta g_{CaSi/SS}$, $\Delta g_{CaCa/OS}$, and $\Delta g_{SiSi/OS}$ are set to zero (i.e. treated as ideal solutions).
- $g_{CaSi/OS}$ is the average of $g_{CaSi/OO}$, $g_{CaSi/SS}$, $g_{CaCa/OS}$ and $g_{SiSi/OS}$.

In order to take into account the two reactions simultaneously,

- Slags are assumed to have cationic and anionic sublattices,
- All possible quadruplets are considered.

Example: $(Ca^{2+},Si^{4+})(O^{2-},S^{2-})$



Gibbs energy of each Quadruplets

- $g_{CaCa/OO}$, $g_{CaCa/SS}$, $g_{SiSi/OO}$, $g_{SiSi/SS}$ are taken from literature (Gibbs energies of pure oxides and sulfides).
- $\Delta g_{CaSi/OO}$ is taken from existing thermodynamic database (**FactSage** database).
- $\Delta g_{CaSi/SS}$, $\Delta g_{CaCa/OS}$, and $\Delta g_{SiSi/OS}$ are set to zero (i.e. treated as ideal solutions).
- $g_{CaSi/OS}$ is the average of $g_{CaSi/OO}$, $g_{CaSi/SS}$, $g_{CaCa/OS}$ and $g_{SiSi/OS}$.

No new adjustable fitting parameters

Gibbs Energy of the Molten Oxysulfide

Gibbs energy of the molten oxide containing sulfur is

$$G = \sum_{\substack{i,j,k,l \\ i,j=\mathrm{Ca,Si}\cdots \\ k,l=\mathrm{O,S}\cdots}} n_{ij/kl} g_{ij/kl} - T\Delta S^{\mathrm{config}}$$

where the configurational entropy is obtained by randomly distributing the quadruplets on the quadruplet sites using an Ising-type approximation:

$$-\frac{\Delta S^{\mathrm{config}}}{\mathrm{R}} = \sum_{\substack{i \\ i=\mathrm{Ca,Si},\cdots,\mathrm{O,S},\cdots}} n_i \ln X_i + \sum_{\substack{i,k \\ i=\mathrm{Ca,Si},\cdots \\ k=\mathrm{O,S},\cdots}} n_{i/k} \ln\left(\frac{X_{i/k}}{Y_i Y_k}\right)$$

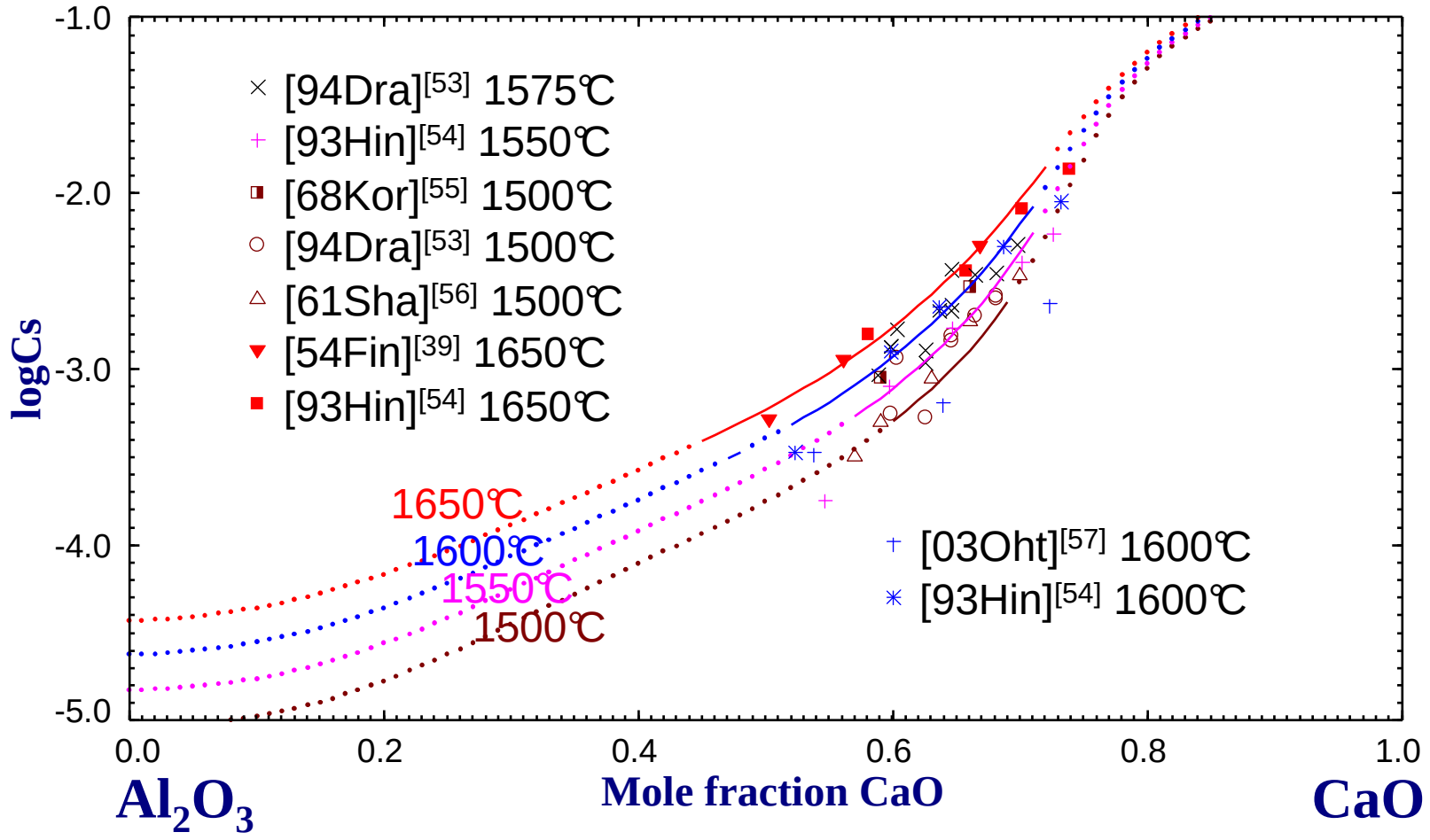
$$+ \sum_{\substack{i,j,k,l \\ i,j=\mathrm{Ca,Si},\cdots \\ k,l=\mathrm{O,S},\cdots}} n_{ij/kl} \ln\left(\frac{X_{ij/kl}}{\frac{(2-\delta_{ij})(2-\delta_{kl}) X_{i/k} X_{i/l} X_{j/k} X_{j/l}}{Y_i Y_j Y_k Y_l}}\right)$$

By minimizing the Gibbs energy of the oxysulfide under given T, P, and n_i , the quadruplet fractions are obtained, and sulfur concentration in the slag is determined.

