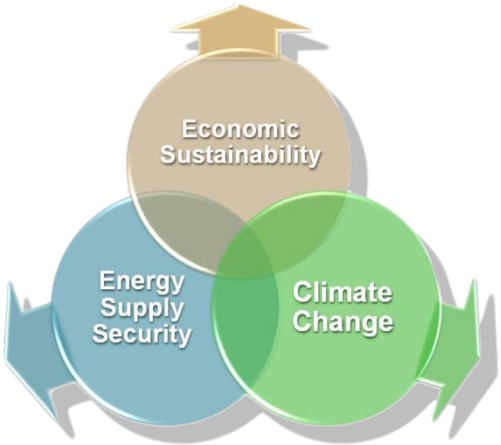


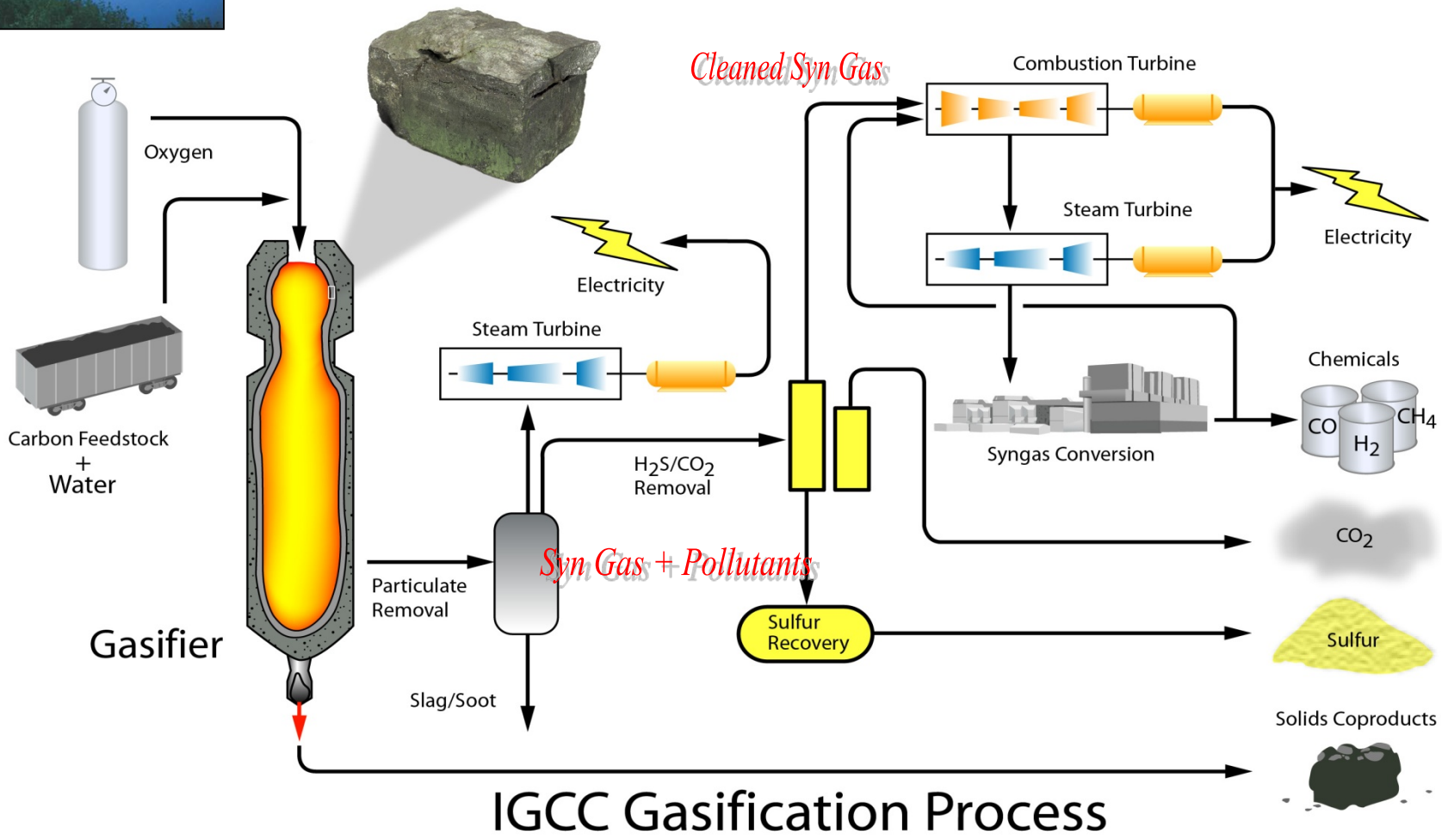
Gasifier Refractories, Coal Slags, and Their Interaction

Kyeising Kwong, James Bennett, Jinichiro Nakano

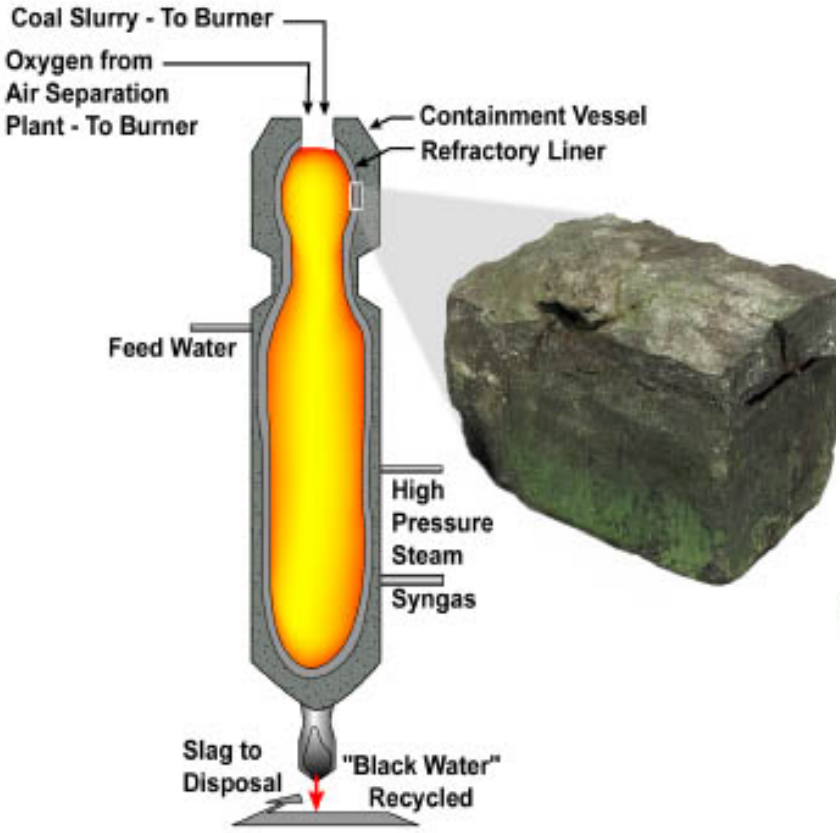
Molten 2012, May 27-30, Beijing, China

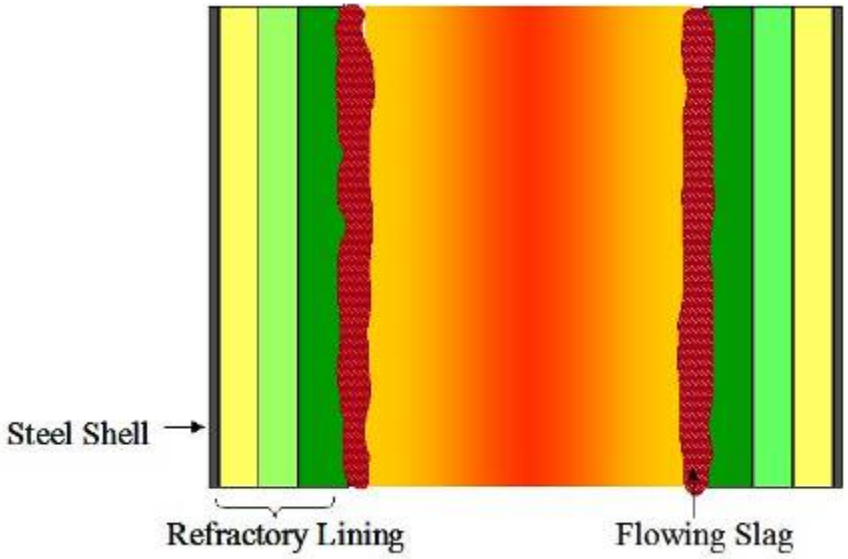
U.S. DEPARTMENT OF ENERGY

Gasification Processes



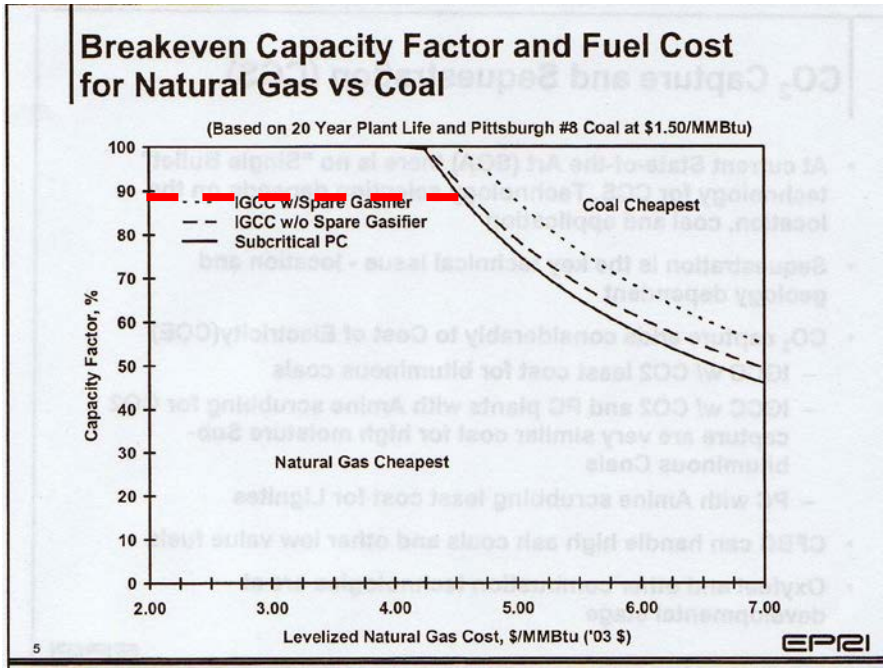
Reliability and Availability of the Gasifier Depends on Materials Performance

