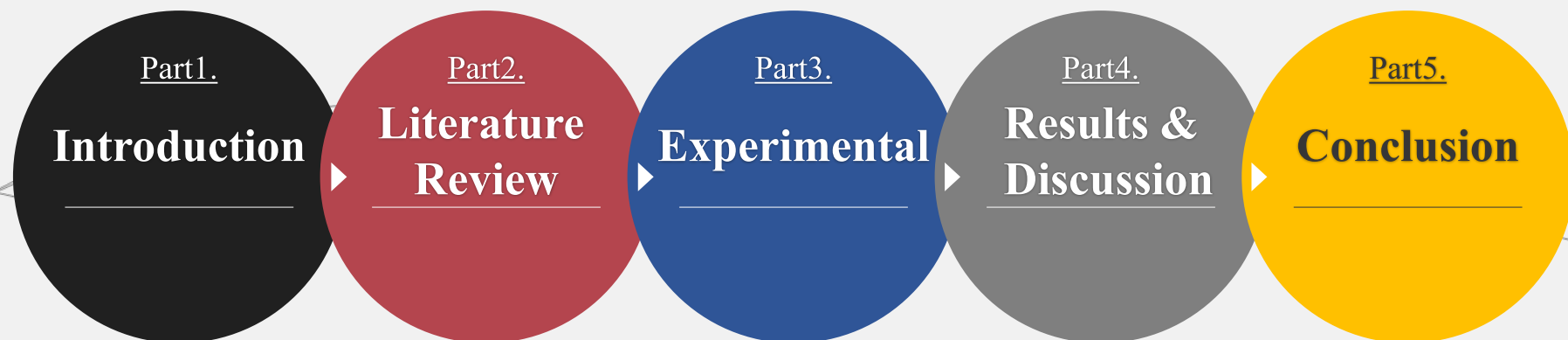




The Effect of Cation Species on the Sulfide Capacity in $\text{CaO-FeO-Al}_2\text{O}_3\text{-SiO}_2$ Melts

Joon Sung Choi*, Youngjoo Park, Sunghee Lee and Dong Joon Min
Department of Materials Science and Engineering

