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Faculty of Engineering
Department of Mining and Materials Engineering

Extracting Rare Metals from Municipal Solid Waste (MSW) Incineration Residues

MIME 572: Computational Thermodynamics

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BACKGROUND

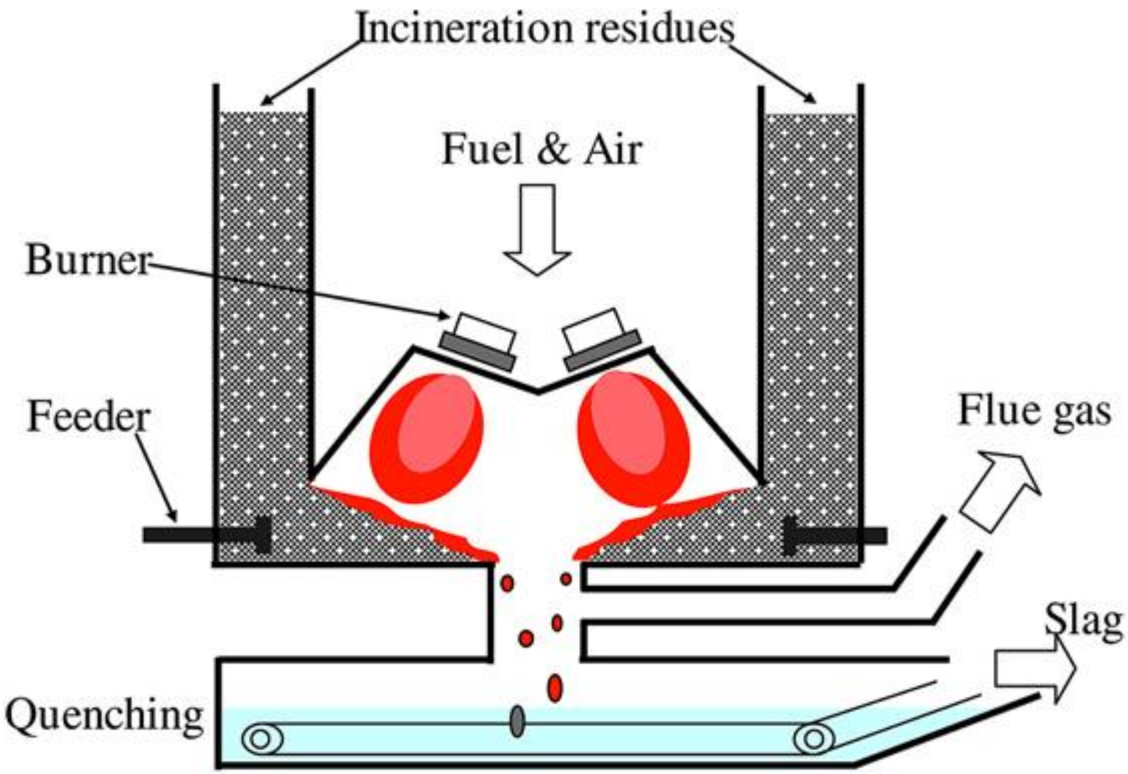
Rare Metals

- Catalytic properties, fluorescence, corrosion resistance
- In modern high technologies
  - Pt and Pd: emission control devices
  - Indium-tin-oxide: thin films for LCDs
- Production and consumption clustering
  - Japan: 30% of annual consumption
  - South Africa: 70% of Cr, Mn, Ta and PGM production

Municipal Solid Waste(MSW)

- MSW incineration residue(bottom ash + fly ash)→1300-1800°C→melting furnace fly ash(MFA)
- MFA generation
  - Reduced volume of residue in landfill
  - Generation of flue gases containing expensive metals
- Japanese government seeks to recover "strategic metals" from flue gas
  - Bi, Ga, Ge, In, Pd, Sb, Pt, Ta, Te, Tl and Zr

Surface Melting Furnace



Surface Melting Furnace

- Two primary operating variables
  - pO_2: varied by changing input fuel composition→CO/CO_2 ratio
  - Furnace temperature: control by changing input fuel and its flow rate
- Surface melting furnace operating optimally
  - Maximizes amount of "strategic metals" reporting to flue gas

Surface Melting Furnace

Input to furnace:

	Plant A 87% BA + 13% FA
O	2.3E+01
C	1.5E+00
N	4.2E−02
P	4.1E−01
S	2.1E−01
Al	2.5E+00
Ca	3.3E+00
Cd	1.8E−04
Cl	8.1E−01
Fe	1.3E+00
K	4.8E−01
Na	1.5E+00
Mg	4.9E−01
Cu	2.1E−01
Pb	5.5E−03
Si	7.0E+00
Zn	1.0E−01
Ag	9.2E−05
Bi	1.5E−05
Co	5.8E−04
Cr	1.3E−02
Ga	2.4E−04
Ge	3.0E−05
In	4.8E−06
Mn	3.7E−02
Mo	3.4E−04
Ni	7.6E−03
Pd	4.7E−06
Sb	2.5E−04
Sn	1.2E−03
Ta	4.3E−05
Te	1.8E−06
Tl	7.0E−07
W	5.6E−05
Zr	8.4E−04

Valuable Metals: Must Volatilise and Recover

Objectives

1) Create FactSAGE model of surface melting furnace operation
2) Use model to investigate influence of pO_2 and temperature on surface melting furnace operation
3) Find optimal operating conditions to maximize "strategic metal" content in flue gas