The present model has been applied to predict sulfide capacities in Al_2O_3-CaO-Fe_tO-MgO-MnO–SiO_2-TiO_X slags systems (from binary to multicomponent) by comparison with large amount of experimental data.

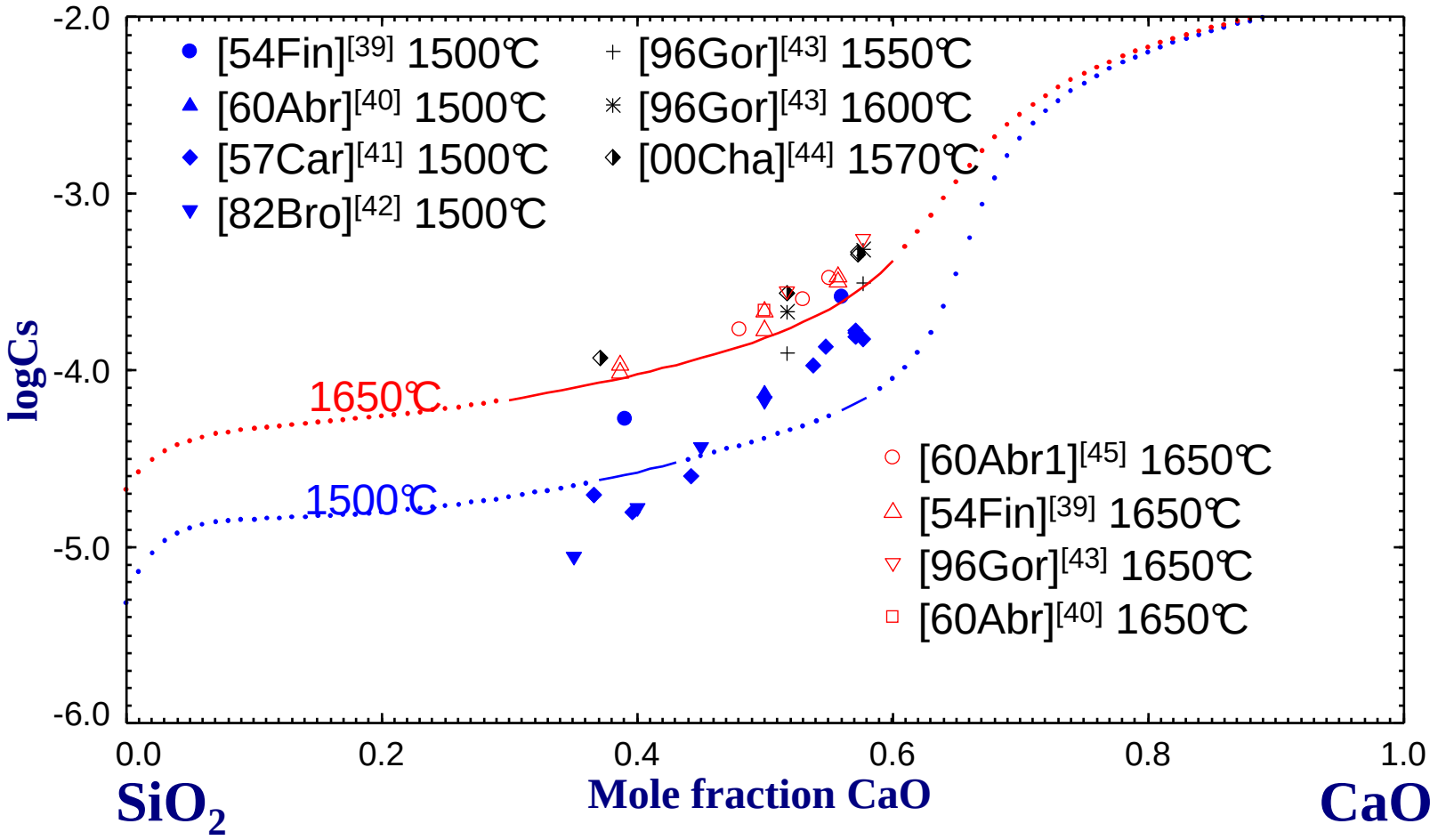
Selected examples in Prediction of Sulfide Capacity

$CaO–Al_2O_3$ slag



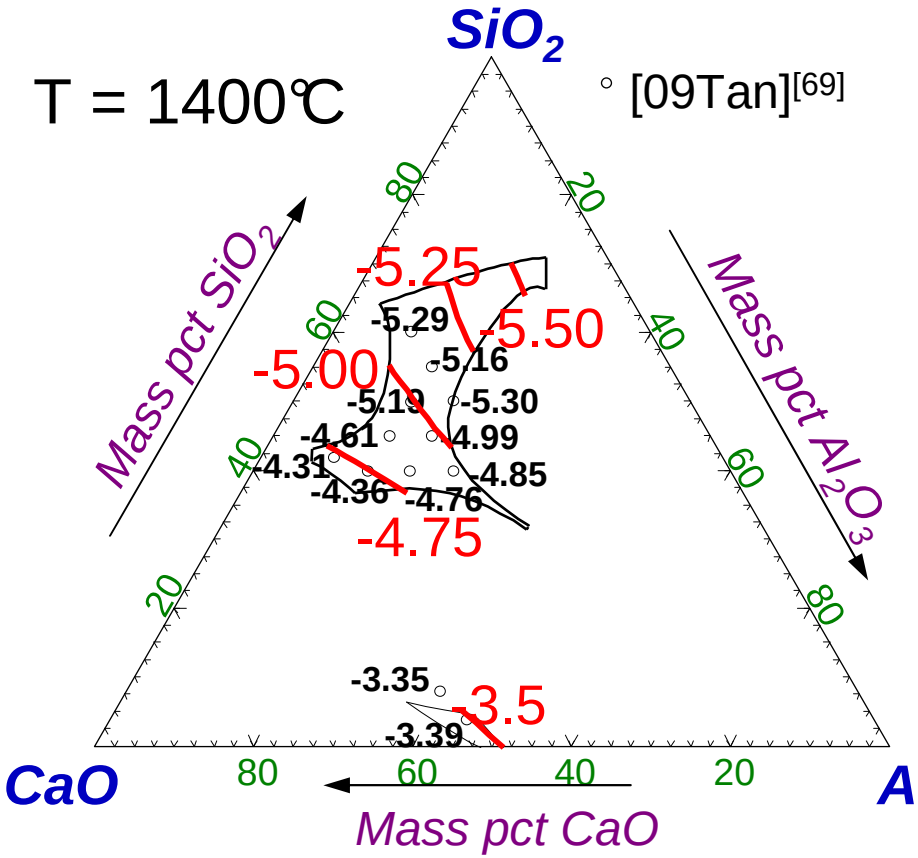
Selected examples in Prediction of Sulfide Capacity