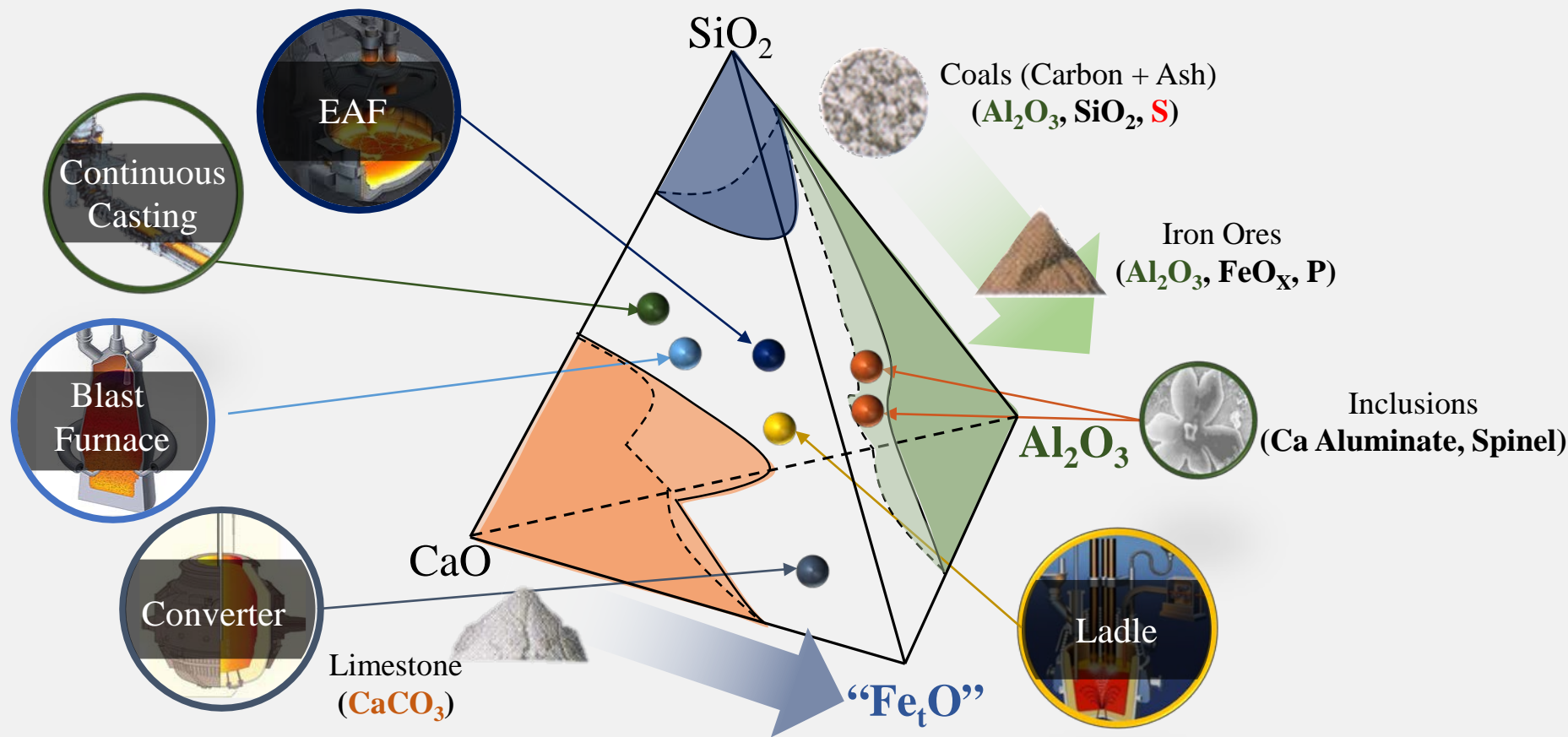




Slag Formation in Iron- and Steelmaking Process

Ores: $\Delta 0.016\%$ (P, Al_2O_3)/yr

Coals : $\Delta 0.015\%$ S/yr, $\Delta 0.08\%$ Ash/yr,

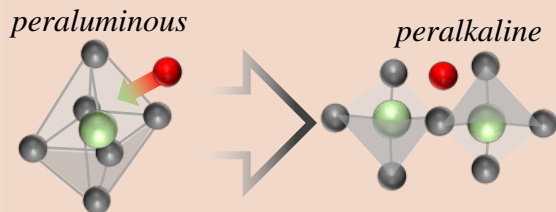


Increase in **FeO, Al_2O_3 & S** Contents in Material

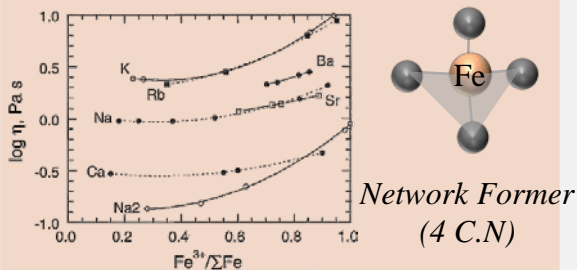
Desulfurization in **High-FeO, Al_2O_3** Bearing Slags?

T³⁺ Ionic Characteristics (T = Al, Fe)

B.O. Mysen (1980)



D.B. Dingwell (1987)



T³⁺ ions form anionic structural unit → TO₄⁵⁻

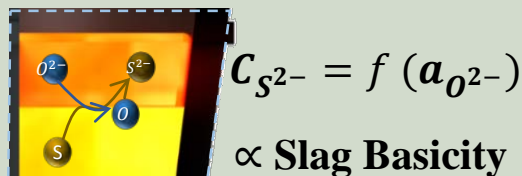
Sulfide Capacity & Basicity

C.J.B. Fincham (1954)

$$C_{S^{2-}} = (wt\%S) \cdot \left(\frac{p_{O_2}}{p_{S_2}}\right)^{1/2}$$

= Slag Property

C. Wagner (1976)



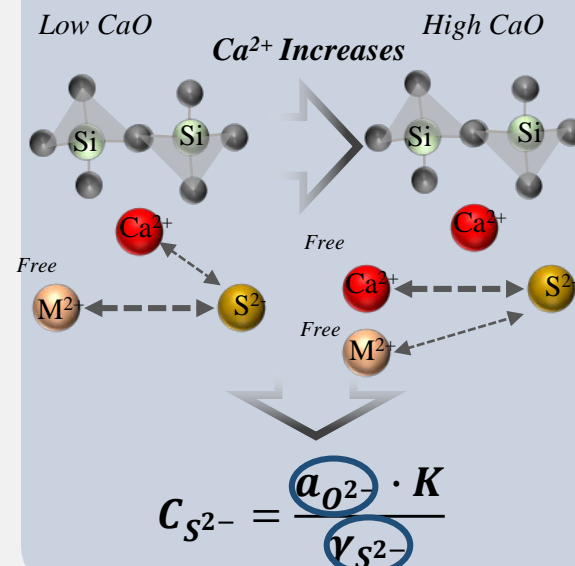
$$C_{S^{2-}} = \frac{a_{O^{2-}} \cdot K}{\gamma_{S^{2-}}}$$

Cationic Effect on C_{S²⁻}

Y.J. Park and D.J. Min (2016)
Y.B. Kang and J.H. Park (2011)

$$C_{S^{2-}} = f(a_{O^{2-}}, \gamma_{S^{2-}})$$

∝ Cation Structure



Study on the **Relationship** Between **Sulfide Capacity** and the **Structure of High-FeO, Al₂O₃ Bearing Slags**

Pauling's Principles for Molten Slag

Electronegativity & Neutrality

Ionic Bonding

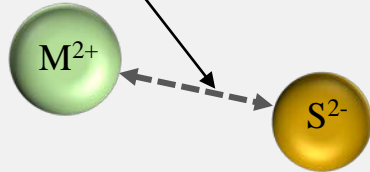
Covalent Bonding

Basic Oxide

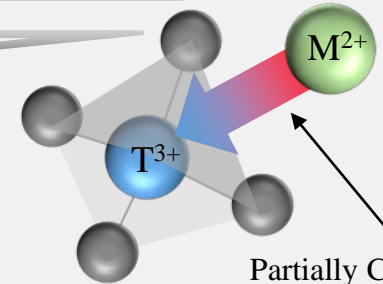
Amphoteric Oxide

Acidic Oxide

Ionic Interaction of M^{2+} with S^{2-}

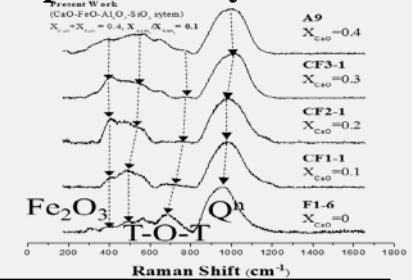


VS.



Partially Covalent

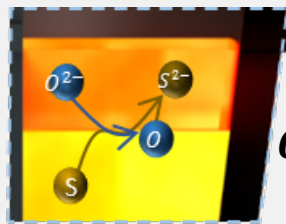
Spectra Analysis



Ionic Interaction

Sulfide Capacity

$\gamma_{S^{2-}}$
(Stability of Sulfur)



$$C_{S^{2-}} = \frac{a_{O^{2-}} \cdot K}{\gamma_{S^{2-}}}$$

Slag Structure

NBO/T, Al C.N

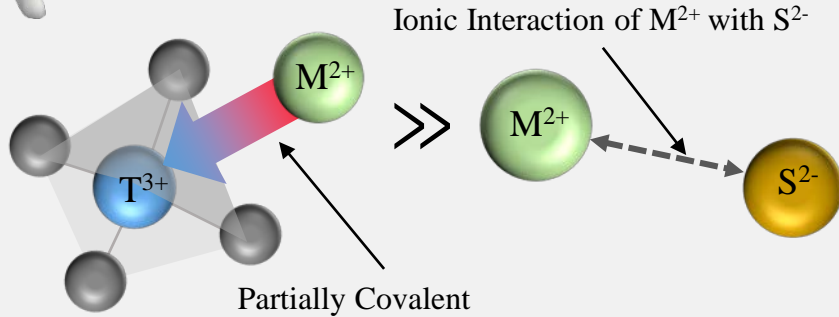
Thermodynamic & Structural Approach to Figure Out the preference of M^{2+}