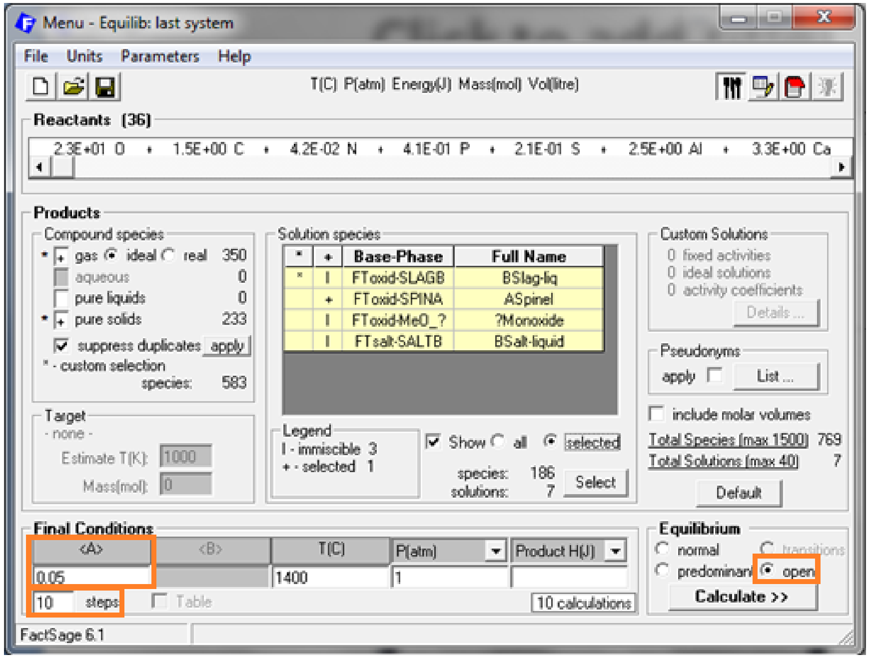
Outline

- Background
- FactSAGE Simulation Setup
- Model validation
- Effects of varying temperature and pO_2
- Furnace optimization
- Conclusion

FACTSAGE SIMULATION SETUP

FactSAGE Simulation Setup

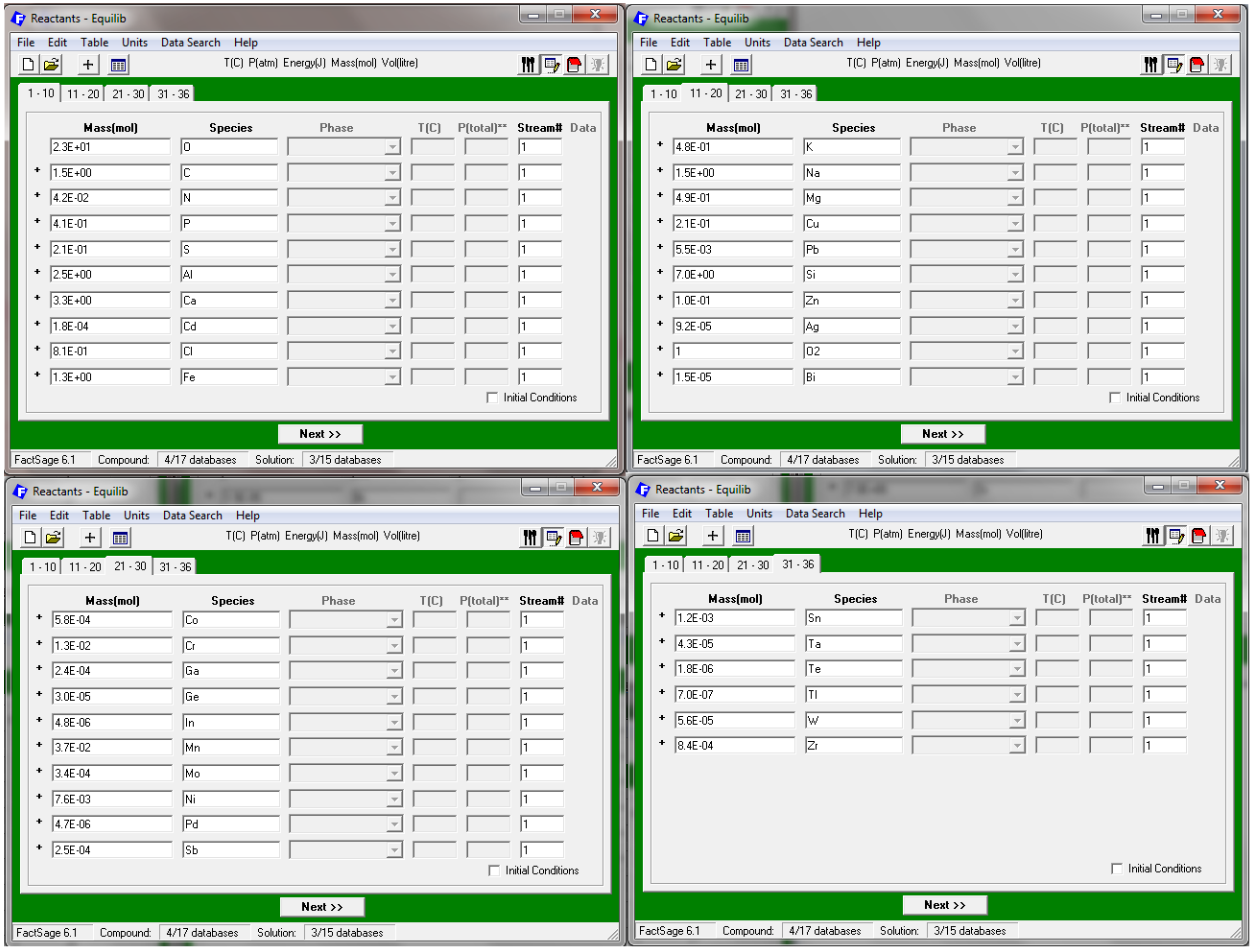
- Originally modeled furnace as an open system
  - 10 step process: <A> consisted in O_2 introduced into system at every step
  - Sough to investigate flue gas generation over time