$CaO–SiO_2$ slag

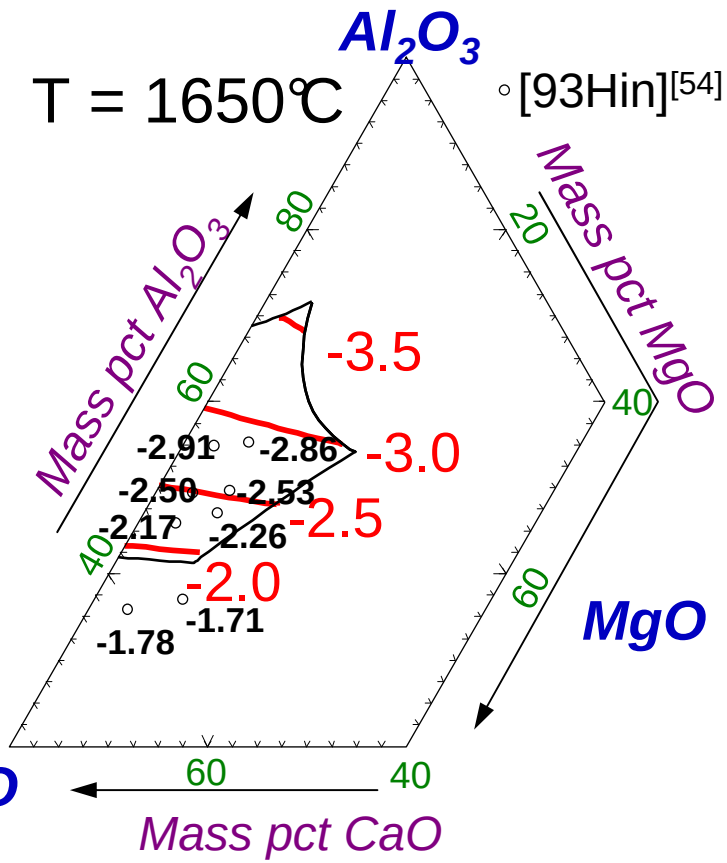


Selected examples in Prediction of Sulfide Capacity

$CaO–Al_2O_3–SiO_2$ slag

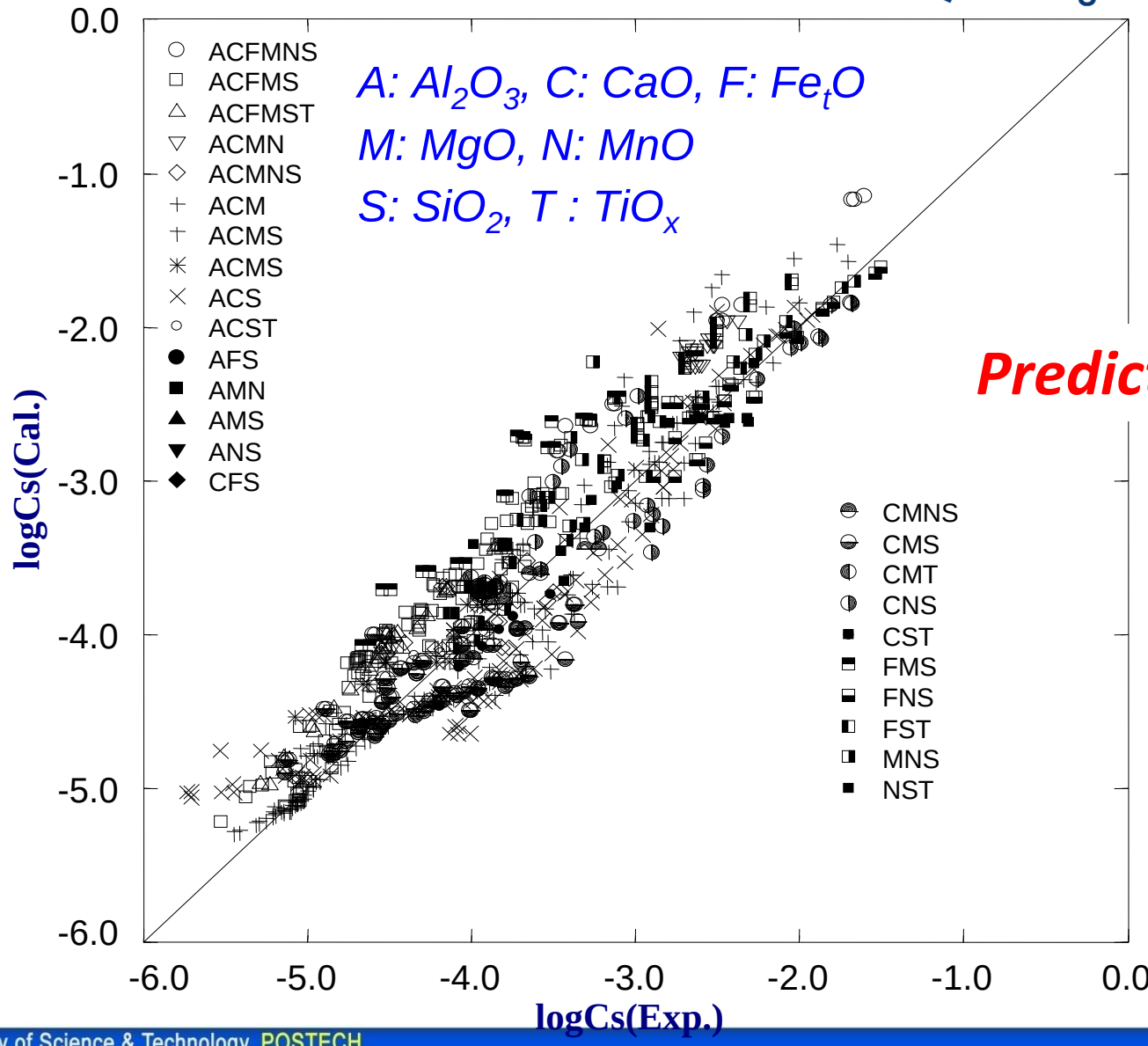


$CaO–Al_2O_3–MgO$ slag



Extention of the Present Model to High Sulfur Content

Multicomponent slags (Al_2O_3-CaO-Fe_tO-MgO-MnO-SiO_2-TiO_x)



Prediction!