Figure out the **Cationic Effect of M^{2+}**
(M : Fe, Ca) on **the Sulfide Capacity**



1

Charge Compensation Effect

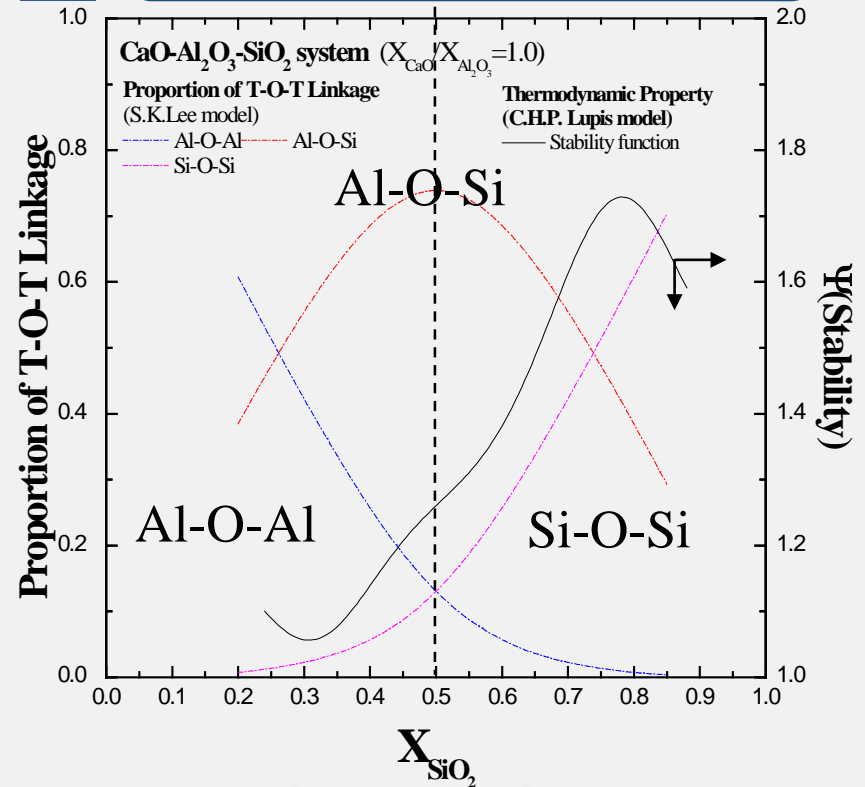


M^+ interacts with TO_4^{5-} prior to S^{2-}
 → charge balancing join
 $(Ca^{2+} + Fe^{2+}) / (Fe^{3+} + Al_2O_3) = 1$

Charge compensation effect
 on $C_{S^{2-}} (= a_{O^{2-}} / \gamma_{S^{2-}})$

2

T-O-T Linkage

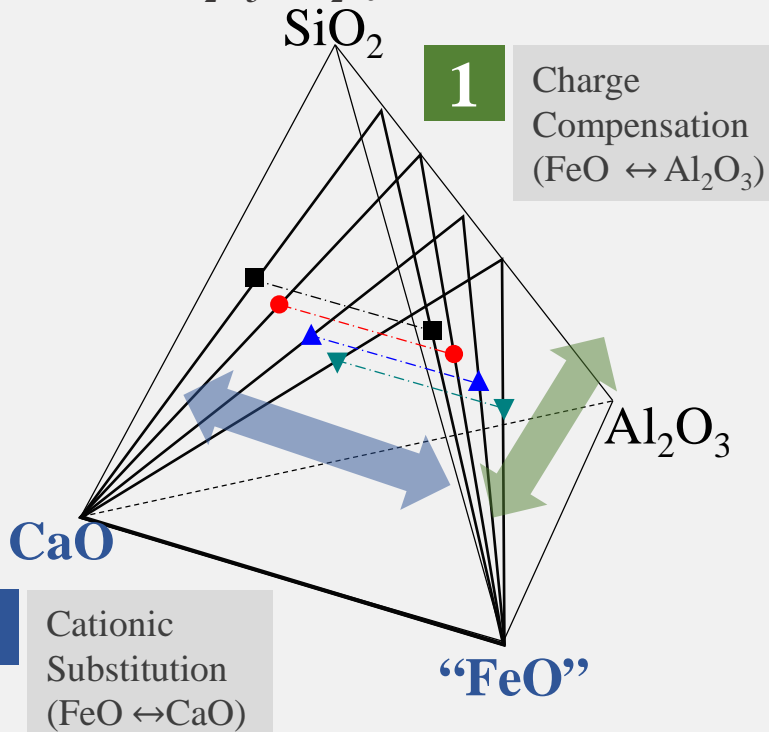


Slag dominant structure (**Matrix**)

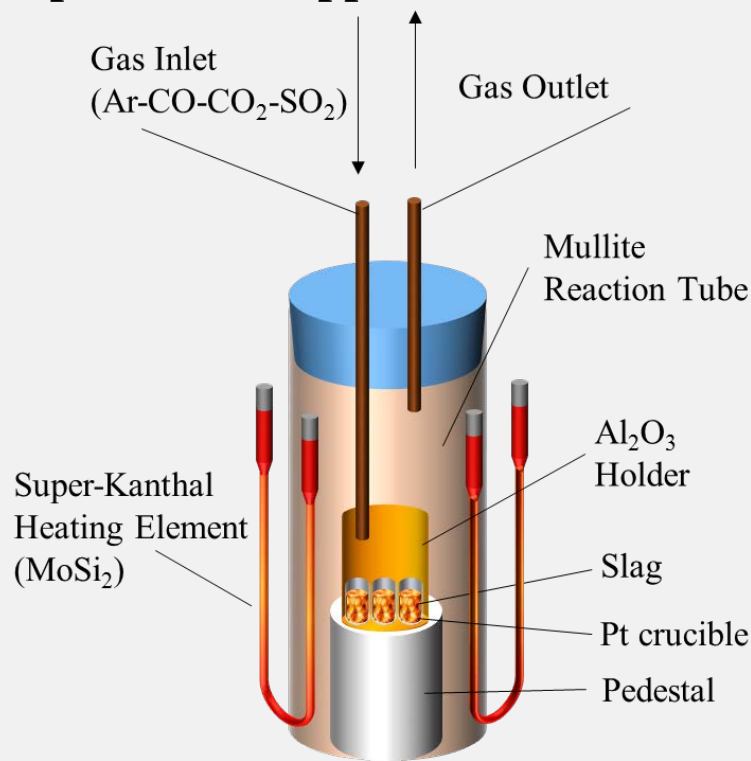
Figure out the **Charge Compensation Effect of M^{2+}**
 (M : Fe, Ca) on the **Sulfide Capacity**