FactSAGE Simulation Setup

- Modeling furnace as open system provided results that did not agree with plant data
- New simulation conducted:
  - Normal system, 1 step
  - Fixed temperature and oxygen partial pressure
- 36 input elements into EQUILIB
  - Original calculations exceed maximum number of computations
  - Solution species had to be carefully selected

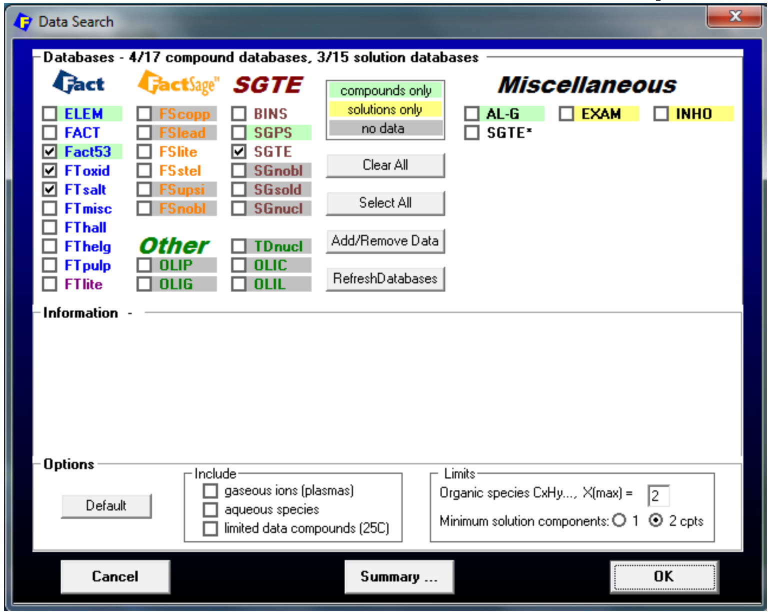
FactSAGE Simulation Setup



FactSAGE Simulation Setup

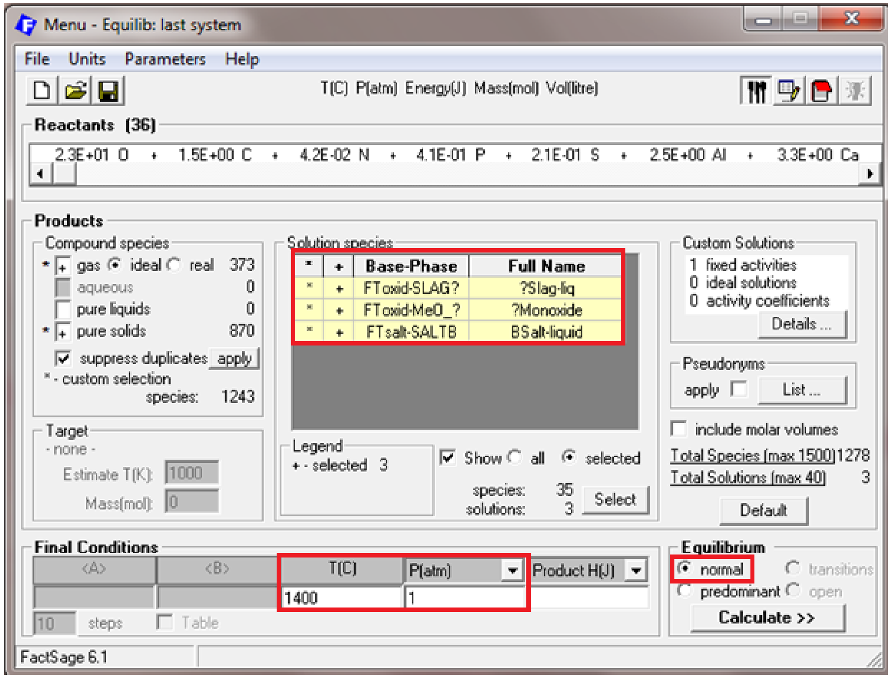
Database selection: in order of priority

- Ftoxid: oxides, ceramic solid solutions, slags
- Ftsalt: pure salts and salt solutions
- Fact53: metals, oxides, salts, C_xH_y, gases