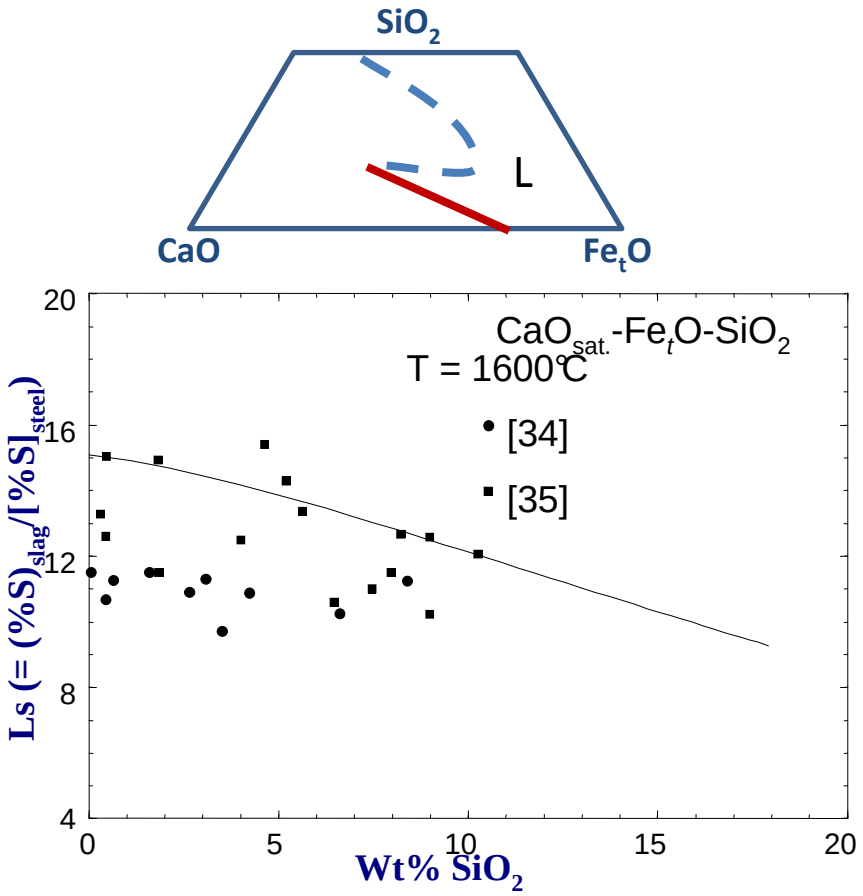
For steel refining purpose,

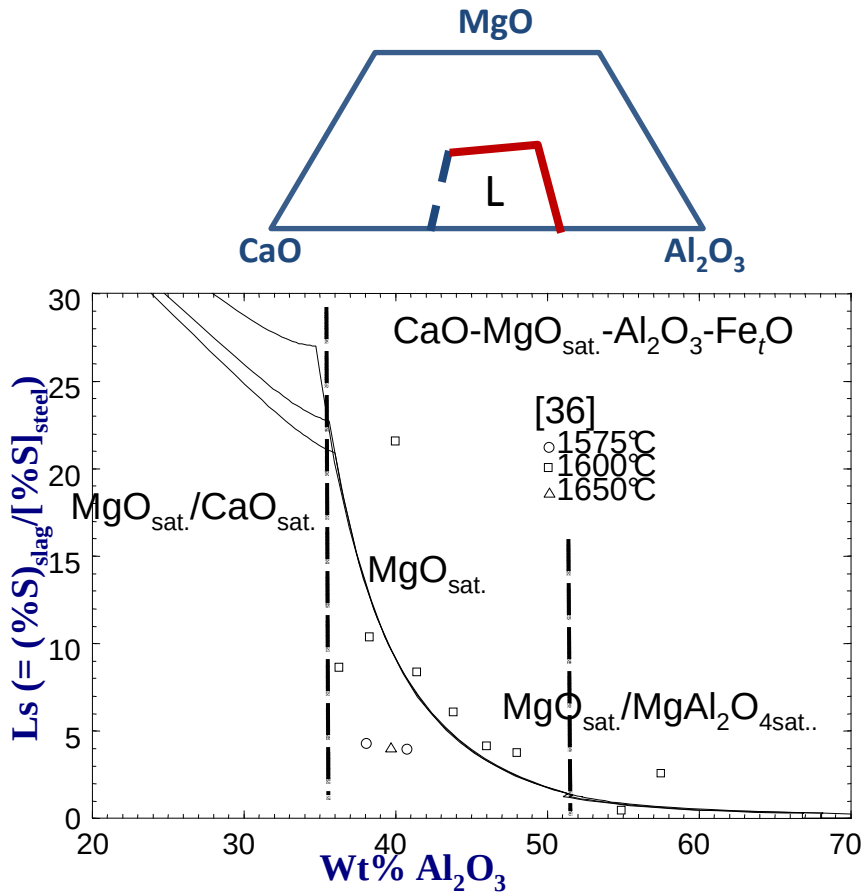
$$L_S = \frac{(\text{mass pct. S})_{slag}}{[\text{mass pct. S}]_{steel}} \quad \Leftrightarrow \quad C_S = (\text{mass pct. S})_{slag}\left(\frac{pO_2}{pS_2}\right)^{\frac{1}{2}}$$

