Ferrous Applications II

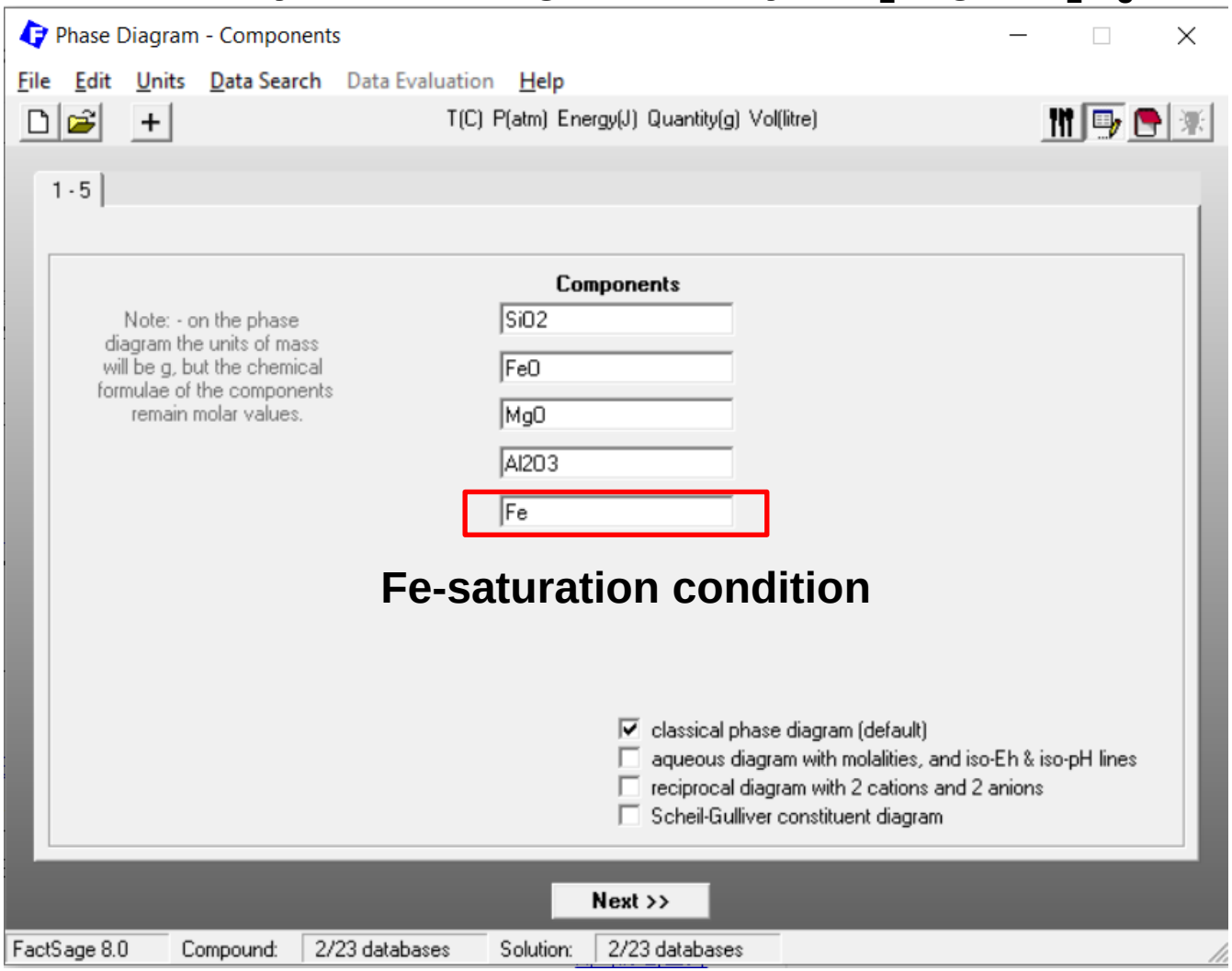
Contents

The effect of SiO_2/MgO and FeO and Al_2O_3 in Slag on the liquidus temperature of the Slag