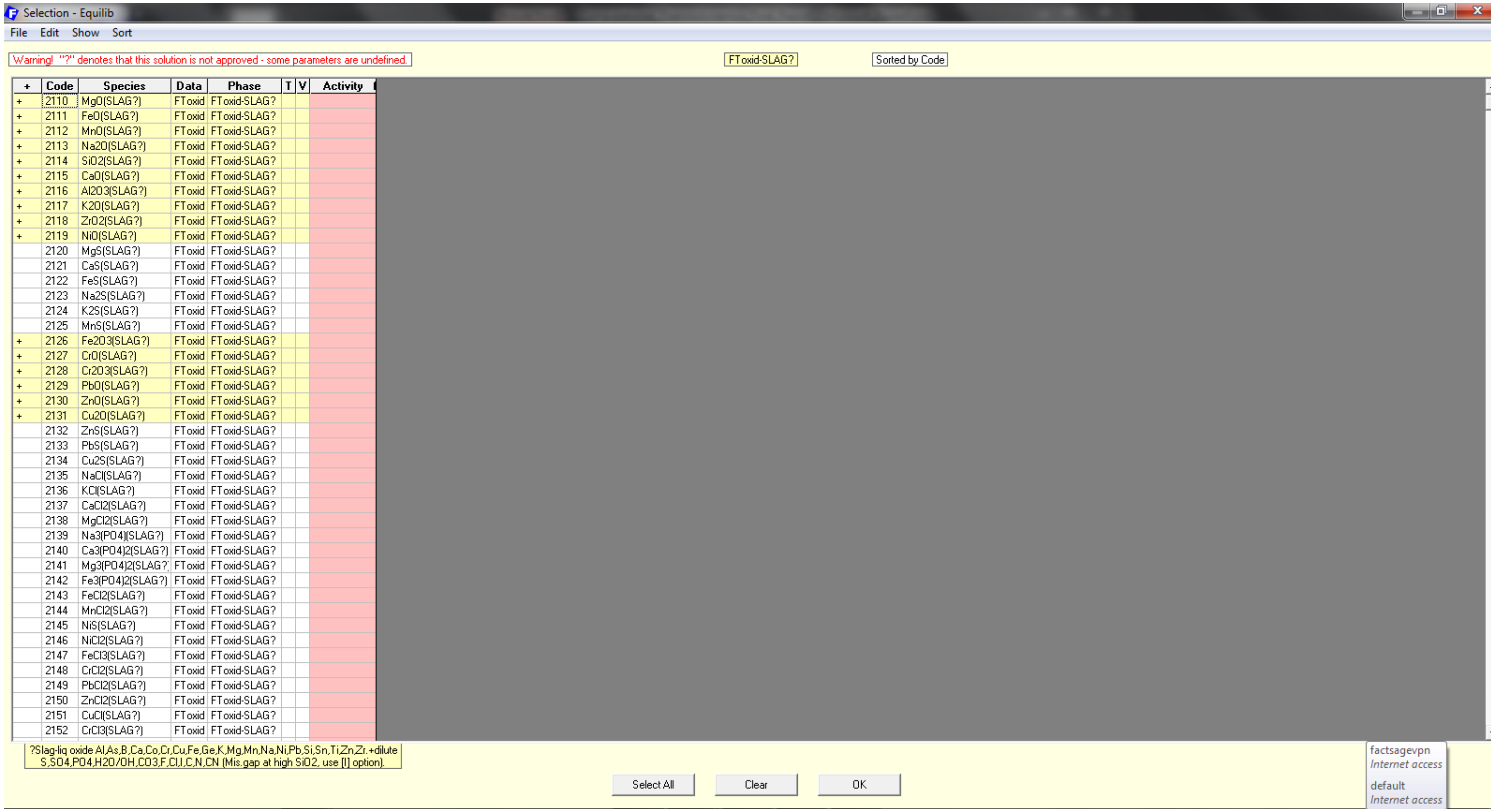
FactSAGE Simulation Setup

- Solution species base phases selected:
  - FToxid-SLAG?
  - Ftoxid-MeO_?
  - FTsalt-SALTB



FactSAGE Simulation Setup

- Species removed from these base phases to speed up calculations



+	Code	Species	Data	Phase	T	V	Activity
+	2110	MgO(SLAG?)	FToxid	FToxid-SLAG?			
+	2111	FeO(SLAG?)	FToxid	FToxid-SLAG?			
+	2112	MnO(SLAG?)	FToxid	FToxid-SLAG?			
+	2113	Na2O(SLAG?)	FToxid	FToxid-SLAG?			
+	2114	SiO2(SLAG?)	FToxid	FToxid-SLAG?			
+	2115	CaO(SLAG?)	FToxid	FToxid-SLAG?			
+	2116	Al2O3(SLAG?)	FToxid	FToxid-SLAG?			
+	2117	K2O(SLAG?)	FToxid	FToxid-SLAG?			
+	2118	ZrO2(SLAG?)	FToxid	FToxid-SLAG?			
+	2119	NiO(SLAG?)	FToxid	FToxid-SLAG?			
	2120	MgS(SLAG?)	FToxid	FToxid-SLAG?			
	2121	CaS(SLAG?)	FToxid	FToxid-SLAG?			
	2122	FeS(SLAG?)	FToxid	FToxid-SLAG?			
	2123	Na2S(SLAG?)	FToxid	FToxid-SLAG?			
	2124	K2S(SLAG?)	FToxid	FToxid-SLAG?			
	2125	MnS(SLAG?)	FToxid	FToxid-SLAG?			
+	2126	Fe2O3(SLAG?)	FToxid	FToxid-SLAG?			
+	2127	CrO(SLAG?)	FToxid	FToxid-SLAG?			
+	2128	Cr2O3(SLAG?)	FToxid	FToxid-SLAG?			
+	2129	PbO(SLAG?)	FToxid	FToxid-SLAG?			
+	2130	ZnO(SLAG?)	FToxid	FToxid-SLAG?			
+	2131	Cu2O(SLAG?)	FToxid	FToxid-SLAG?			
	2132	ZnS(SLAG?)	FToxid	FToxid-SLAG?			
	2133	PbS(SLAG?)	FToxid	FToxid-SLAG?			
	2134	Cu2S(SLAG?)	FToxid	FToxid-SLAG?			
	2135	NaCl(SLAG?)	FToxid	FToxid-SLAG?			
	2136	KCl(SLAG?)	FToxid	FToxid-SLAG?			
	2137	CaCl2(SLAG?)	FToxid	FToxid-SLAG?			
	2138	MgCl2(SLAG?)	FToxid	FToxid-SLAG?			
	2139	Na3(PO4)(SLAG?)	FToxid	FToxid-SLAG?			
	2140	Ca3(PO4)2(SLAG?)	FToxid	FToxid-SLAG?			
	2141	Mg3(PO4)2(SLAG?	FToxid	FToxid-SLAG?			
	2142	Fe3(PO4)2(SLAG?)	FToxid	FToxid-SLAG?			
	2143	FeCl2(SLAG?)	FToxid	FToxid-SLAG?			
	2144	MnCl2(SLAG?)	FToxid	FToxid-SLAG?			
	2145	NiS(SLAG?)	FToxid	FToxid-SLAG?			
	2146	NiCl2(SLAG?)	FToxid	FToxid-SLAG?			
	2147	FeCl3(SLAG?)	FToxid	FToxid-SLAG?			
	2148	CrCl2(SLAG?)	FToxid	FToxid-SLAG?			
	2149	PbCl2(SLAG?)	FToxid	FToxid-SLAG?			
	2150	ZnCl2(SLAG?)	FToxid	FToxid-SLAG?			
	2151	CuCl(SLAG?)	FToxid	FToxid-SLAG?			
	2152	CrCl3(SLAG?)	FToxid	FToxid-SLAG?			