$$[S] + 1/2O_2(g) = [O] + 1/2S_2(g);\ K$$

$$\log L_S = \log C_S + \log f_{[S]} - \log a_{[O]} + \log K$$

Applications in Sulfur Distribution Coefficient

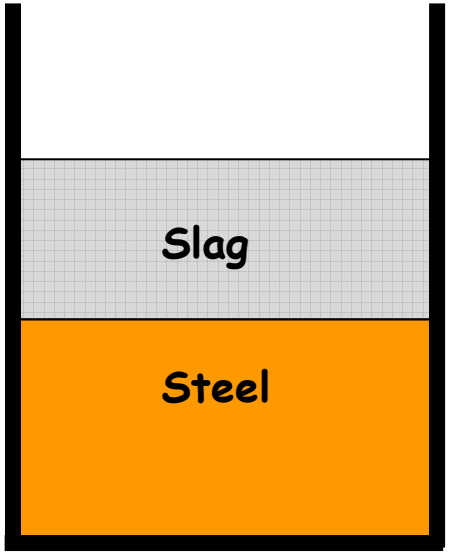




Extention of the Present Model to High Sulfur Content

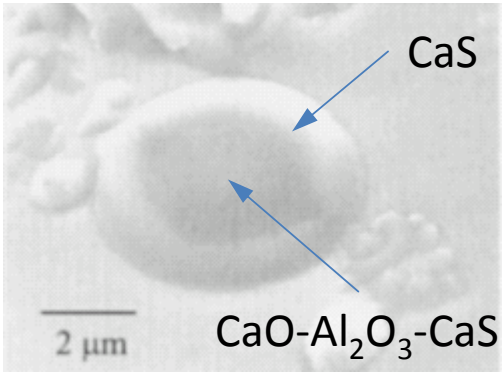
Steel/slag reaction

- Low (wt%S) in slag
- Sulfide capacity



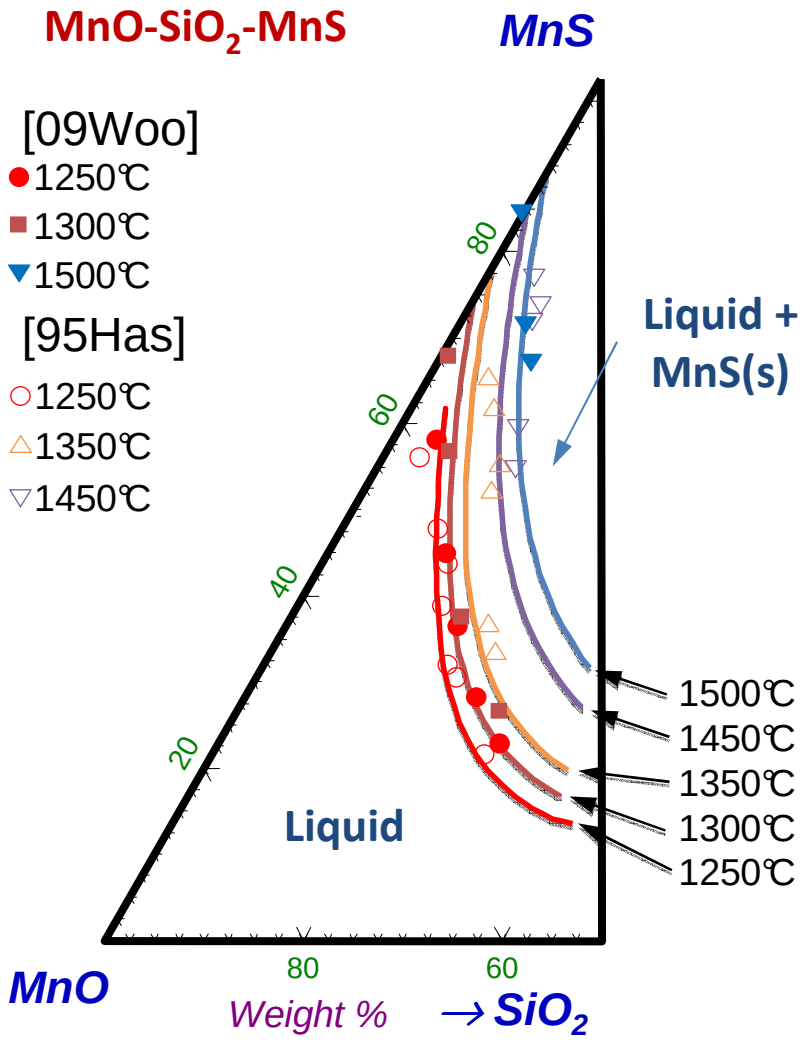
Steel/inclusion reaction

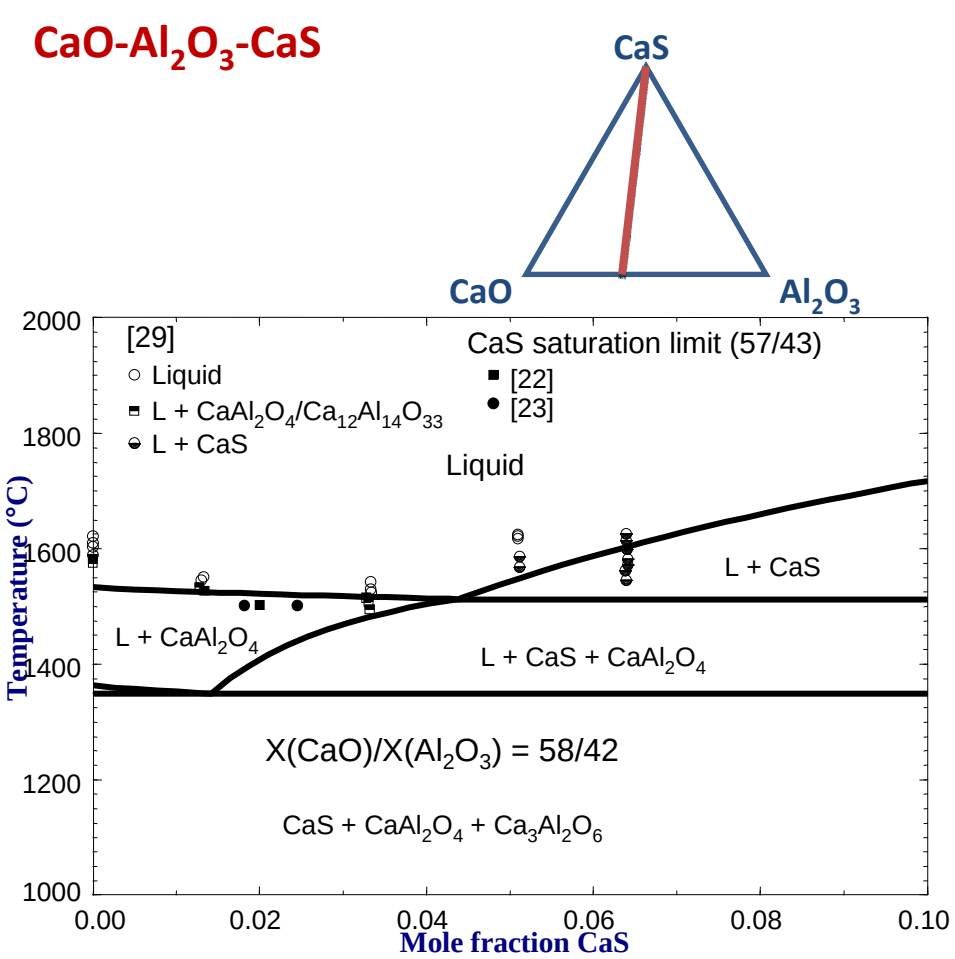
- High S content (oxysulfide, sulfide)
- Solubility limit of sulfide