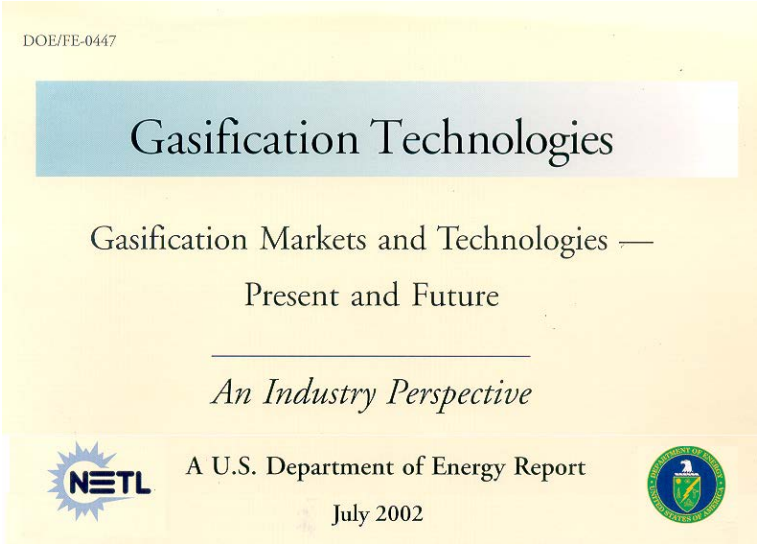




Refractory replacement cycle can be as frequently as every 3-6 months

Gasification Technology Barriers



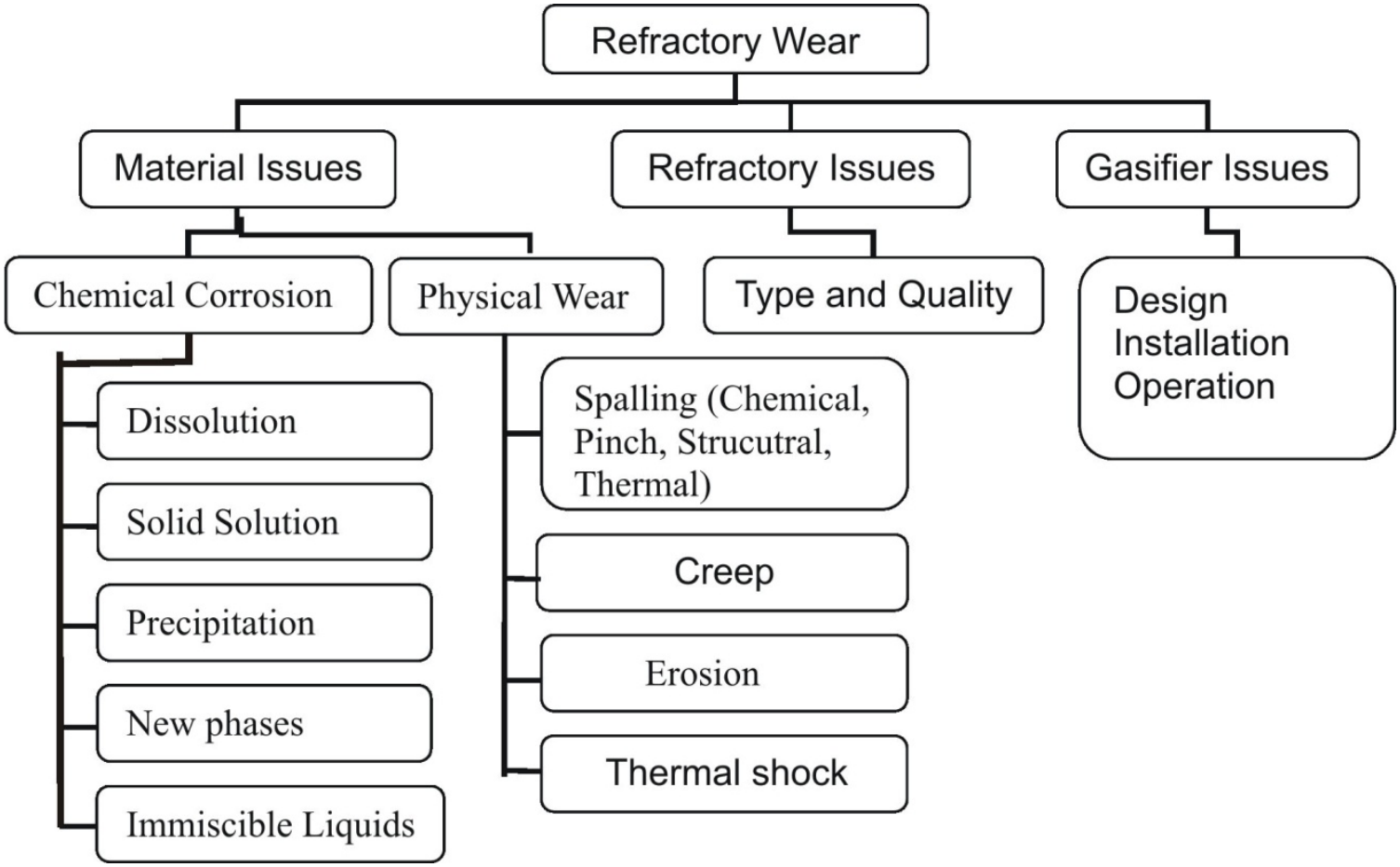


*A gasifier availability of 85-95% for utility applications is required. Gasifier users identified refractory service life as **the** most important limitation to on-line availability.*

Materials Challenges Associated with Slagging Gasifiers

- Process temperatures of 1325° to 1575 ° C.
- Frequent thermal cycling.
- Reducing and oxidizing environments.
- Corrosive slags of variable chemistry.
- Corrosive gases.
- Pressures ≥ 400 psi.

Refractory Wear Issues



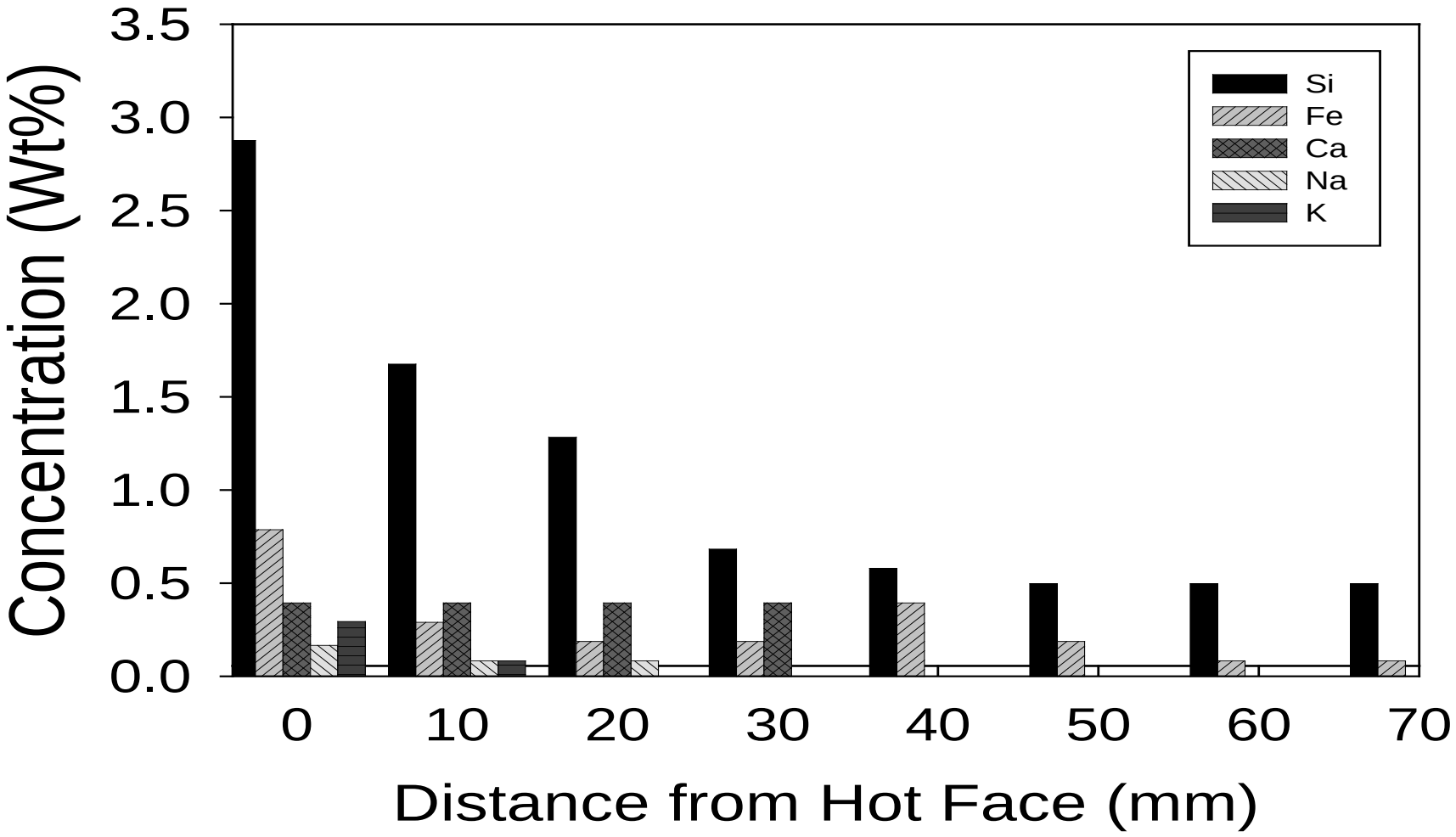
Cross Section of a Gasifier Spent Refractory