Phase Diagram / Equilib

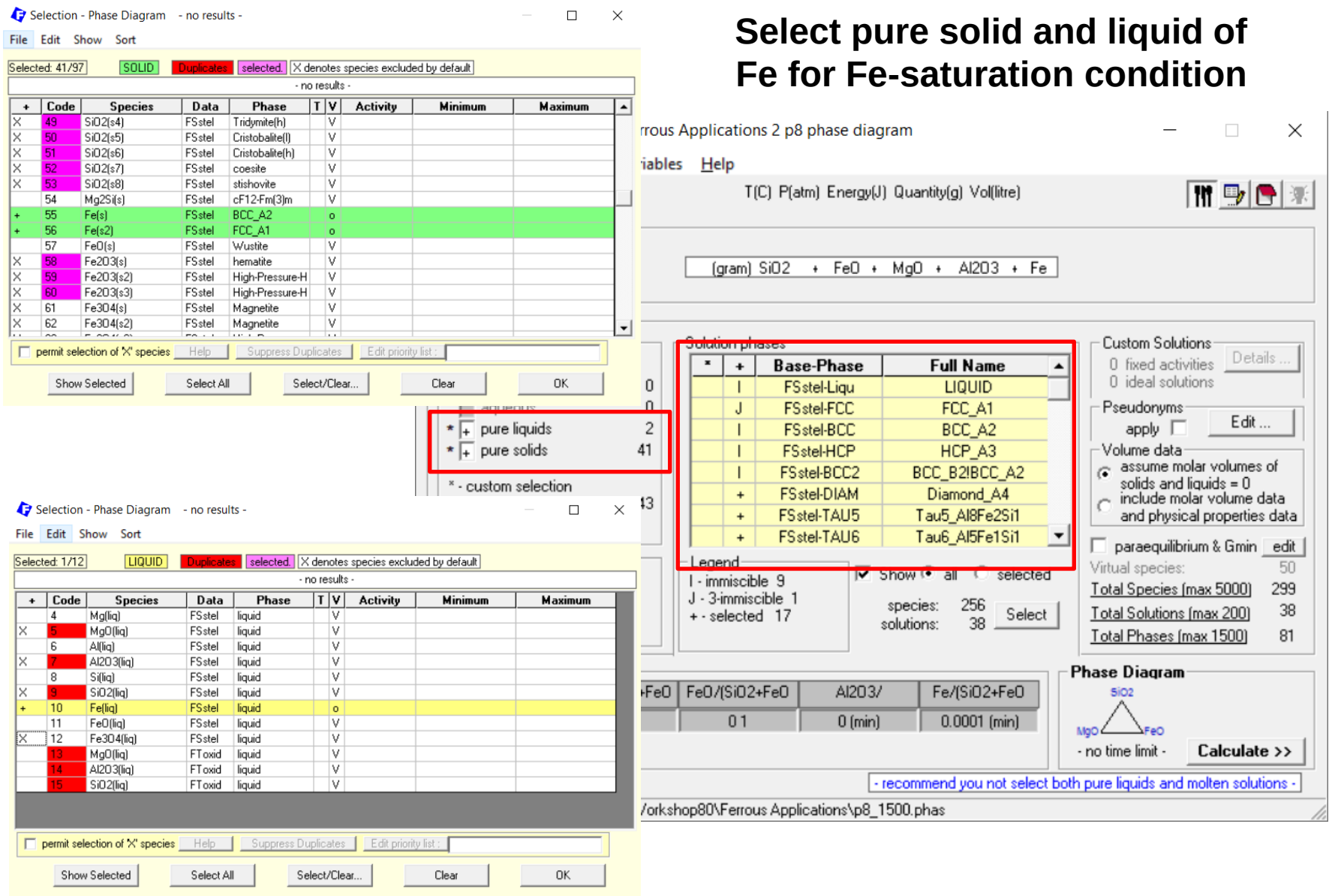
Phase diagram of SiO_2-MgO-Al_2O_3-FeO-Fe

Actually, SiO_2/MgO of Laterite is almost same as that of the produced Slag
The main system of Slag is virtually SiO_2-MgO-Al_2O_3-FeO