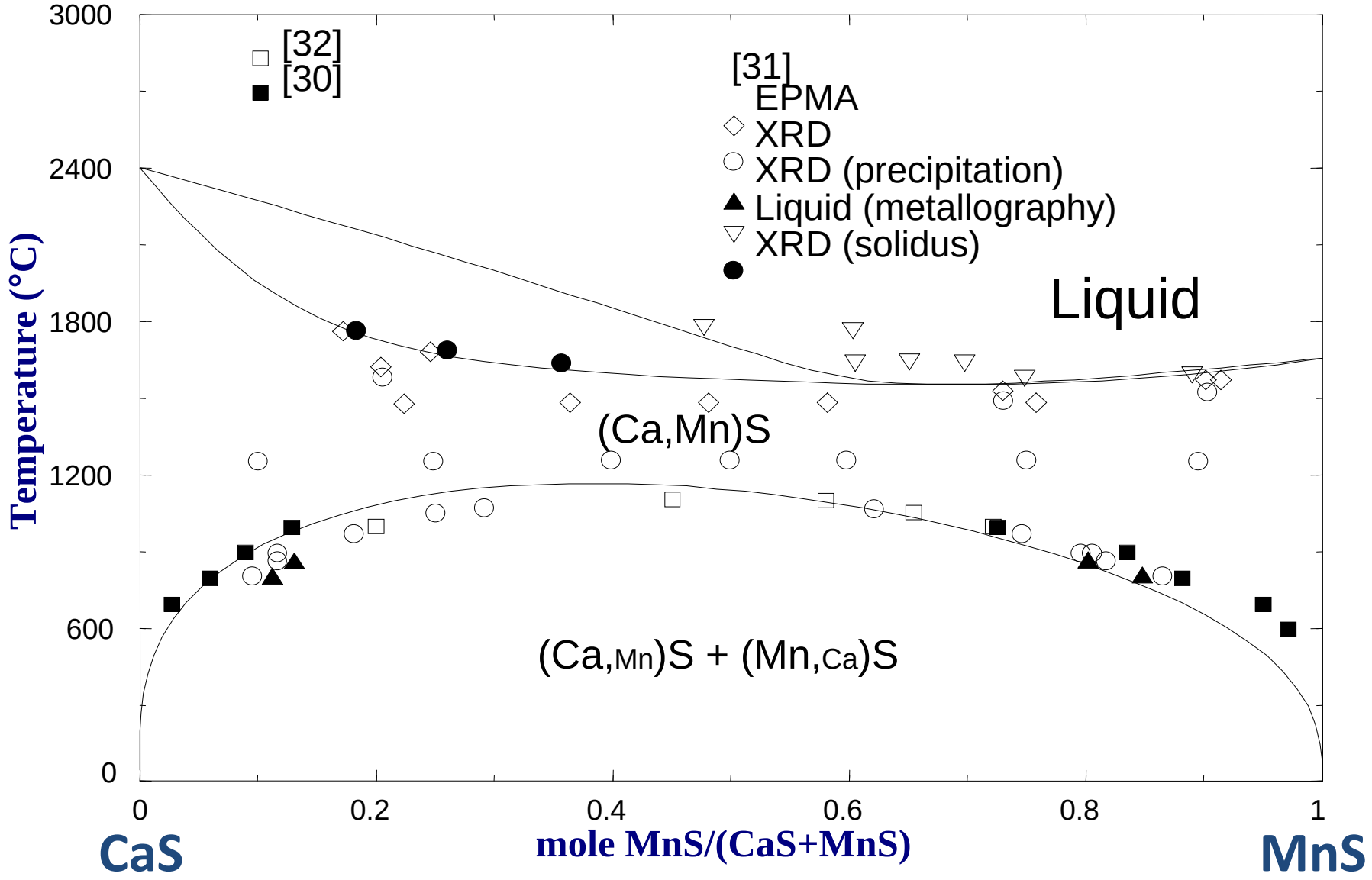
Wang et al., Met.B. (2002)

Predicted Solubility Limit (Phase Diagram) of OxySulfide Systems





Phase Equilibria in Sulfide Systems: CaS-MnS



After Ca injection in steel

Refining

- ❑ Modifiy Al_2O_3 (solid inclusion) to $CaO\text{-}Al_2O_3$ (liquid inclusion)
- ❑ CaS (either $CaO\text{-}Al_2O_3\text{-}CaS$ (liquid inclusion) or CaS (solid inclusion) forms if [S] in the steel is high