Interior cross section

Slag Penetration of 40-50 mm

Change in chemistry of the spent refractory

With Distance from the Hot Face

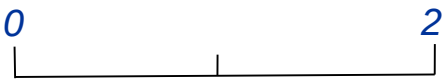


Refractory Solution:
Phosphate Modified Cr_2O_3 Refractory
Developed and Patented by the NETL

- **Decreases slag penetration**
- **Minimizes spalling**
- **Improves refractory chemical corrosion resistance**

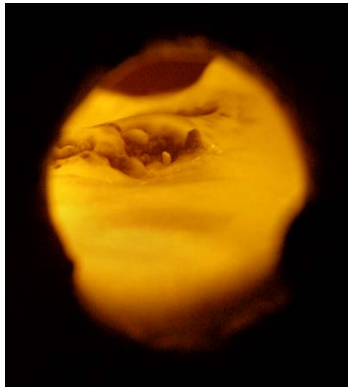
NETL Refractory

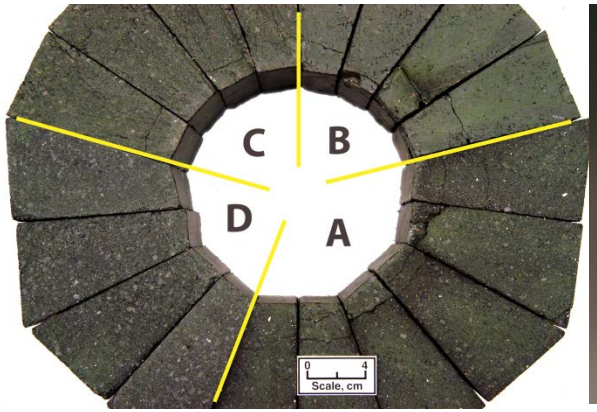
Previous Commercial "Best"