Slag Compositions

CaO-"FeO"-Al₂O₃-SiO₂ system



Experimental Apparatus



Experimental Analysis



XRF

CS Analyzer

K₂Cr₂O₇ Titration

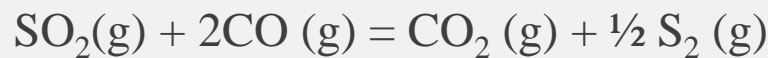
Slag Compositions

Sulfur Contents

Fe²⁺/T.Fe Content

Slag Structure with Micro-Raman Spectroscopy

-Sulfur potential controlled by mixture gas

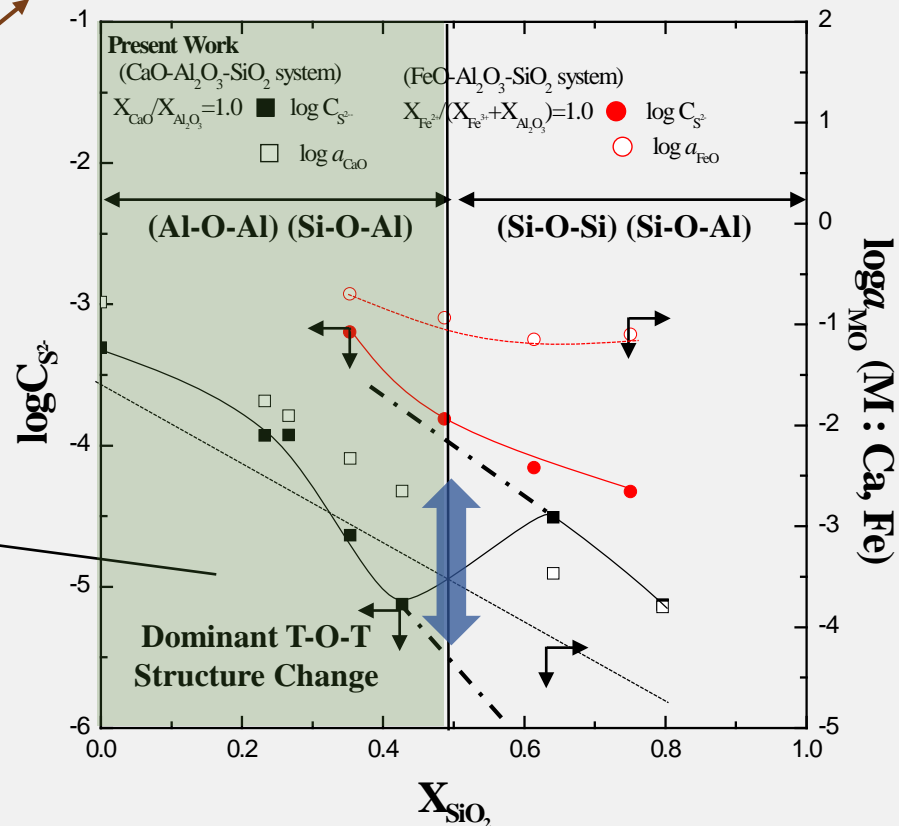
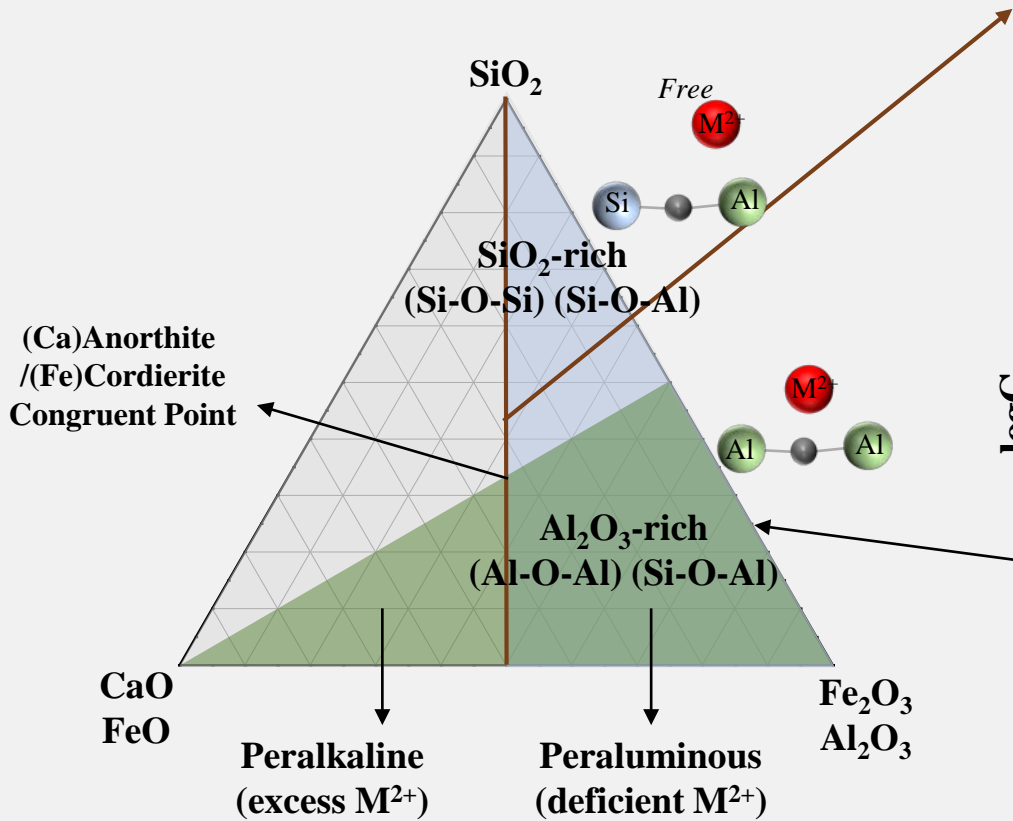


$$\Delta G = 258.5 \text{ KJ/mol}$$

Temp.	Partial Pressure (atm)				p_{S_2}	p_{O_2}	$(p_{\text{S}_2}/p_{\text{O}_2})^{1/2}$
	Ar	CO	CO ₂	SO ₂			
1873K	0.196	0.435	0.348	0.0217	6.01×10^{-3}	1.33×10^{-7}	212