?Slag-liq oxide Al,As,B,Ca,Co,Cr,Cu,Fe,Ge,K,Mg,Mn,Na,Ni,Pb,Si,Sn,Ti,Zn,Zr.+dilute S,SO4,PO4,H2O/OH,CO3,F,Cl,I,C,N,CN (Mis.gap at high SiO2, use [I] option).

Select All | Clear | OK

factsagevpn *Internet access*
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FactSAGE Simulation Setup

Selection - Equilib

File Edit Show Sort

Se Warning! It is recommended that you select all the components of a solution phase.

FTsalt-SALTB

Sorted by Code

+	Code	Species	Data	Phase	T	V	Activity
+	2902	NaCl(SALTB)	FTsalt	FTsalt-SALTB			
+	2903	KCl(SALTB)	FTsalt	FTsalt-SALTB			
+	2904	MgCl2(SALTB)	FTsalt	FTsalt-SALTB			
+	2905	CaCl2(SALTB)	FTsalt	FTsalt-SALTB			
+	2906	FeCl2(SALTB)	FTsalt	FTsalt-SALTB			
+	2907	FeCl3(SALTB)	FTsalt	FTsalt-SALTB			
+	2908	MnCl2(SALTB)	FTsalt	FTsalt-SALTB			
+	2909	CoCl2(SALTB)	FTsalt	FTsalt-SALTB			
+	2910	NiCl2(SALTB)	FTsalt	FTsalt-SALTB			
	2911	CaO(SALTB)	FTsalt	FTsalt-SALTB			
	2912	Na2O(SALTB)	FTsalt	FTsalt-SALTB			
	2913	K2O(SALTB)	FTsalt	FTsalt-SALTB			
	2914	MgO(SALTB)	FTsalt	FTsalt-SALTB			
	2915	FeO(SALTB)	FTsalt	FTsalt-SALTB			
	2916	Fe2O3(SALTB)	FTsalt	FTsalt-SALTB			
	2917	MnO(SALTB)	FTsalt	FTsalt-SALTB			
	2918	CoO(SALTB)	FTsalt	FTsalt-SALTB			
	2919	NiO(SALTB)	FTsalt	FTsalt-SALTB			

Selection - Equilib

File Edit Show Sort

Warning! "?" denotes that this solution is not approved - some parameters are undefined.

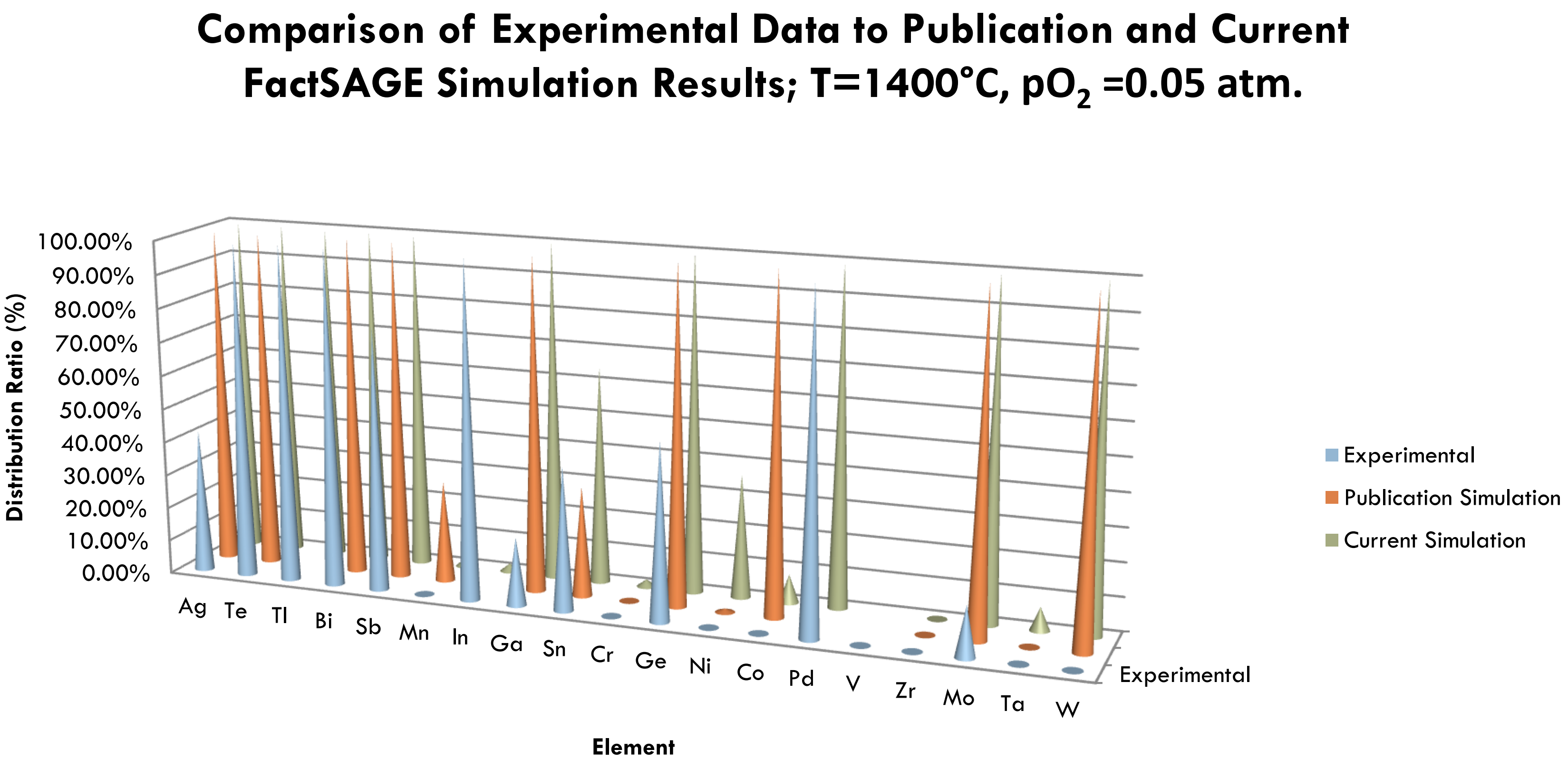
FToxid-MeO_?