Scale, Inches

Rotary Slag Test

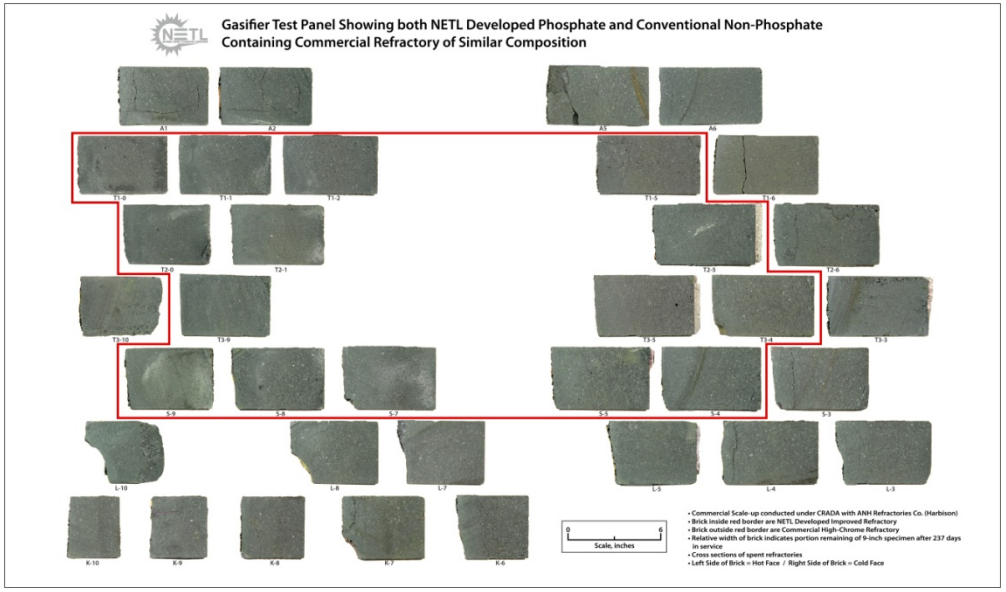




Commercial Refractory

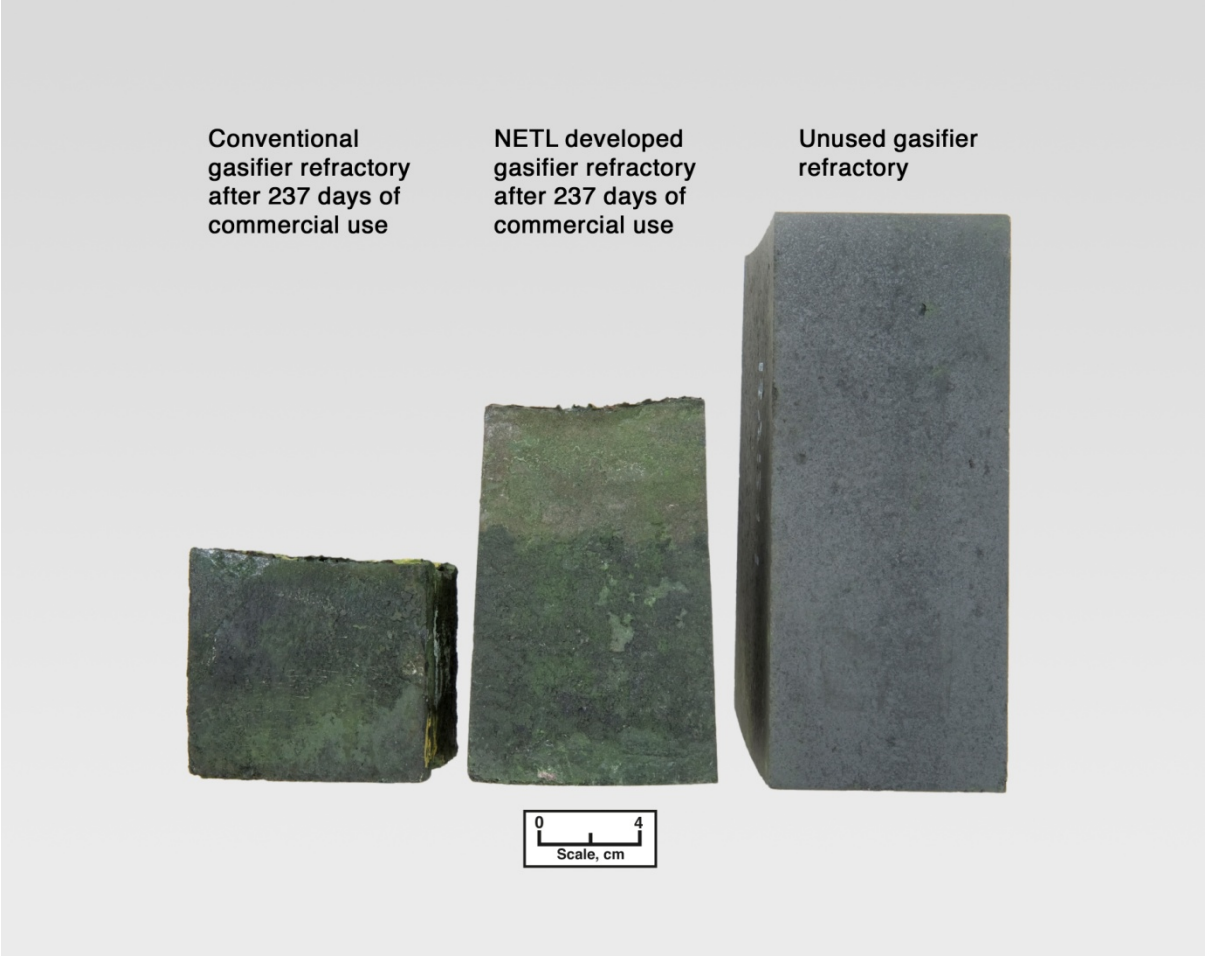
NETL Developed

Field Tests

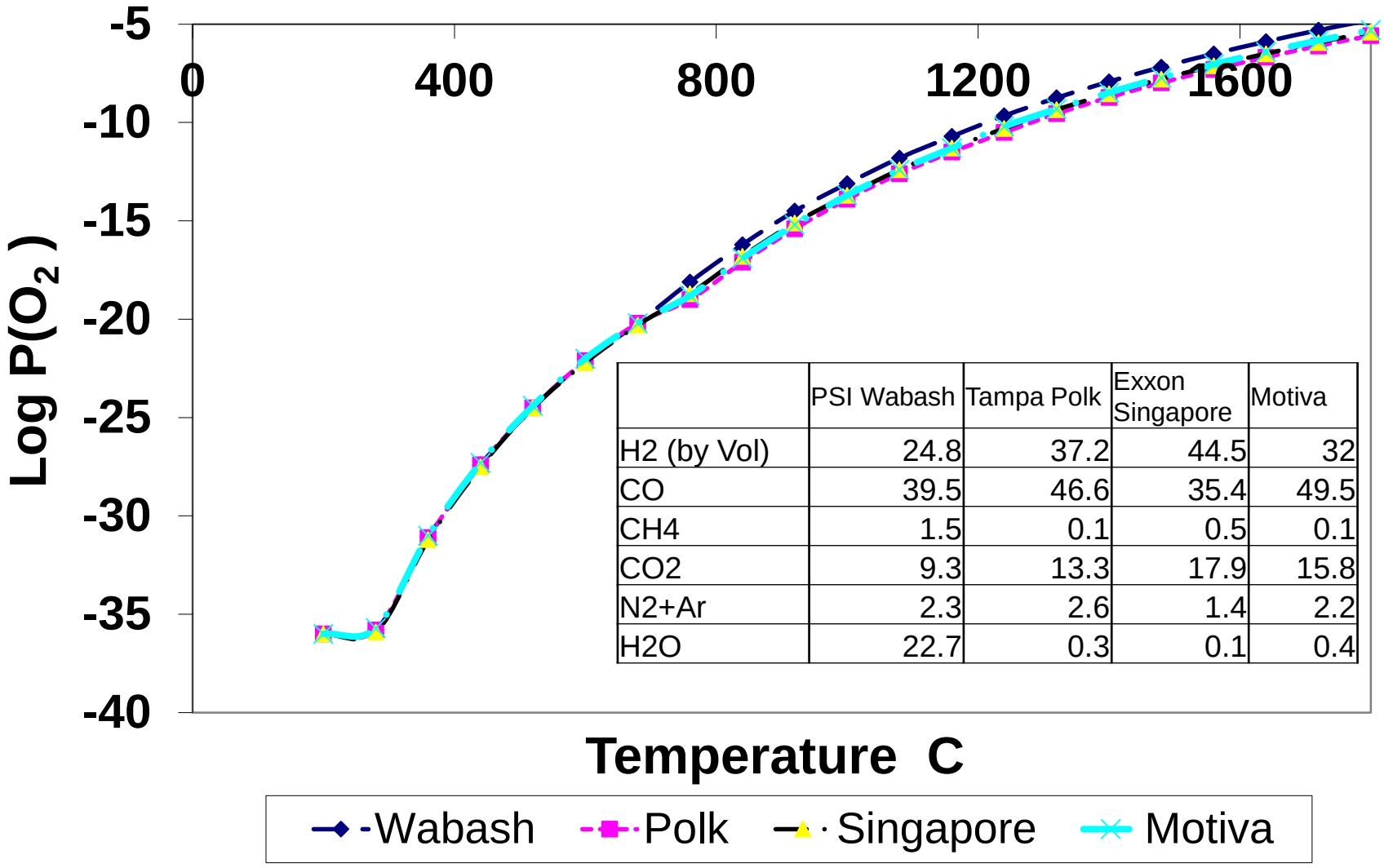


U.S. Patent 6,815,386 "Use of Phosphates to Reduce Slag Penetration in Cr_2O_3-Based Refractories." Licensed by NETL in May, 2007, to Harbison-Walker Refractories Company

Refractory Comparison



Gasifier Atmosphere



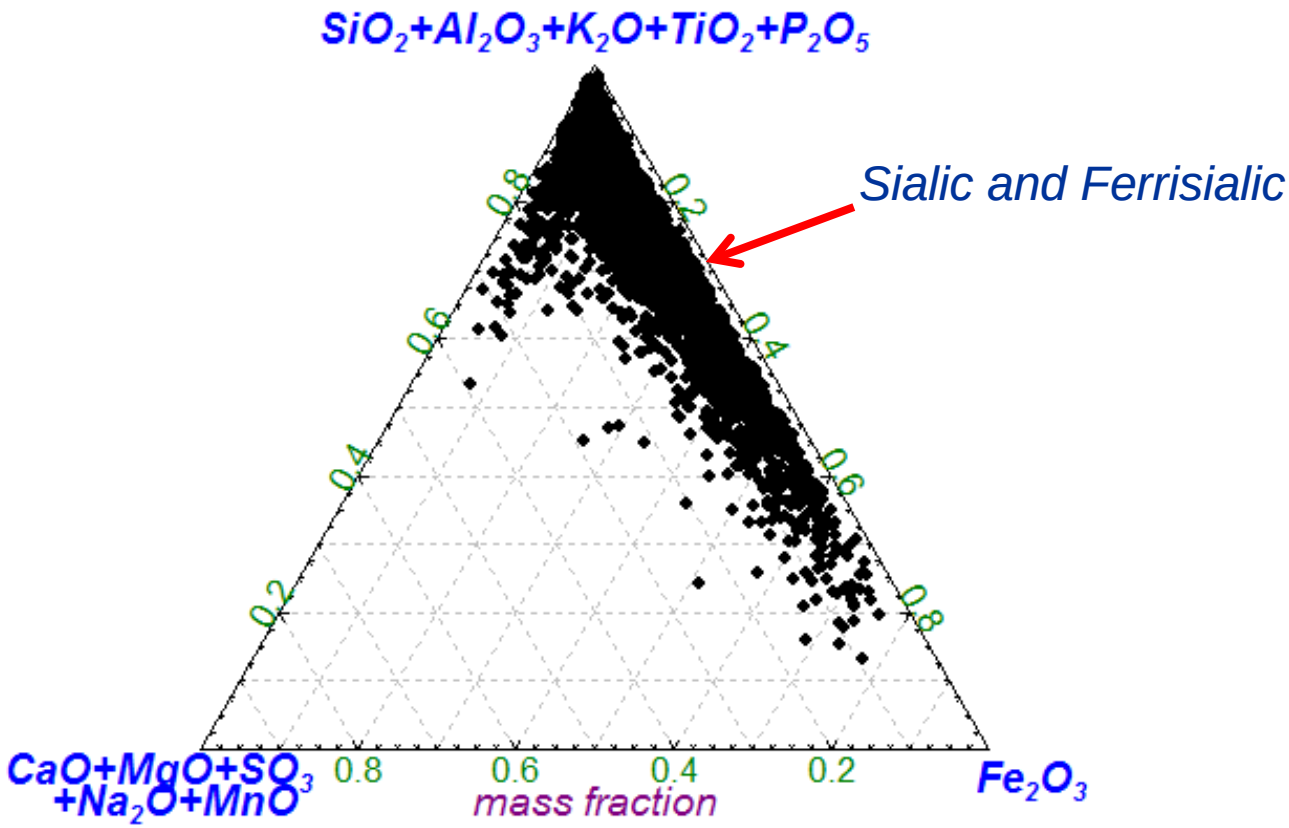
	PSI Wabash	Tampa Polk	Exxon Singapore	Motiva
H2 (by Vol)	24.8	37.2	44.5	32
CO	39.5	46.6	35.4	49.5
CH4	1.5	0.1	0.5	0.1