Effect of Al_2O_3/SiO_2 on Charge Balancing Join ($MO/Al_2O_3=1$)



1) Silicate Dominant Structure ($A/S \leq 0.5$)

- Si-O-Si, Al-O-Si dominant (SiO_2 stability Increase)
- M^{2+} - SiO_4^{4-} interaction, Fe-O-Si bonding
- M^{2+} - S^{2-} attraction increases (**lower $\gamma_{S^{2-}}$**)

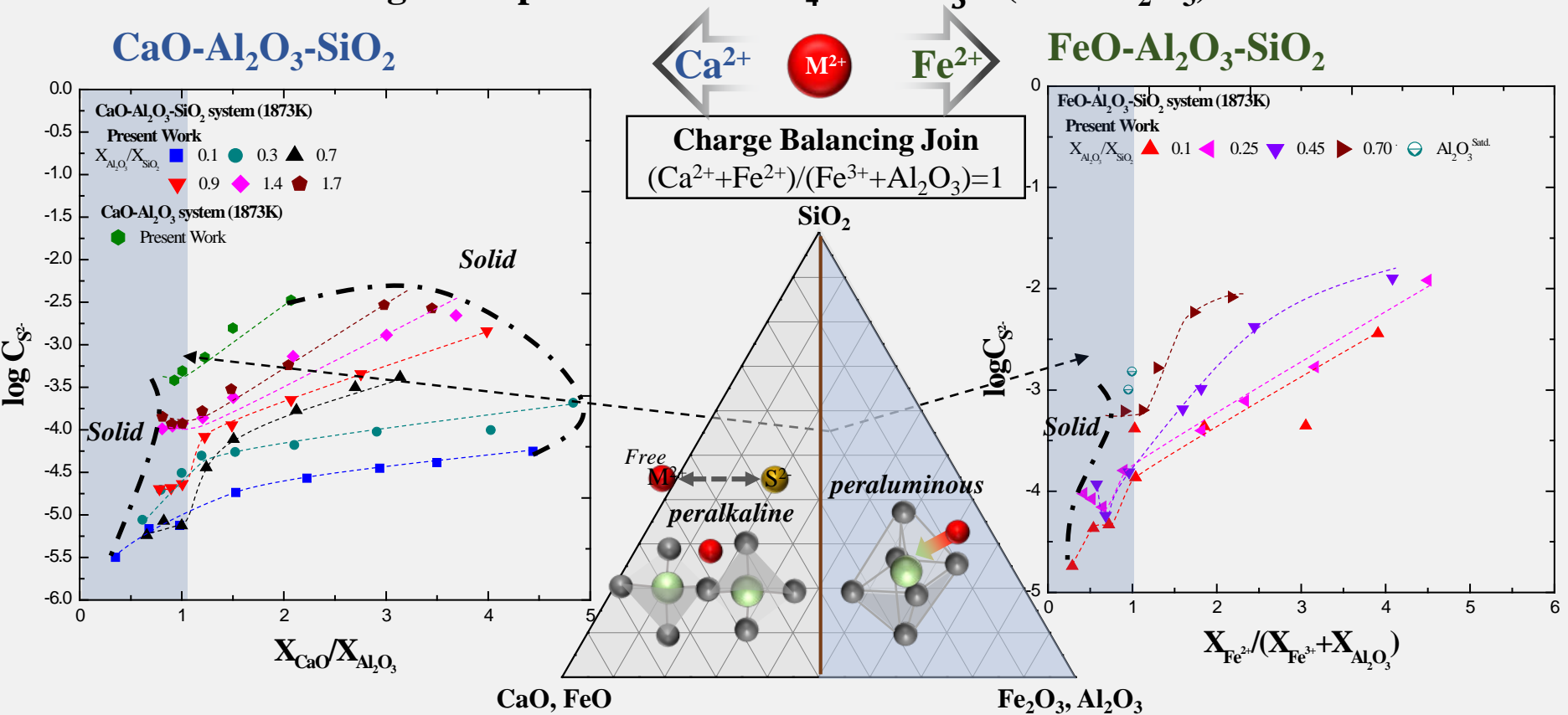
2) Aluminate Dominant Structure ($A/S \geq 0.5$)

- Al-O-Al, Al-O-Si dominant (SiO_2 stability decrease)
- M^{2+} - AlO_4^{5-} interaction, Fe-O-Al bonding
- M^{2+} - S^{2-} attraction decreases (**larger $\gamma_{S^{2-}}$**)

**The Charge Compensation Domain Determined
by Al_2O_3/SiO_2 (T-O-T Dominant Structure)**



Effect of M^{2+} on Charge Compensation of AlO_4^{5-} and $C_{S^{2-}}$ (MO/Al_2O_3)



1) Charge Compensation Effect of Ca^{2+}

- $C_{S^{2-}}$ is independent as basicity changes below meta-aluminous join ($X_{CaO}/X_{Al_2O_3}=1$) in high- Al_2O_3 region ($A/S > 0.7$)