Sorted by Code

+	Code	Species	Data	Phase	T	V	Activity
+	2443	FeO(MeO_?)	FToxid	FToxid-MeO_?			
	2444	Fe2O3(MeO_?)	FToxid	FToxid-MeO_?			
+	2445	CaO(MeO_?)	FToxid	FToxid-MeO_?			
+	2446	MgO(MeO_?)	FToxid	FToxid-MeO_?			
+	2447	ZnO(MeO_?)	FToxid	FToxid-MeO_?			
+	2448	Al2O3(MeO_?)	FToxid	FToxid-MeO_?			
+	2449	NiO(MeO_?)	FToxid	FToxid-MeO_?			
+	2450	CoO(MeO_?)	FToxid	FToxid-MeO_?			
+	2451	MnO(MeO_?)	FToxid	FToxid-MeO_?			
	2452	Cr2O3(MeO_?)	FToxid	FToxid-MeO_?			
	2453	Mn2O3(MeO_?)	FToxid	FToxid-MeO_?			
	2454	ZrO2(MeO_?)	FToxid	FToxid-MeO_?			
	2455	Cu2O(MeO_?)	FToxid	FToxid-MeO_?			

MODEL VALIDATION

Model Validation

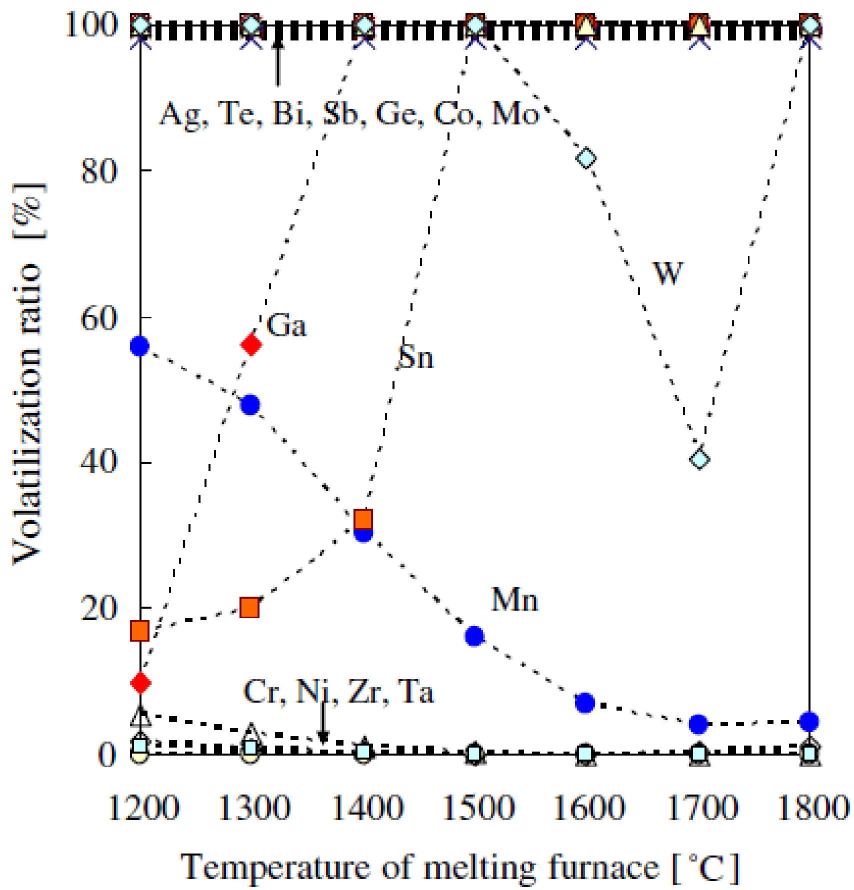


Model Validation

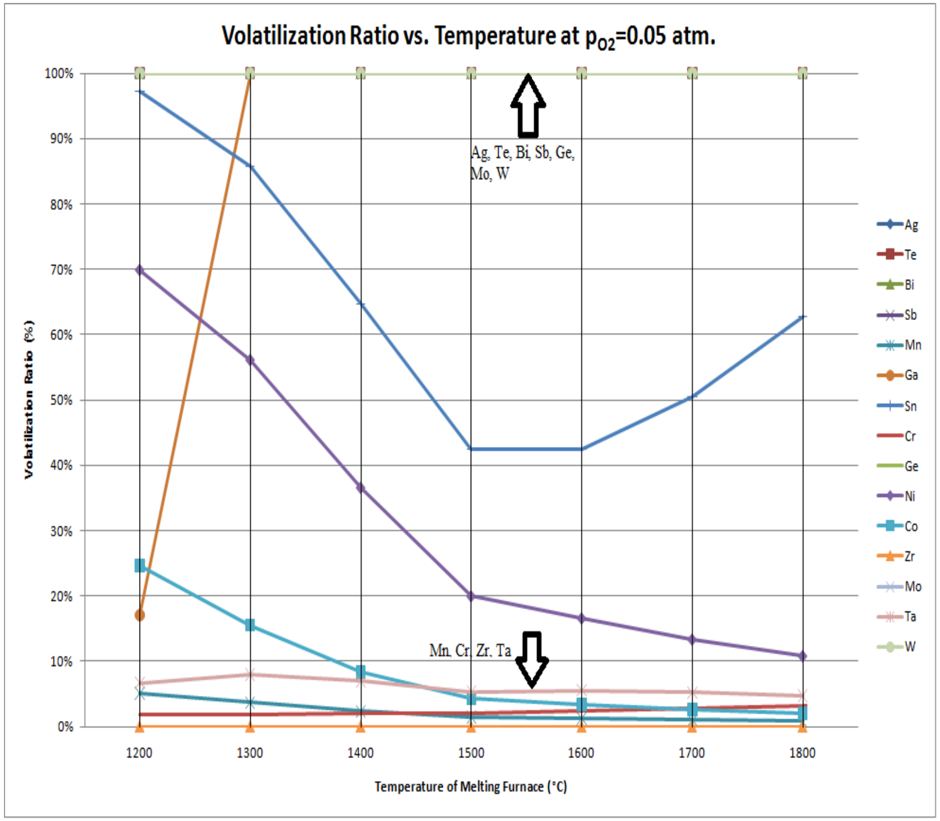
	Distribution ratio (%)			Error Sum of Squares	
Element	Experimental	Publication Simulation	Current Simulation	Publication Simulation	Current Simulation
Ag	42.50%	100.00%	100.00%	33.06%	33.06%
Te	100.00%	100.00%	100.00%	0.00%	0.00%
Tl	100.00%		100.00%	100.00%	0.00%
Bi	100.00%	100.00%	100.00%	0.00%	0.00%
Sb	78.00%	100.00%	100.00%	4.84%	4.84%
Mn	0.00%	30.00%	2.35%	9.00%	0.06%
In	100.00%		2.23%	100.00%	95.58%
Ga	20.00%	99.00%	100.00%	62.41%	64.00%
Sn	42.50%	32.50%	64.61%	1.00%	4.89%
Cr	0.00%	0.00%	2.09%	0.00%	0.04%
Ge	52.50%	100.00%	100.00%	22.56%	22.56%
Ni	0.00%	1.00%	36.55%	0.01%	13.36%
Co	0.00%	100.00%	8.33%	100.00%	0.69%
Pd	100.00%		100.00%	100.00%	0.00%
V	0.00%			100.00%	100.00%
Zr	0.00%	0.00%	0.00%	0.00%	0.00%
Mo	15.00%	100.00%	100.00%	72.25%	72.25%
Ta	0.00%	0.00%	6.90%	0.00%	0.48%
W	0.00%	100.00%	100.00%	100.00%	100.00%
All Data				**42%**	**27%**
Excluding Database Omissions				**23.78%**	**17.43%**

Model Validation

Publication Simulation:



Current Simulation:



Model Validation

- FactSAGE simulation presented here matches plant results more closely than publication
  - ~30% lower error sum of squares
  - Includes more elements, notably Tl and In
- Superior results due to
  - Newer version of FactSAGE
  - Better starting assumptions
- Inaccurate Mo results in both simulations
  - No Mo slag database

TEMPERATURE AND OXYGEN PARTIAL PRESSURE EFFECTS

Varying pO_2 at T=1300°C

T=1300											
	Distribution Ratio (%)										
PO2 (atm.)	**0**	**0.01**	**0.02**	**0.03**	**0.04**	**0.05**	**0.06**	**0.07**	**0.08**	**0.09**	**0.1**