CO2	9.3	13.3	17.9	15.8
N2+Ar	2.3	2.6	1.4	2.2
H2O	22.7	0.3	0.1	0.4

US Coal Ash Compositon

	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O	K_2O	TiO_2	P_2O_5	SO_3
Avg	43.4	23.0	3.7	17.3	1.11	0.66	1.71	1.15	0.43	3.93
Max	93.0	46.0	42.0	88.0	19.00	13.00	6.80	5.60	9.70	37.00
Min	7.4	1.6	0.1	0.3	0.00	0.00	0.01	0.01	0.00	0.00
Std	11.8	6.9	4.7	14.3	1.12	1.07	0.96	0.50	0.58	4.80

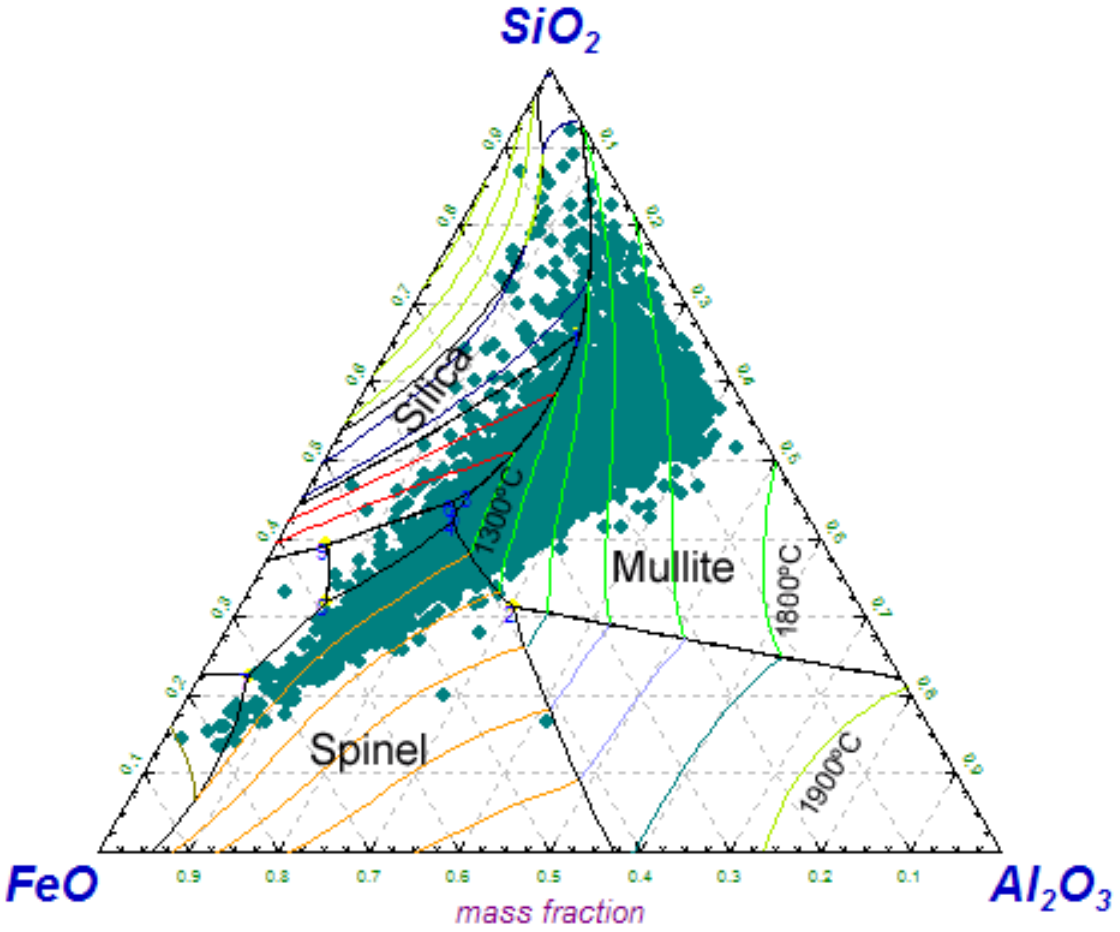
- *Eastern coal slag contains high FeO and SiO_2 while Western coal slag contains high Cao and less SiO_2; both slags are acidic slags because SiO_2/CaO ratio higher than 1.*