2) Charge Compensation Effect of Fe^{2+}

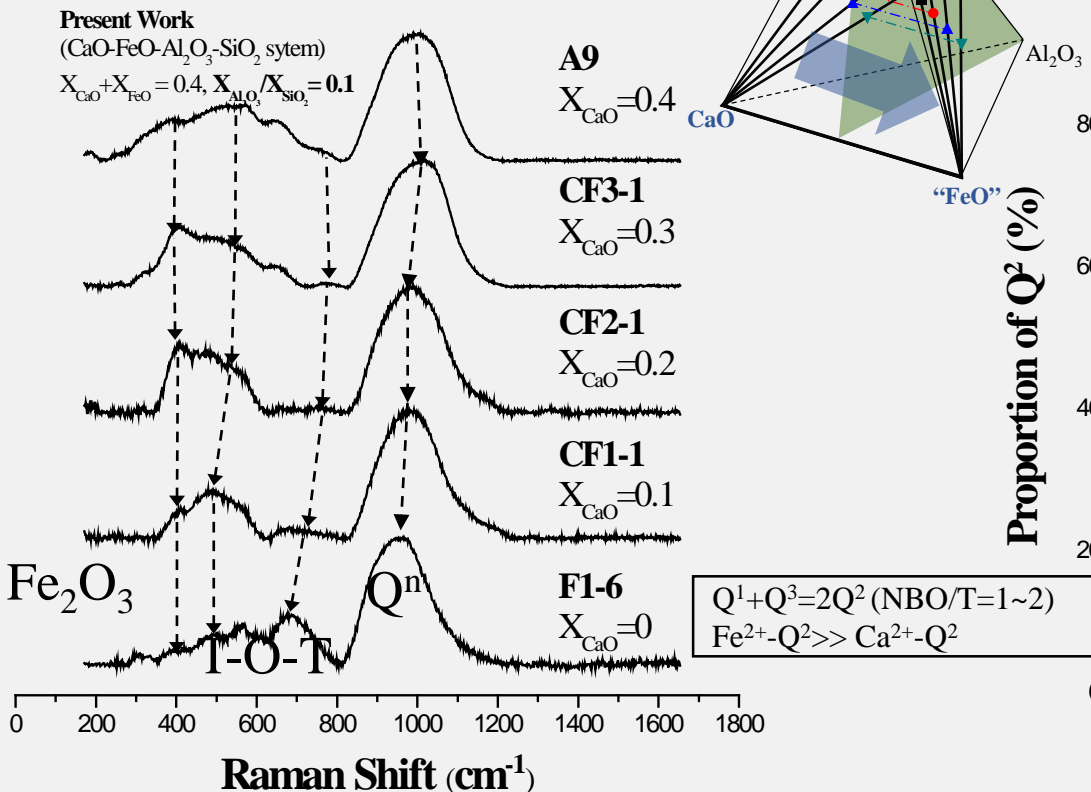
- $C_{S^{2-}}$ is independent as basicity changes below charge balancing join ($X_{Fe^{2+}}/(X_{Fe^{3+}} + X_{Al_2O_3})=1$)

The Charge Compensation Effect on the Sulfide Capacity (Deficit or Excess of M^{2+})

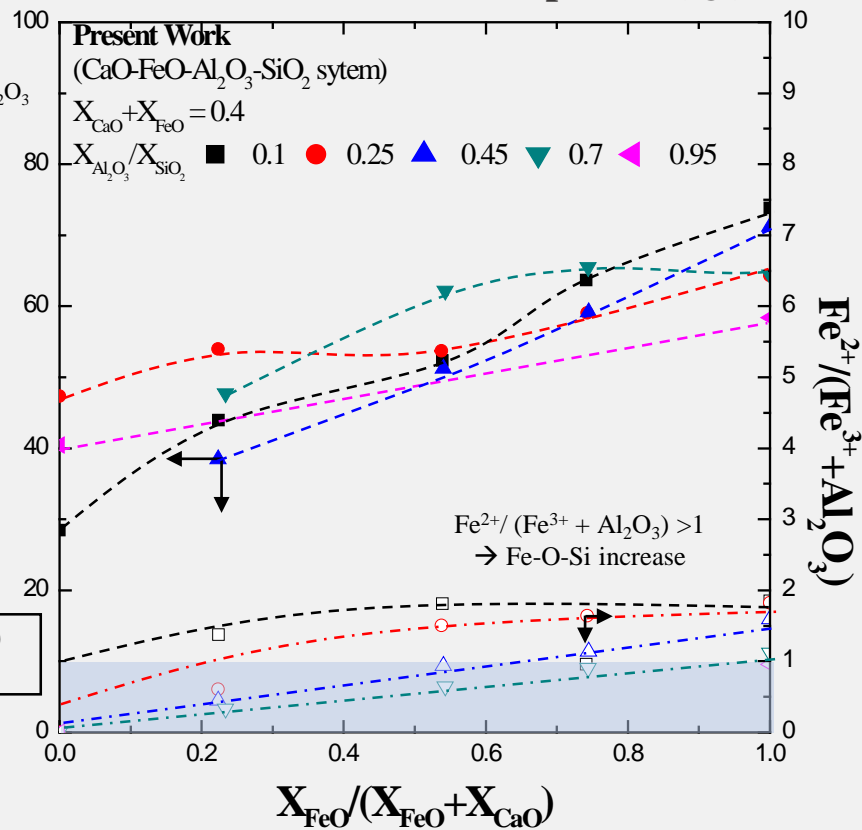


Slag Structural Analysis ($\text{CaO} \leftrightarrow \text{FeO}$)

Raman Spectroscopy



Deconvolution of Raman Spectra (Q^2)



1) Interpretation of Raman Spectra

- $X_{\text{Al}_2\text{O}_3} + X_{\text{Al}_2\text{O}_3} = 0.6$, Q^n unit ($\text{Q}^1, \text{Q}^2, \text{Q}^3$)
- **Increases FeO** : $400\sim 600\text{cm}^{-1}$ Fe_2O_3 peak decreases, $600\sim 700\text{cm}^{-1}$ T-O-T peak Increases, $800\sim 1200\text{cm}^{-1}$ Q^n peak left chemical shift