Bi	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	96.18%	91.86%
Ga	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
Ge	100.00%	0.30%	0.18%	0.13%	0.11%	0.09%	0.08%	0.07%	0.07%	0.06%	0.06%
In	11.45%	36.30%	36.96%	37.65%	38.34%	39.05%	39.78%	40.52%	41.28%	42.05%	42.85%
Pd	55.12%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
Sb	32.31%	6.82%	7.35%	7.66%	7.83%	7.93%	7.99%	8.02%	8.03%	8.02%	8.00%
Ta	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
Te	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
Tl	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
Zr	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%

Varying pO_2 at T=1300°C

- At 1300°C, only Ge, In, Pd and Sb see changes in distribution ratio with varying oxygen partial pressure
- As pO_2 ↑, different compounds containing these species form
  - $GeS(g) \rightarrow GeO(g) \rightarrow GeO(g) + GeCl_4(g)$
  - $In(g)+In_2S(g) \rightarrow In(g)+InO\ (g)$
  - $Pd(g) \rightarrow Pd(g)+PdO_2(g)$
  - $Sb(g) \rightarrow SbCl_3(g)$

Varying pO_2 at T=1400°C

T=1400											
	Distribution Ratio (%)										
PO2 (atm.)	**0**	**0.01**	**0.02**	**0.03**	**0.04**	**0.05**	**0.06**	**0.07**	**0.08**	**0.09**	**0.1**
Bi	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
Ga	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	91.86%
Ge	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
In	100.00%	7.17%	4.30%	3.21%	2.61%	2.23%	1.97%	1.77%	1.62%	1.41%	0.06%
Pd	73.37%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	42.85%
Sb	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
Ta	31.45%	6.12%	6.54%	6.74%	6.84%	6.90%	6.93%	6.94%	6.94%	6.89%	8.00%
Te	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
Tl	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
Zr	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%

Varying pO_2 at T=1400°C

- At 1400°C, only In, Pd and Ta see changes in distribution ratio with varying oxygen partial pressure
- As $pO_2 \uparrow$, different compounds containing these species form
  - $In_{(g)}+In_2S(g) \rightarrow In(g)+InO\ (g)$
  - $Pd(g) \rightarrow Pd(g)+PdO(g)+PdO_2(g)$
  - $TaOCl_3$ forms less favourably, increase in oxides doesn't compensate