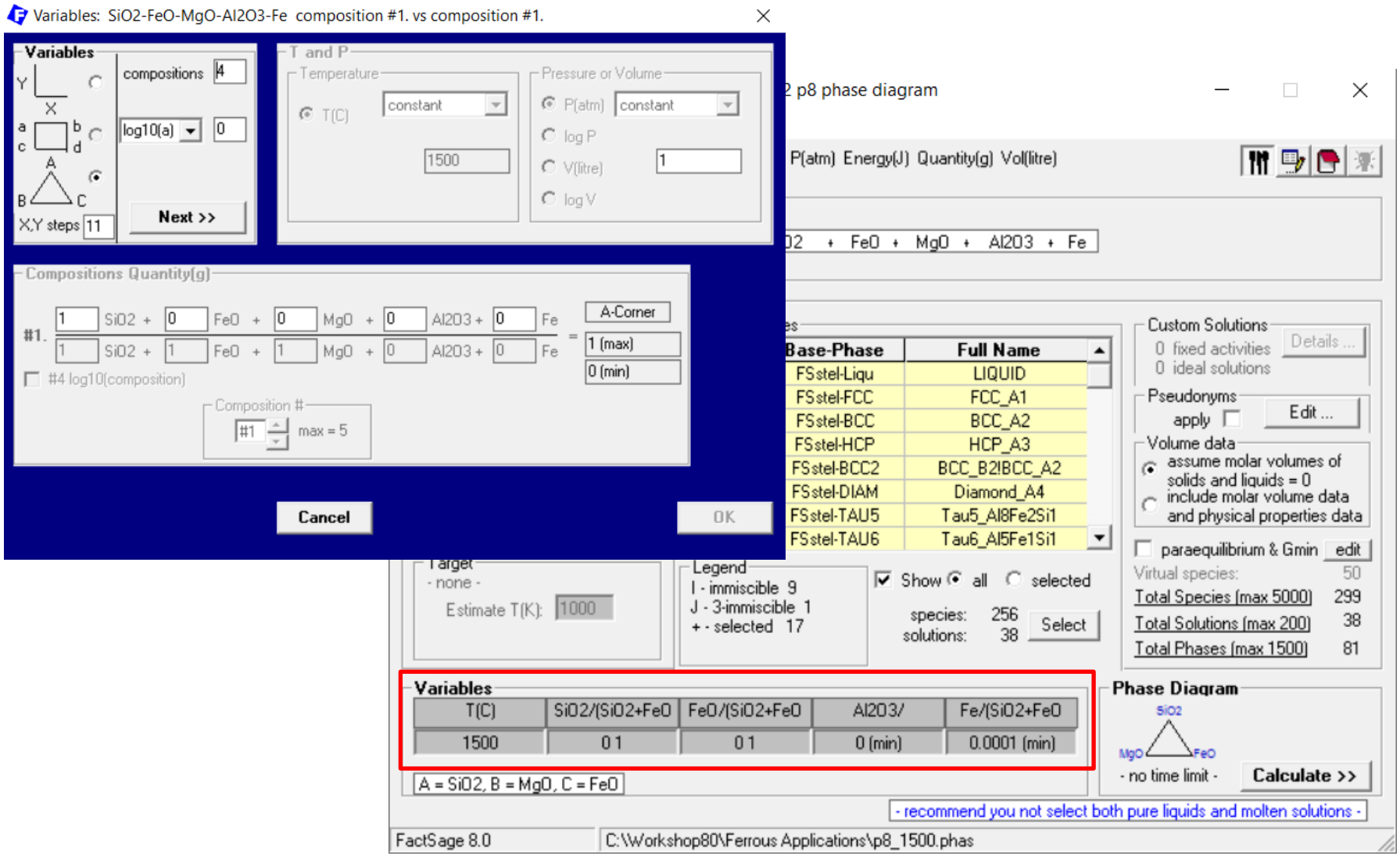


Phase diagram of SiO_2-MgO-Al_2O_3-FeO-Fe