Classification of Coal Ash

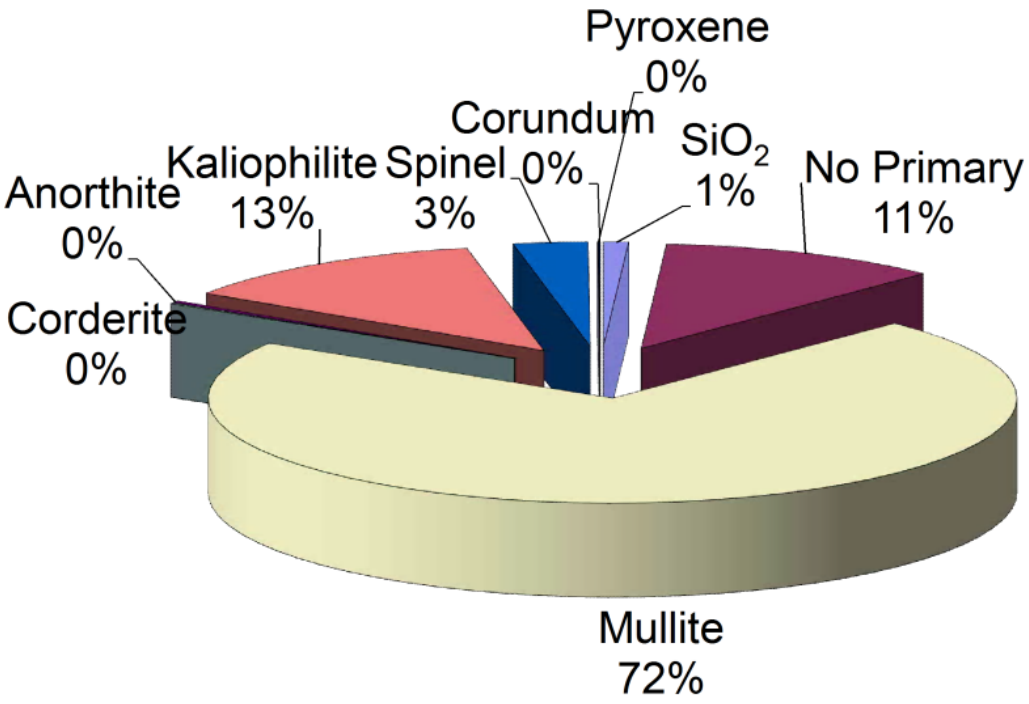


Slag Composition in SiO_2-Al_2O_3-FeO

Ternary Phase Diagram

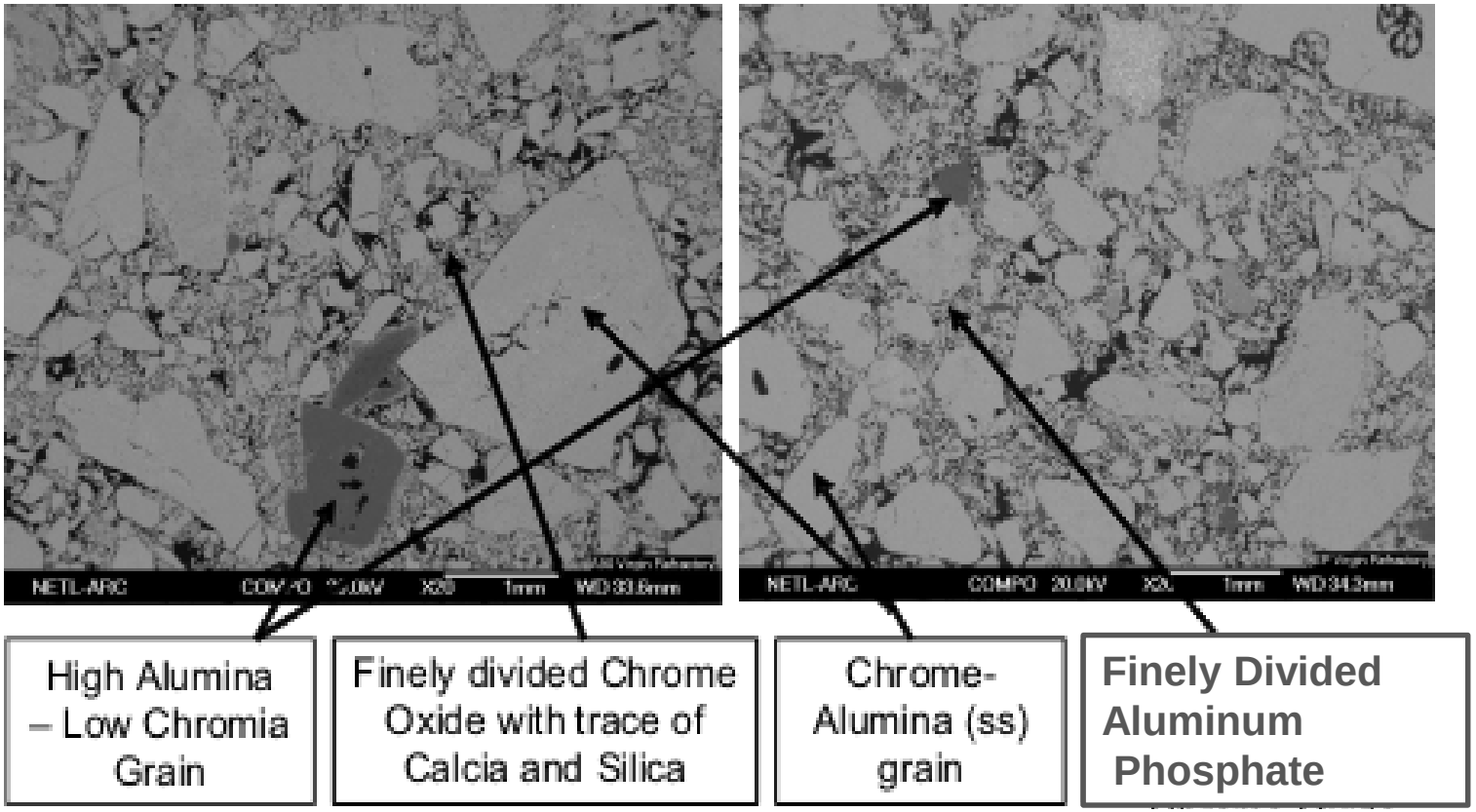


The Distribution of Primary Phase of US coal Slag – Thermodynamic Prediction

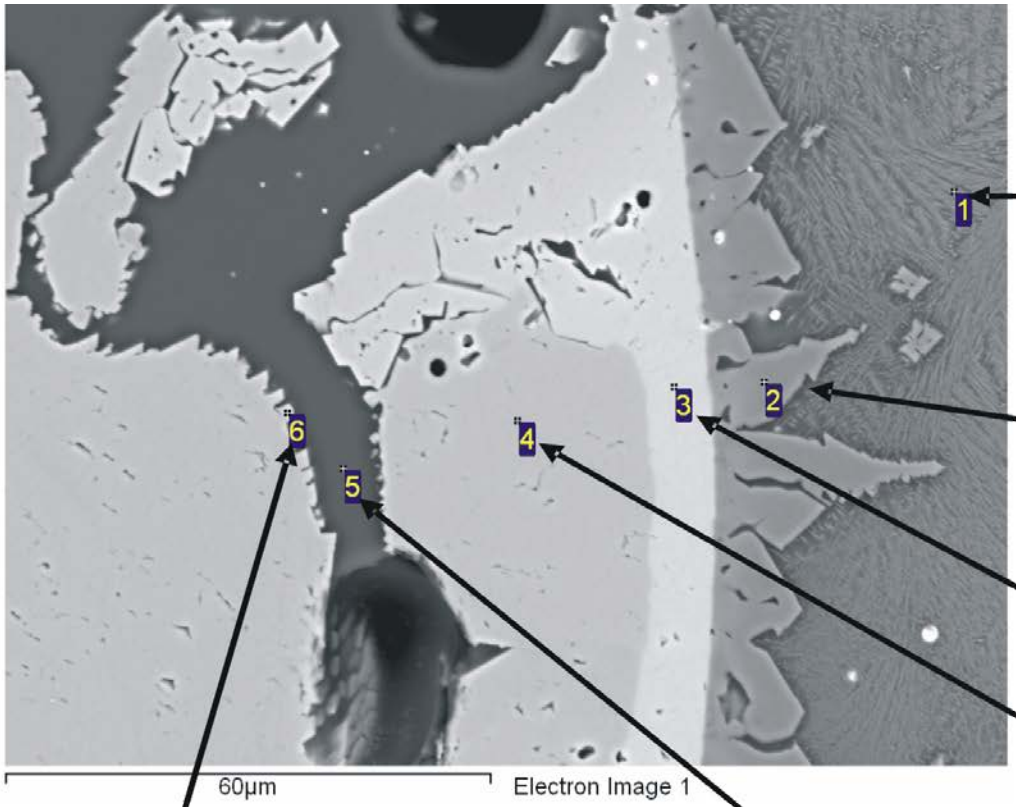


The micrograph of

a) virgin commercial and b) NETL-developed chrome refractories



The Microstructure of Gasifier Refractory
by SEM



Hercynite ($FeAl_2O_4$) Dendritic Recrystallization on cool-down

Formation of Iron-Aluminum Spinel

Formation of Iron-Chrome Spinel

Silica and Corundum with Chrome substitution

Slag Penetrated Region

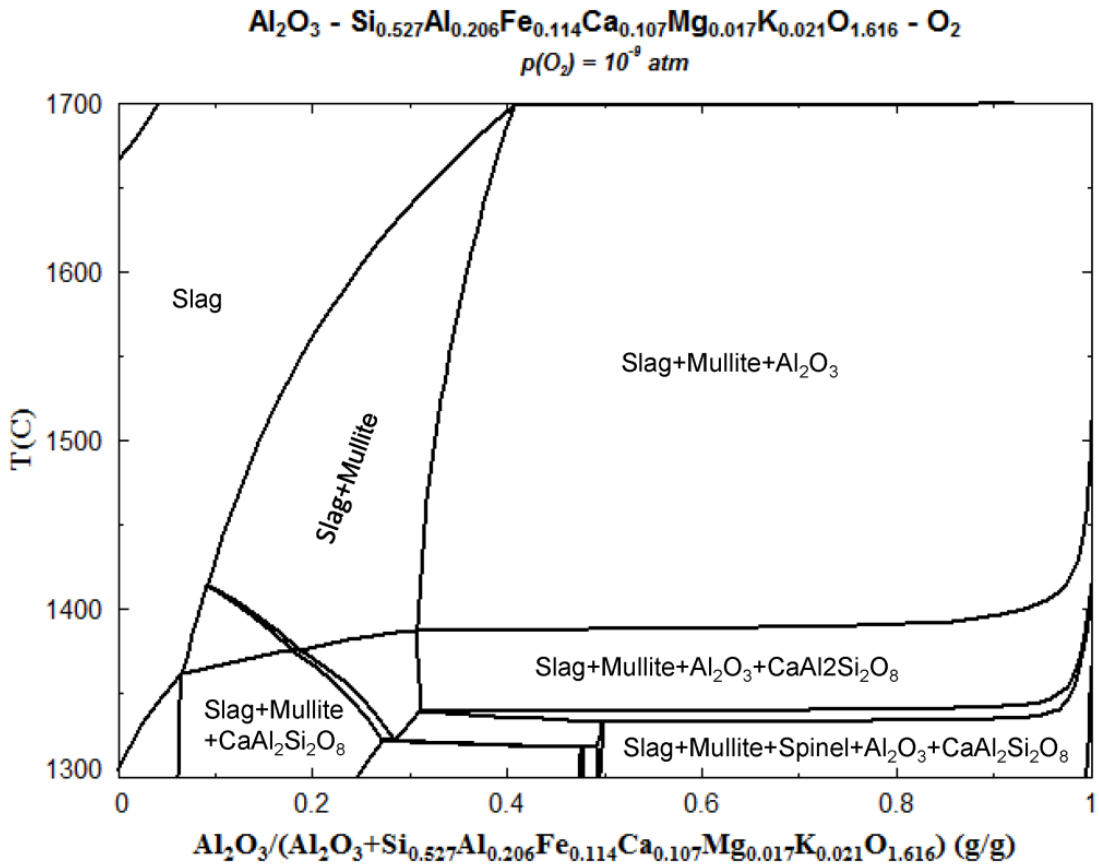
Chrome-Alumina Solid Solution

Examples

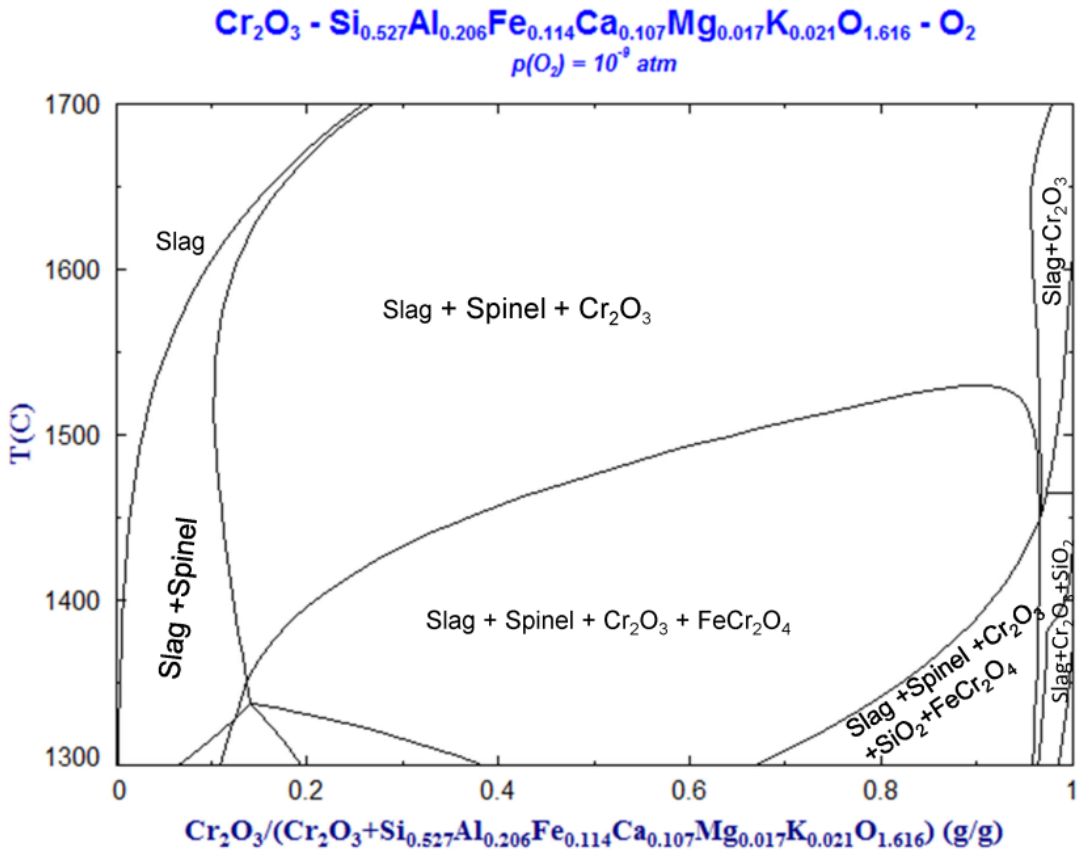
Reactions between Cr_2O_3 Refractory and Coal Slags

Wt%	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3
Illinois #6	54.31	18.00	14.04	10.33	1.18	0.41	1.69	0.05
Powder River Basin (PRB)	32.15	16.48	4.55	34.14	9.77	2.61	0.31	0.00