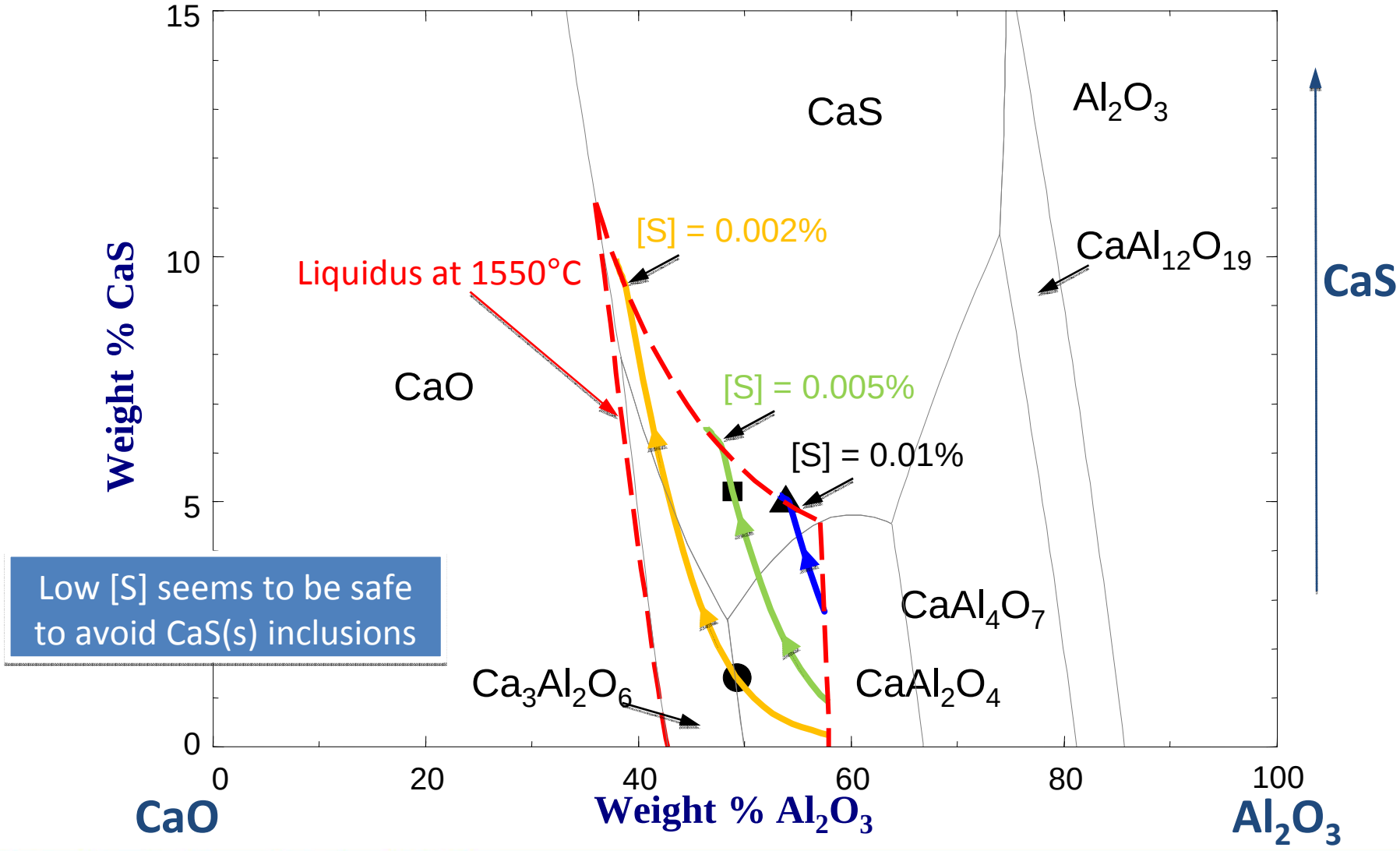
Solidification

- ❑ forms (Ca,Mn)S solid solution as inclusions
  - (Ca,$_{Mn}$)S: hard and non-deformable causing cracks
  - (Mn,$_{Ca}$)S: easily deformed

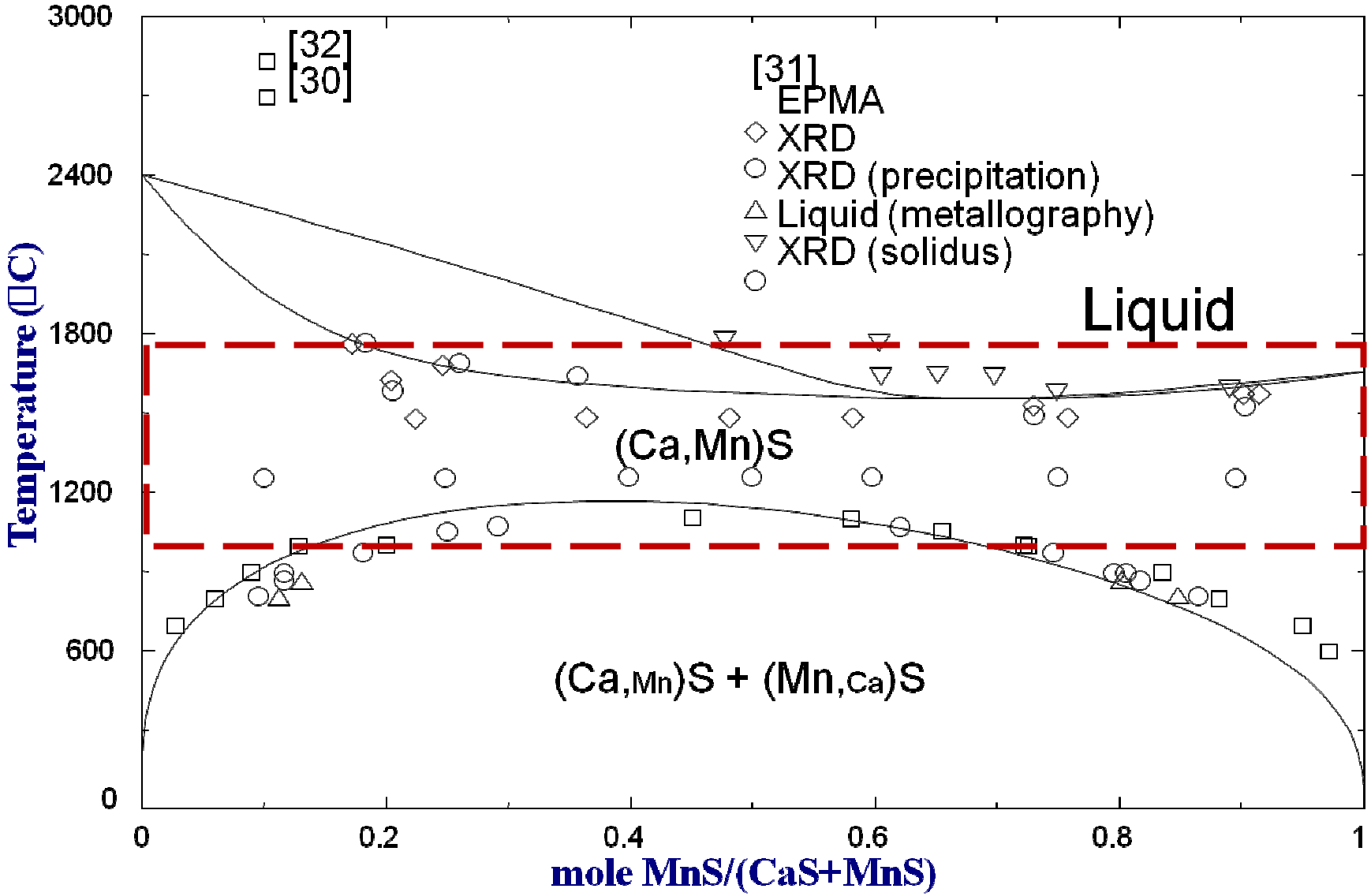
Therefore, depending on the steel grade, proper control of the S content of the steel is necessary.