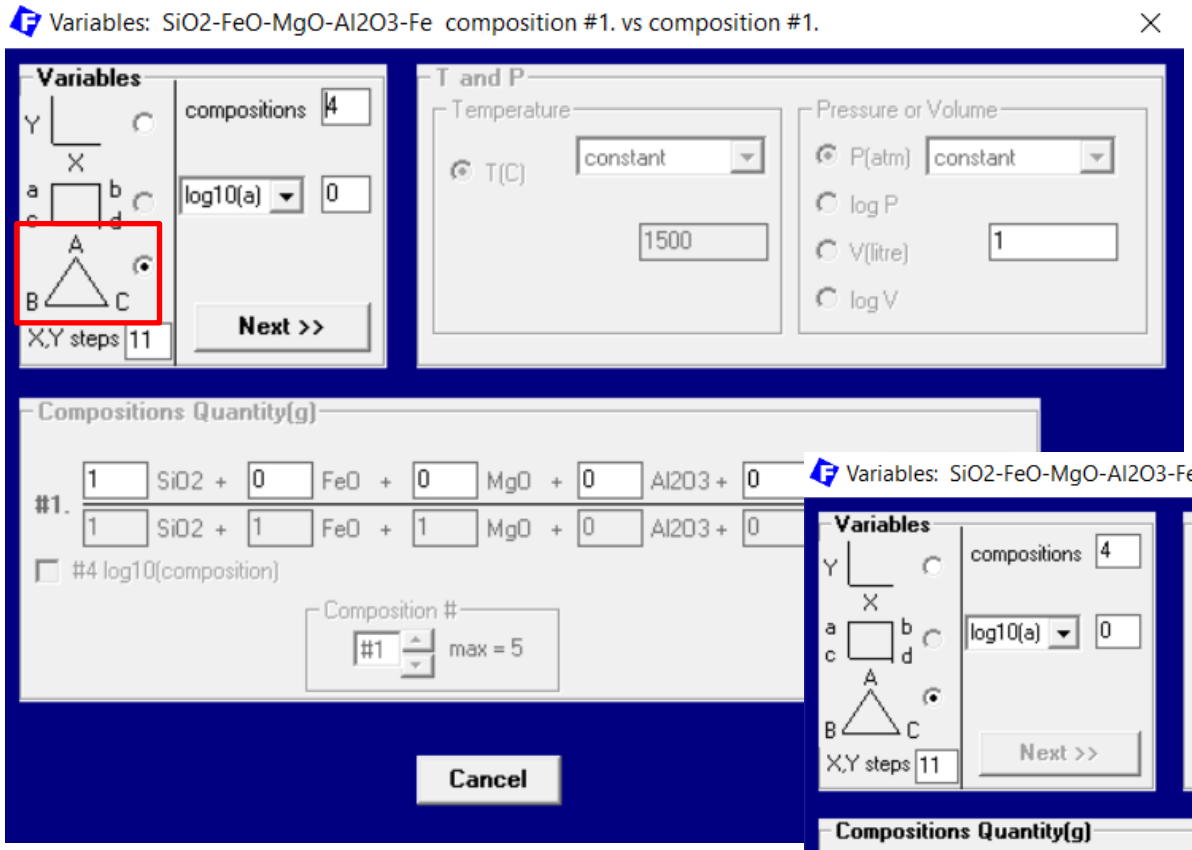
Select pure solid and liquid of Fe for Fe-saturation condition