2) Q^2 Unit : $\text{Fe}^{2+} - \text{Q}^2$

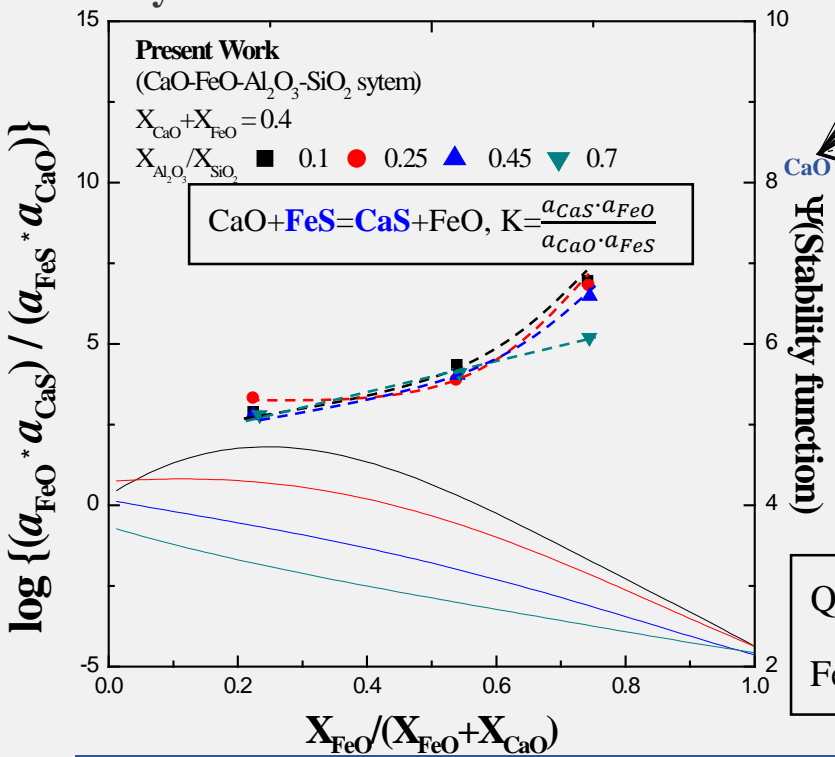
- **Increases FeO** : Prefer $\text{Fe}^{2+} - \text{Q}^2$ unit
- **Role of Fe^{2+}** : $\text{Fe}^{2+} - \text{O} - \text{Al}^{3+}$ (-41000J/mol), $\text{Fe}^{2+} - \text{O} - \text{Fe}^{3+}$ (-18660J/mol) \rightarrow $\text{Fe}^{2+} - \text{O} - \text{Si}^{4+}$ (-41840J/mol)
- **FeS dominant** \rightarrow Fe-O-Si prefer & CaS dominant

Q^2 Increases ($F/(C+F) > 0.5$) \rightarrow $\text{Fe}^{2+} - \text{Q}^2$ Increases

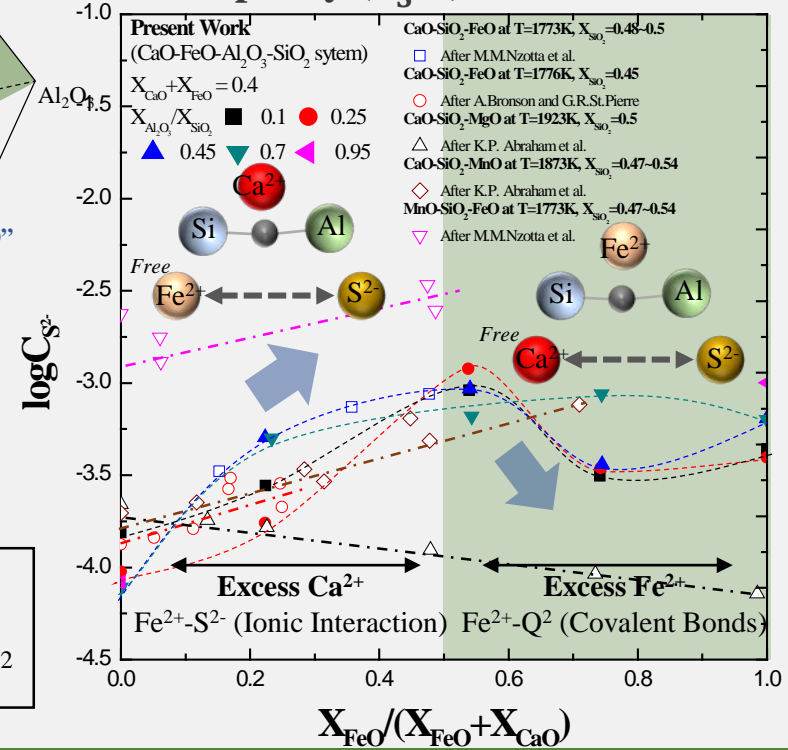


Thermodynamic Facotrs ($\text{CaO} \leftrightarrow \text{FeO}$)

Stability Function & CaS/FeS Preference



Sulfide Capacity ($\text{C}_{\text{S}^{2-}}$)



1) Stability Function & CaS/FeS

- **Stability Function** : Upward concave as FeO increases (Low Al₂O₃), Linearly decreases (High Al₂O₃)
- **CaS/FeS** : Increases CaS preferncy rather than FeS as FeO increases

2) FeO ↔ CaO Substitution Effect

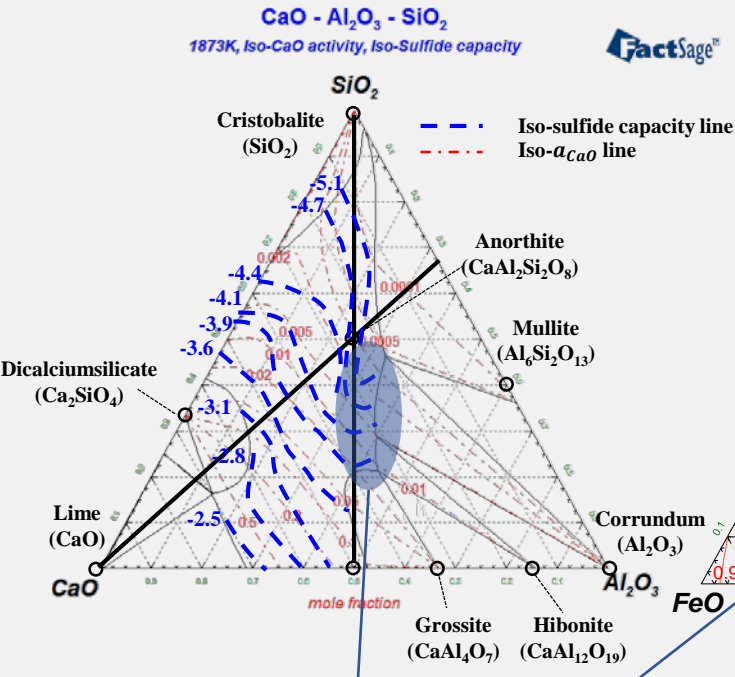
- **Ionic Interaction** ($F/(C+F) \leq 0.5$) : $\epsilon_{\text{S}^{2-}}^{\text{Ca}} < \epsilon_{\text{S}^{2-}}^{\text{Fe}}$, $\gamma_{\text{MS}} \downarrow, C_{\text{S}^{2-}} \uparrow$ (γ_{FeS}) as FeO Increases
- **Fe-Q² effect** ($F/(C+F) \geq 0.5$) : $\gamma_{\text{MS}} \uparrow, C_{\text{S}^{2-}} \downarrow$ (γ_{CaS}) as FeO Increases