Varying pO_2 at T=1500°C

T=1500											
	Distribution Ratio (%)										
PO2 (atm.)	**0**	**0.01**	**0.02**	**0.03**	**0.04**	**0.05**	**0.06**	**0.07**	**0.08**	**0.09**	**0.1**
Bi	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
Ga	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
Ge	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
In	100.00%	100.00%	72.43%	54.02%	44.02%	37.65%	33.20%	29.90%	27.35%	25.32%	23.66%
Pd	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
Sb	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
Ta	39.42%	5.60%	5.54%	5.47%	5.41%	5.34%	5.30%	5.33%	5.35%	5.35%	5.34%
Te	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
Tl	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
Zr	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%

Varying pO_2 at T=1500°C

- At 1500°C, only In and Ta see changes in distribution ratio with varying oxygen partial pressure
- As pO_2 ↑, different compounds containing these species form
  - $In(g)+In_2S(g) \rightarrow In(g)+InO\ (g)$
  - $TaOCl_3$ forms less favourably, increase in oxides doesn't compensate

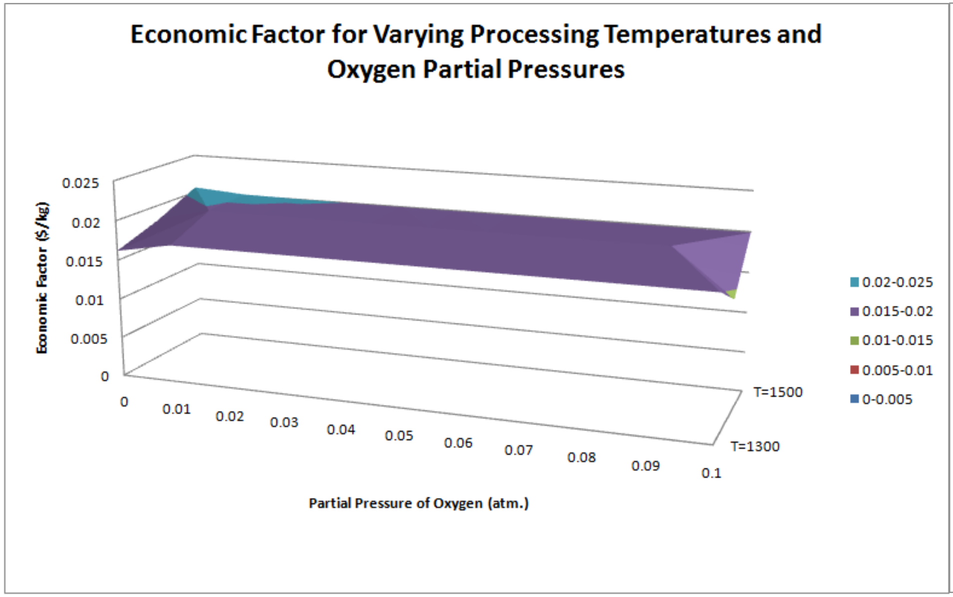
FURNACE OPTIMIZATION

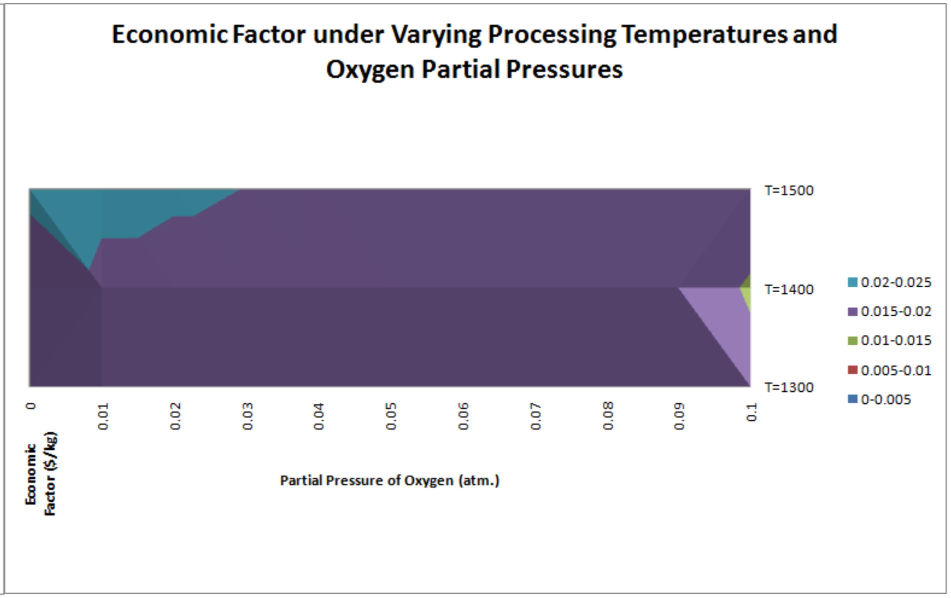
Furnace Optimization

- Want to know optimal operating conditions to maximize value of “strategic metals” in flue gas
- Used previously calculations
  - pO_2(atm.)=0 0.1 0.01
  - T(°C)=1300 1500 100
- Used most up to date metal prices to find operating conditions of maximum flue gas monetary value

Furnace Optimization

- Optimal operating conditions
  - T=1500°C and pO_2 = 0.01 atm.
  - $20.13 of "strategic metals" per tonne of MFA processed





Conclusion

- FactSAGE simulation of surface melting furnace more accurate than publication
- Used to investigate the effects of temperature and oxygen partial pressure on composition of flue gas
- Optimal furnace operating conditions estimated at T=1500°C and pO_2 = 0.01 atm.

References

- C.-H. Jung, M. Osako / *Chemosphere* **69** (2007) 279–288
- *www.**kitco**.com/*
- http://www.metalprices.com/