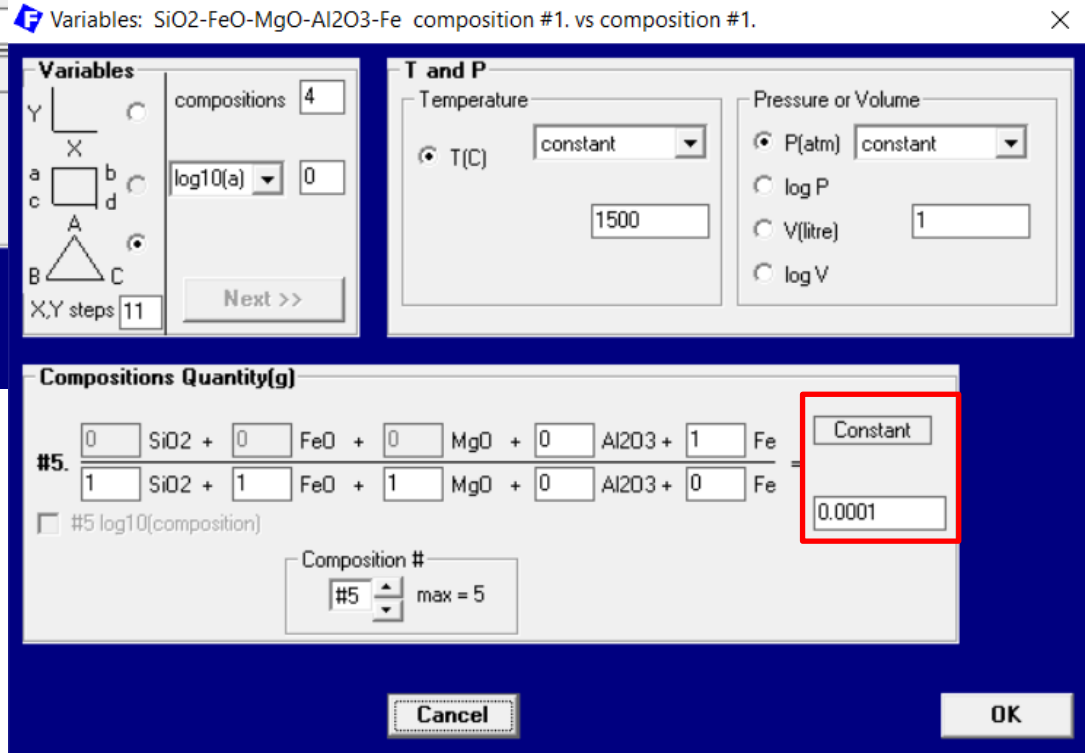
Phase diagram of SiO_2-MgO-Al_2O_3-FeO-Fe