($F/(C+F) < 0.5$) : **Fe²⁺-S²⁻ Ionic Interaction (γ_{FeS})**,
($F/(C+F) > 0.5$) : **Fe-Q² Effect (γ_{CaS})**

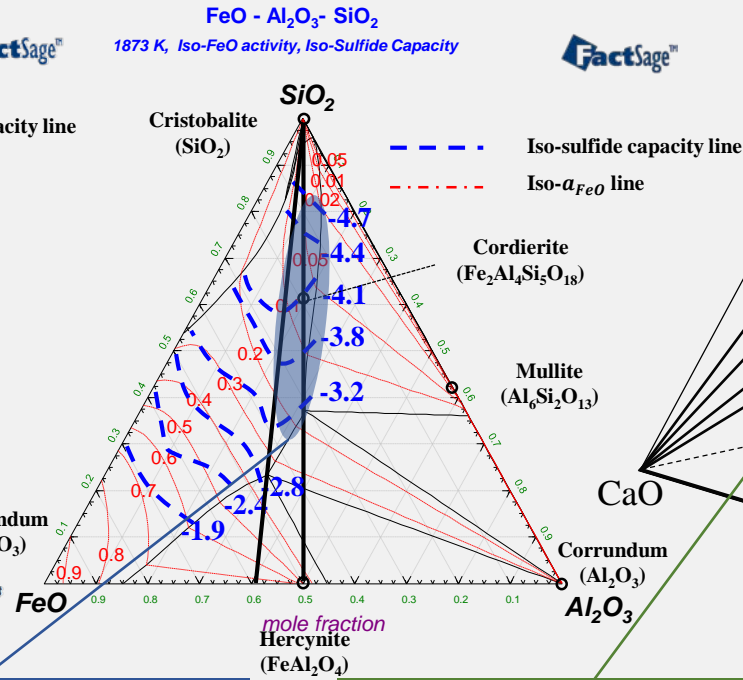


Iso-Sulfide Capacity Line & Iso- a_{MO} Line (M : Ca,Fe)

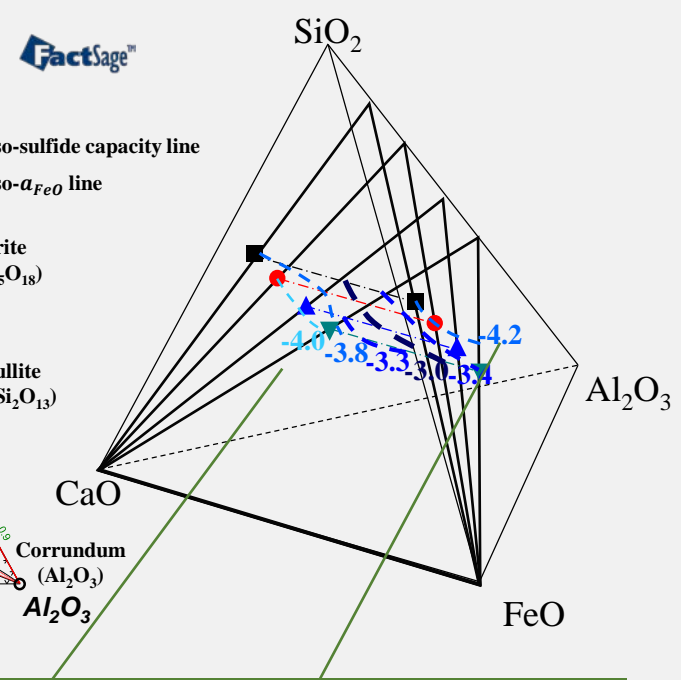
CaO-Al₂O₃-SiO₂ System



FeO-Al₂O₃-SiO₂ System



CaO-FeO-Al₂O₃-SiO₂ System



1) MO-Al₂O₃-SiO₂ Ternary System (M:Ca,Fe)

- CaO-Al₂O₃-SiO₂: Ca²⁺ interact with AlO₄⁵⁻
- FeO-Al₂O₃-SiO₂: Fe²⁺ interact with AlO₄⁵⁻, FeO₄⁵⁻
- Not stabilize sulfur in peraluminous ($\gamma_{S^{2-}}$)

2) CaO-FeO-Al₂O₃-SiO₂ Quaternary System

- CaO-rich (F/(C+F) ≤ 0.5) : Ionic Interaction dominant, FeO stabilize sulfur (γ_{FeS})
- FeO-rich (F/(C+F) ≥ 0.5) : Fe-Q² effect, CaO stabilize sulfur (γ_{CaS})

The **Cationic Substitution Effect** on the Sulfide Capacity
 (Maximum : F/(C+F) = 0.5)

The effect of **anionic slag structure** and **charge compensation behavior** on sulfide capacity of CaO-FeO-Al₂O₃-SiO₂ system is investigated by measurement of **sulfide capacity** and **Micro-Raman spectroscopy**. From the results of present work, findings are summarized as followings:



01

The charge compensation of M²⁺ (M:Fe,Ca) : The Inflection Point of the sulfide capacity in the charge balancing join due to the deficit or excess charge compensator.

02

The cationic substitution (CaO ↔ FeO) : The Fe-Q² units increases as CaO→FeO substitution ($F/(C+F) > 0.5$) by figure out the deconvolution of raman spectra

03

The cationic substitution (CaO ↔ FeO) : The strong interaction between Fe²⁺ and S²⁻ in the CaO-rich region. The weak interaction between Fe²⁺ and S²⁻ in the FeO-rich region.




Thank you