Thermodynamic Predictions
Illinois #6 with Al_2O_3 Refractory

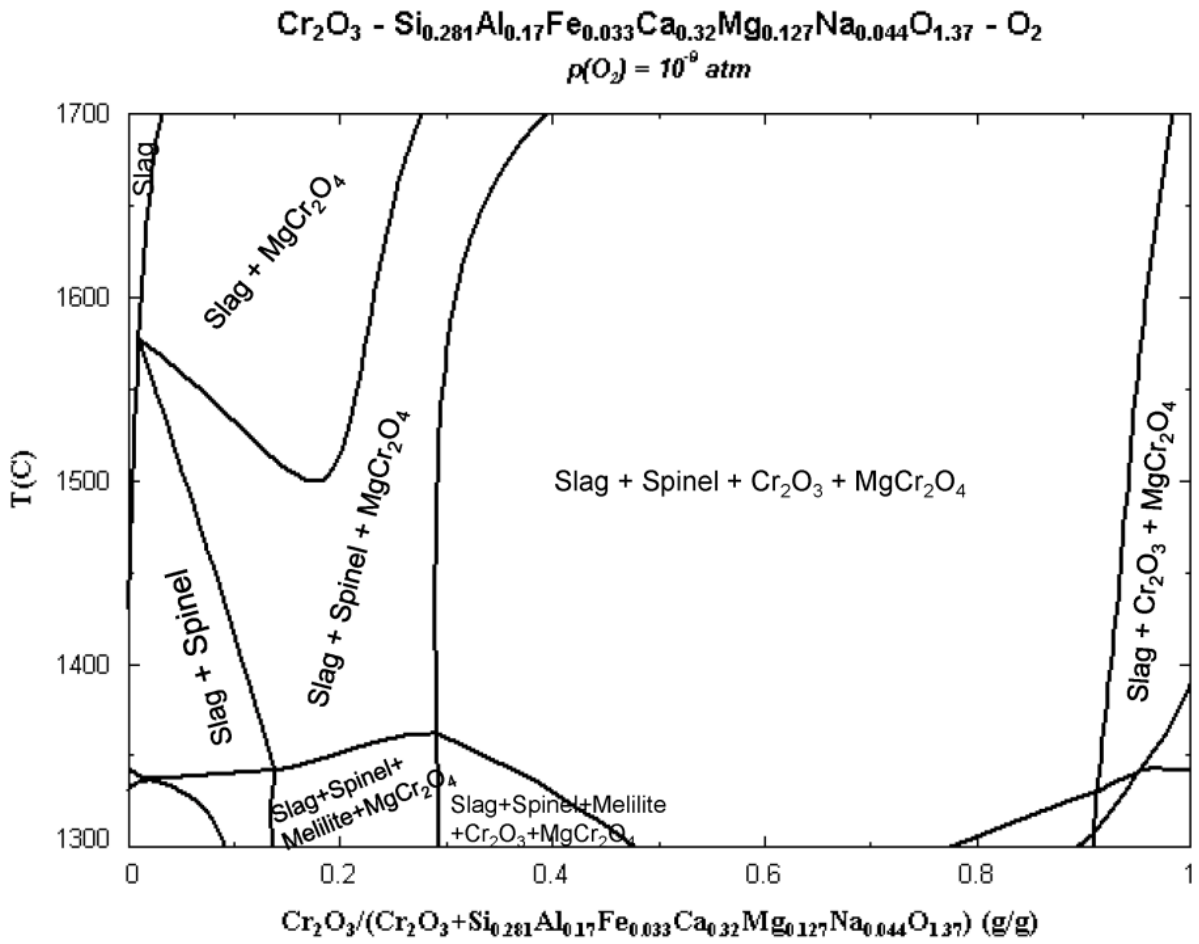


Thermodynamic Predictions
Illinois #6 with Cr_2O_3 Refractory



Thermodynamic Predictions

PRB with Cr_2O_3 Refractory

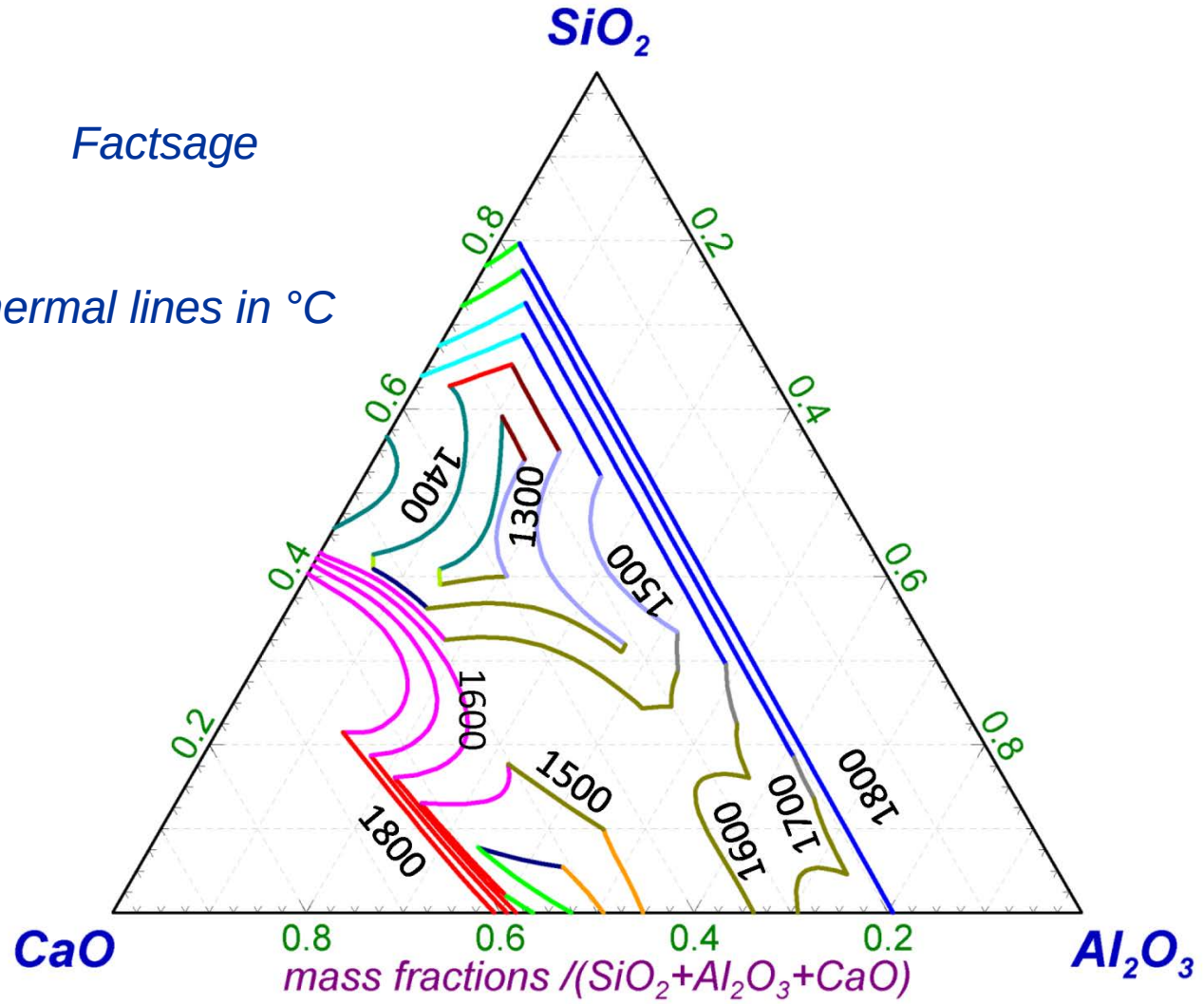


Phosphate Additive Effects

SiO_2 - Al_2O_3 - CaO - 0.01 P_2O_5 Phase Diagram

Factsage

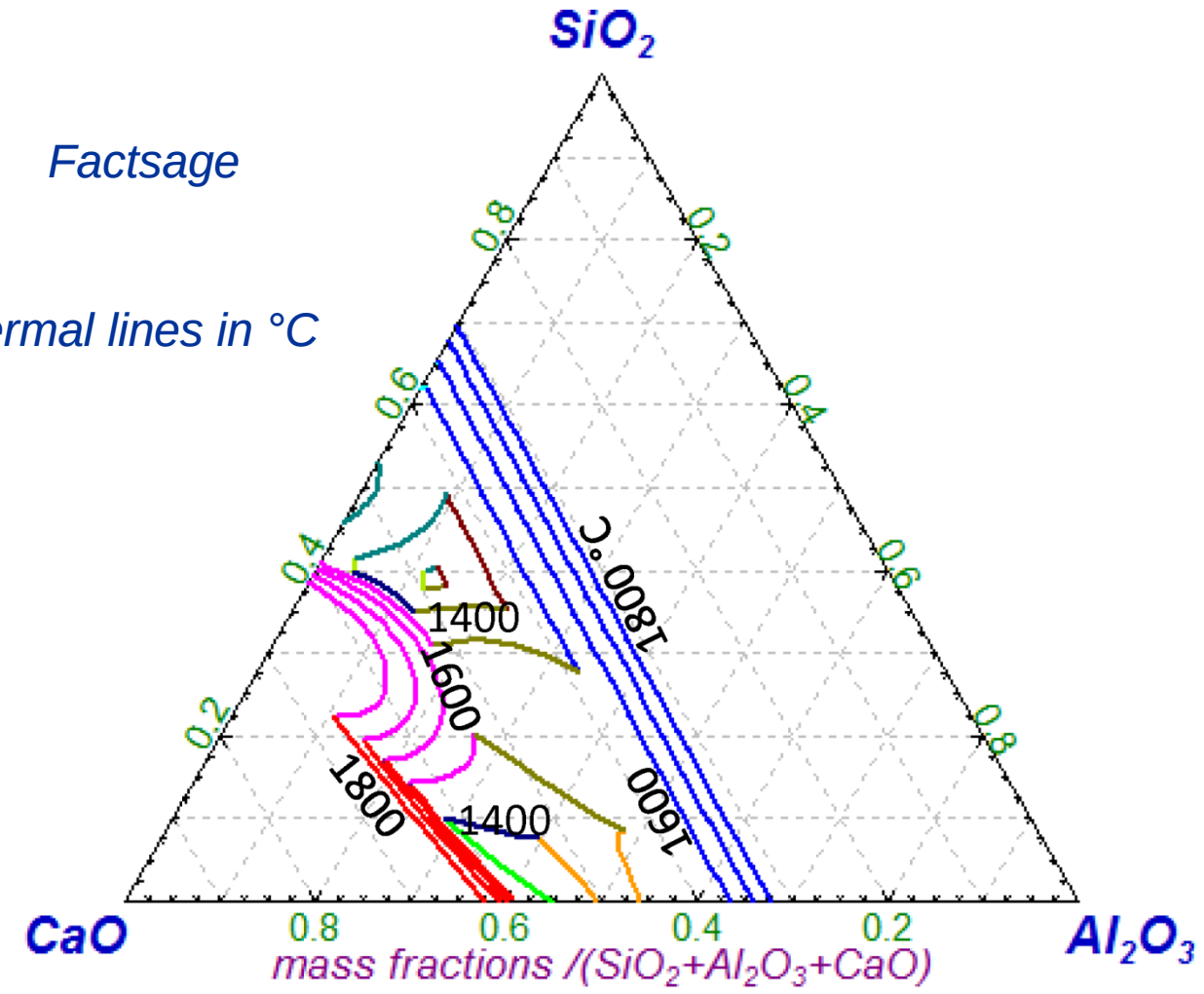
Isothermal lines in °C



SiO_2 - Al_2O_3 - CaO - 0.03 P_2O_5 Phase Diagram

Factsage

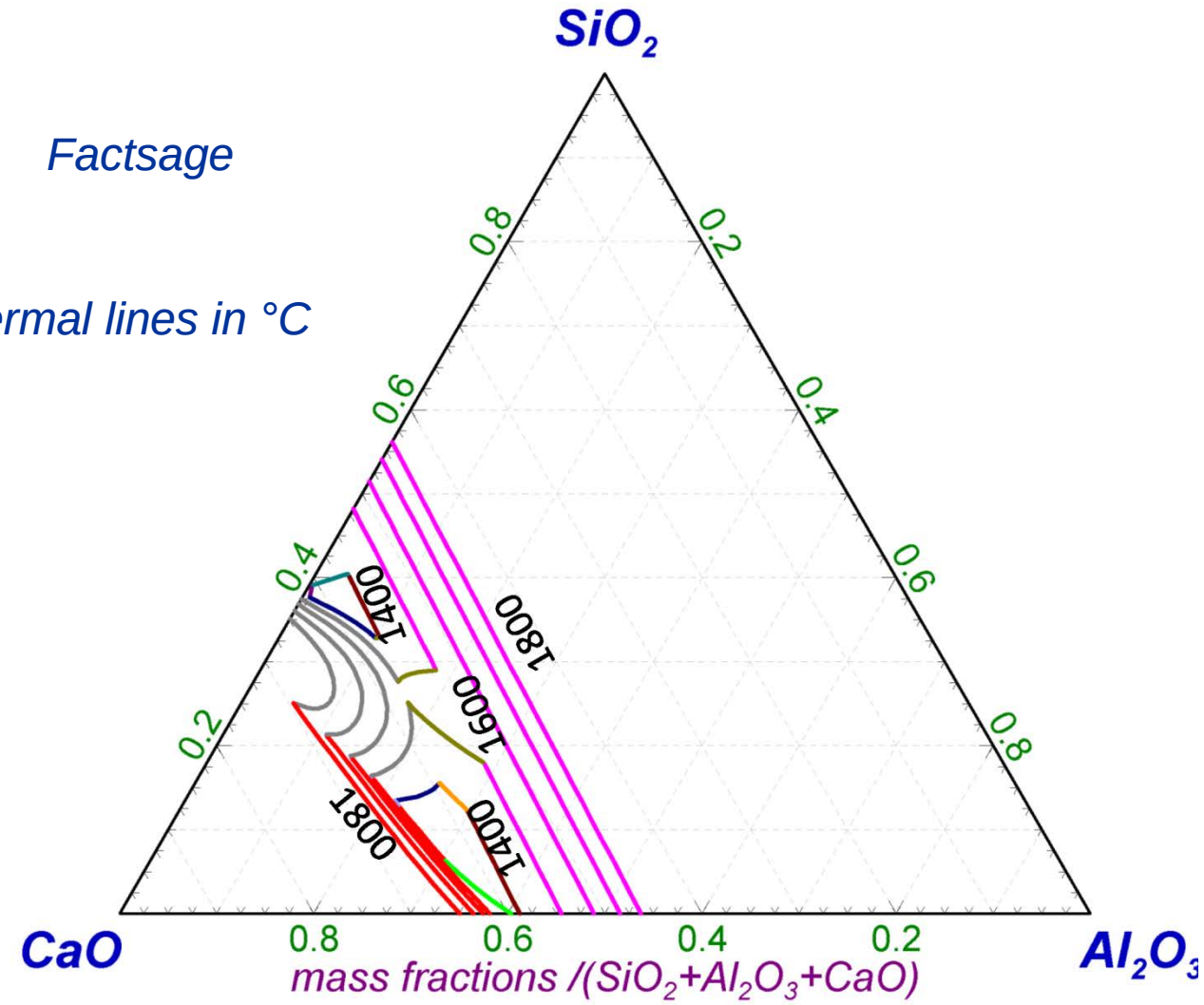
Isothermal lines in °C



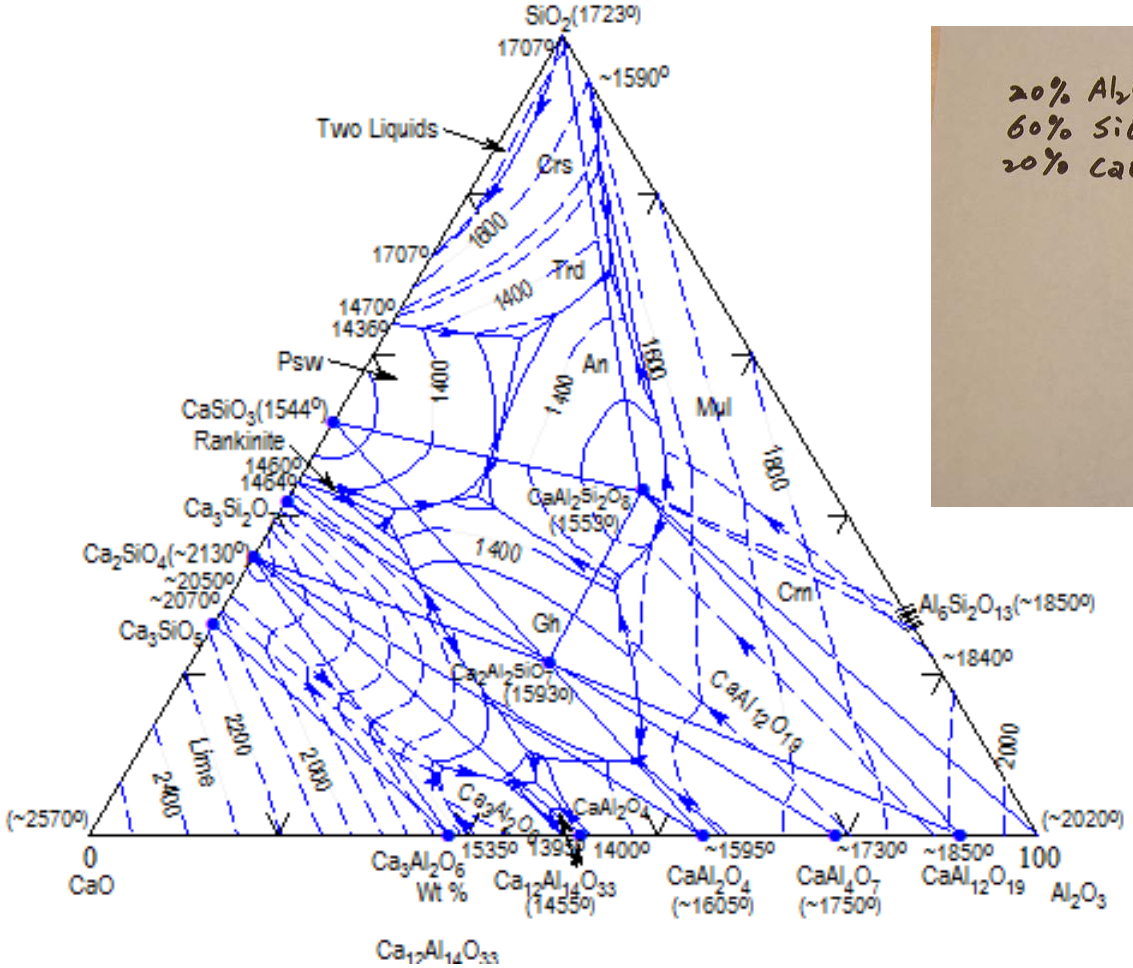
SiO_2 - Al_2O_3 - CaO - 0.07 P_2O_5 Phase Diagram

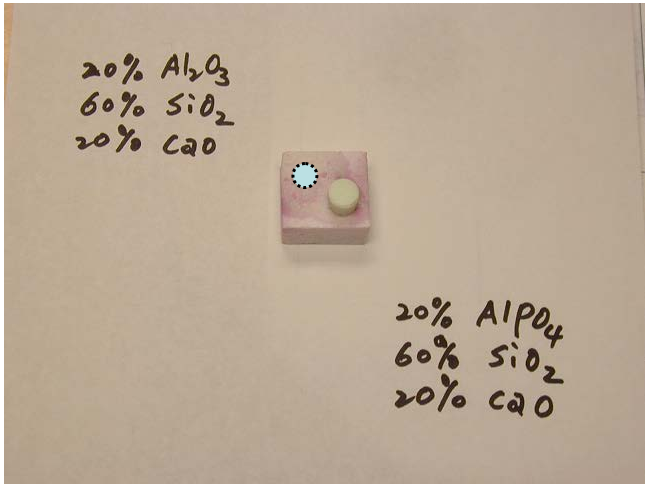
Factsage

Isothermal lines in °C



Experimental Evidence





1500 °C for 1 hour

Conclusions

- **Structural spalling is one of the major failure mechanisms of gasifier refractory linings. It is promoted by slag penetration into the refractory.**
- **Phosphate containing Cr_2O_3 refractory can effectively stop/decrease slag penetration and extend the service life of refractory.**
- **Mechanisms by which phosphates reduce refractory wear:**

  1) phosphates react with basic oxides and increase slag viscosity;

  2) phosphates can fill up pores in the refractory and decrease porosity;

  3) phosphates can increase the melting point of penetrated slag.

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."