Phase diagram of SiO_2-MgO-Al_2O_3-FeO-Fe



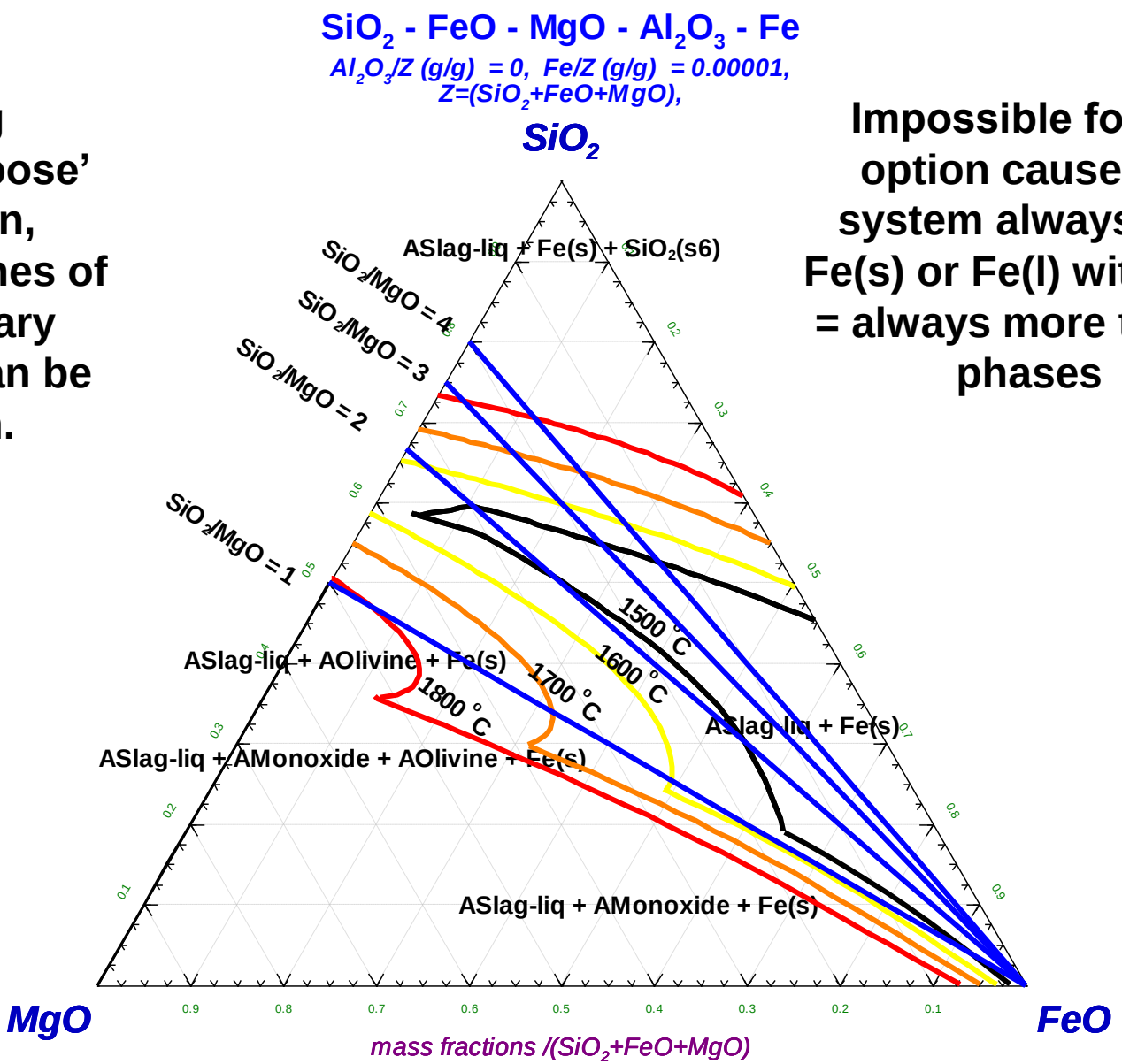
Ternary phase diagram of FeO-MgO-SiO_2 at constant Al_2O_3 with Fe-saturation



Add small amount of Fe

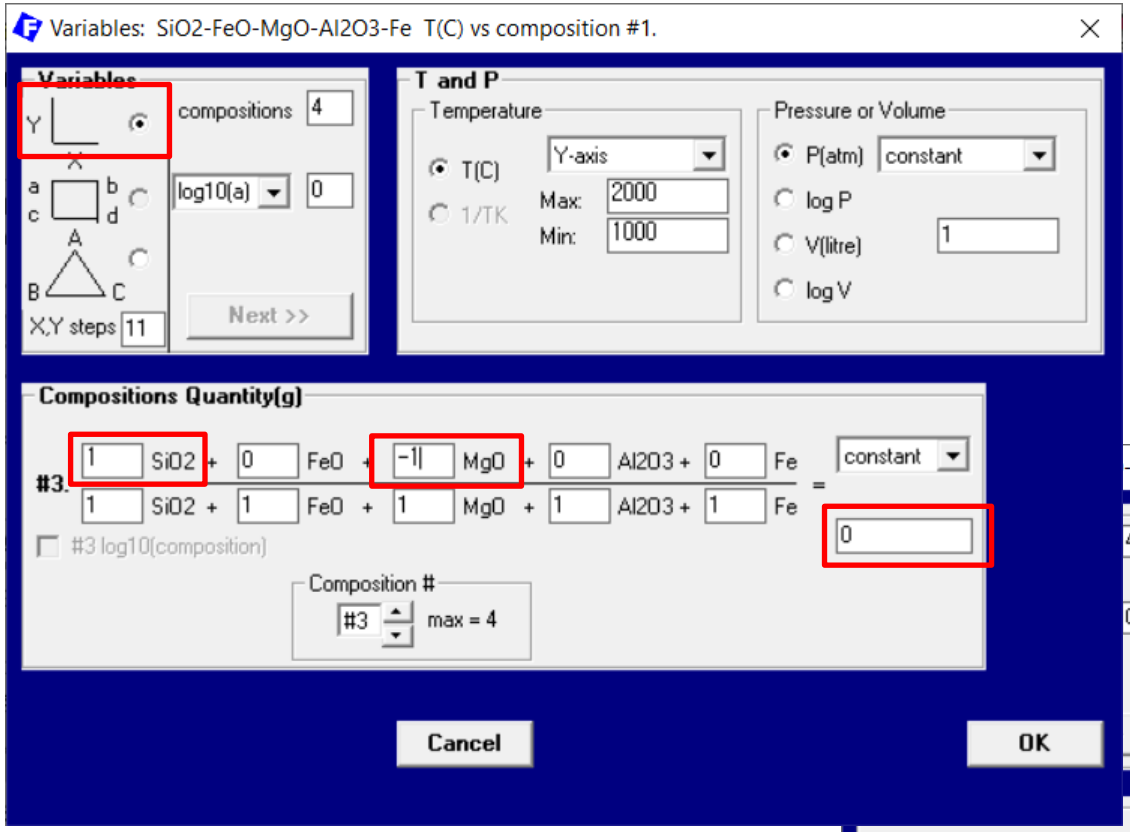
Phase diagram of SiO_2-MgO-Al_2O_3-FeO-Fe