CaO-Al_2O_3-CaS type inclusions in Steel; during refining steels

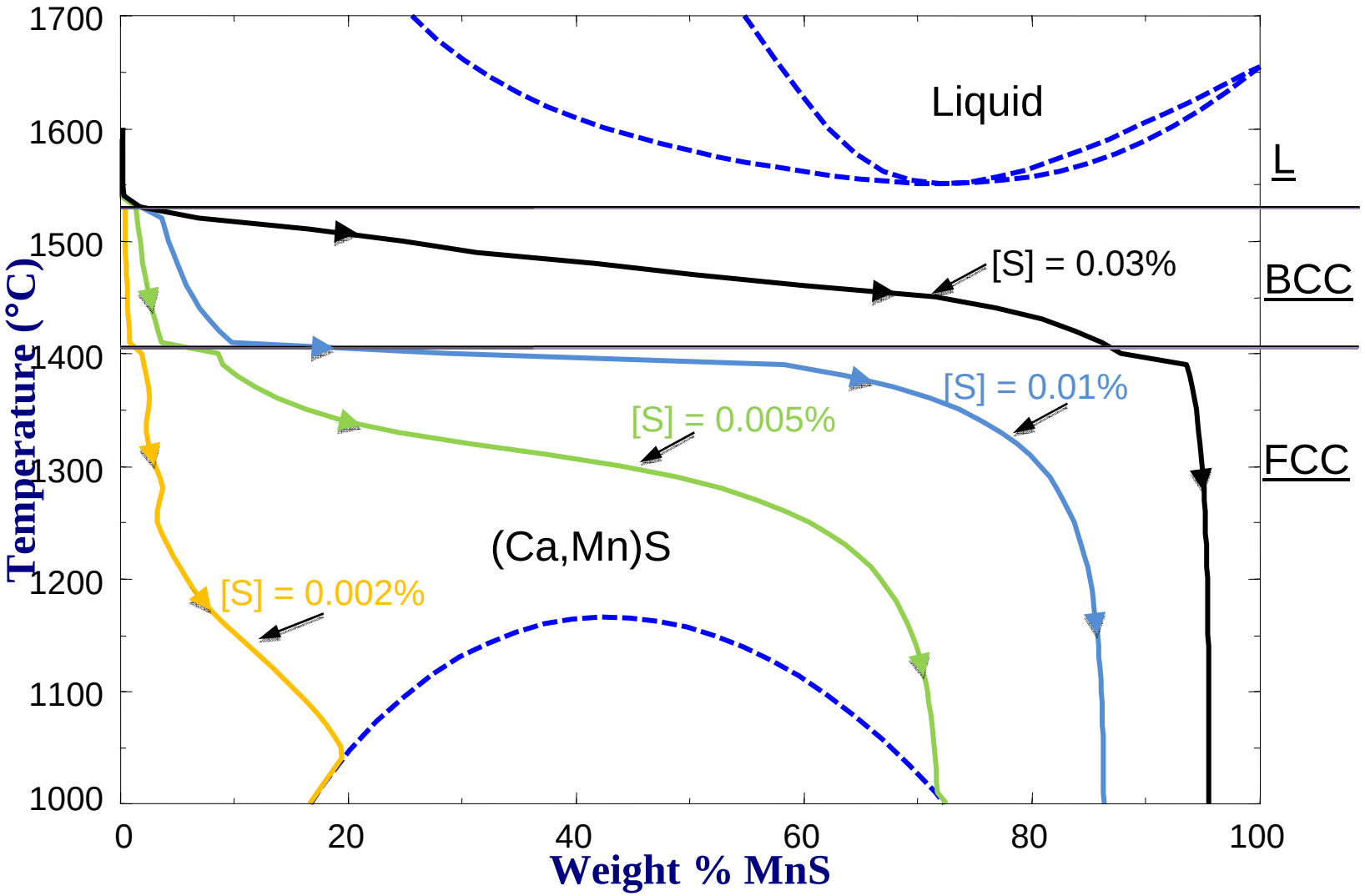
Fe-0.5Mn-0.03Al-0.002O-*x*Ca-*y*S (wt%) steel at 1550℃ (*y* = 0.002, 0.005, and 0.01).



$CaO-Al_2O_3$-CaS type inclusions in Steel; during refining steels



$CaO-Al_2O_3$-CaS type inclusions in Steel; during solidification of steels



CaS

Too low [S] forms $(Ca,_{Mn})S$ inclusions

Enough [S] transforms $(Ca,_{Mn})S$ to $(Mn,_{Ca})S$ inclusions

MnS

Concluding Remarks

- Thermodynamic database in FactSage system for oxide (solid and liquid) has been developed for many years at the CRCT, using Quasichemical model for liquid phase.

- A **thermodynamic model and database for sulfur dissolved in molten oxide** has been also developed. Modified Quasichemical Model in the Quadruplet Approximation was used to describe sulfur dissolution behavior in the molten oxide.

- The model was also applied to predict **sulfide solubility** limit in molten oxysulfide melts.

- The model was used to calculated **sulfur distribution coefficient** between slag and steel (L_S), and (oxy)sulfide inclusions evolution in steel during refining and solidificaiton.