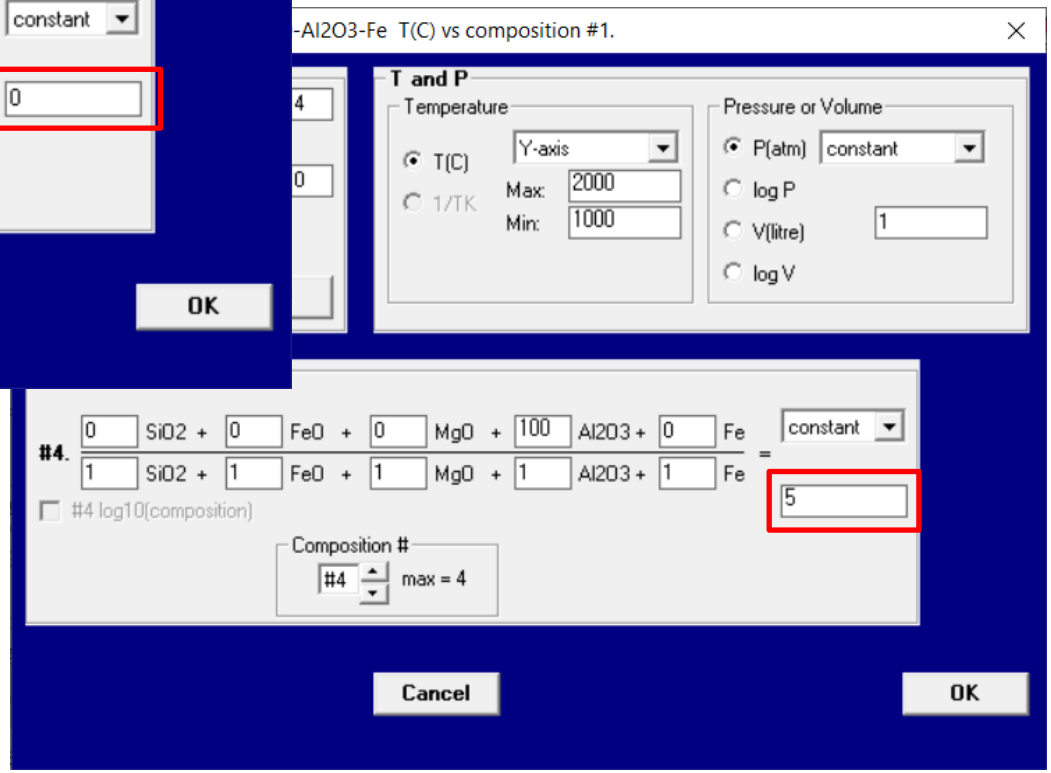
Using 'superimpose' function, liquidus lines of the ternary system can be drawn.



Impossible for 'O' option cause the system always has Fe(s) or Fe(l) with slag = always more than 2 phases

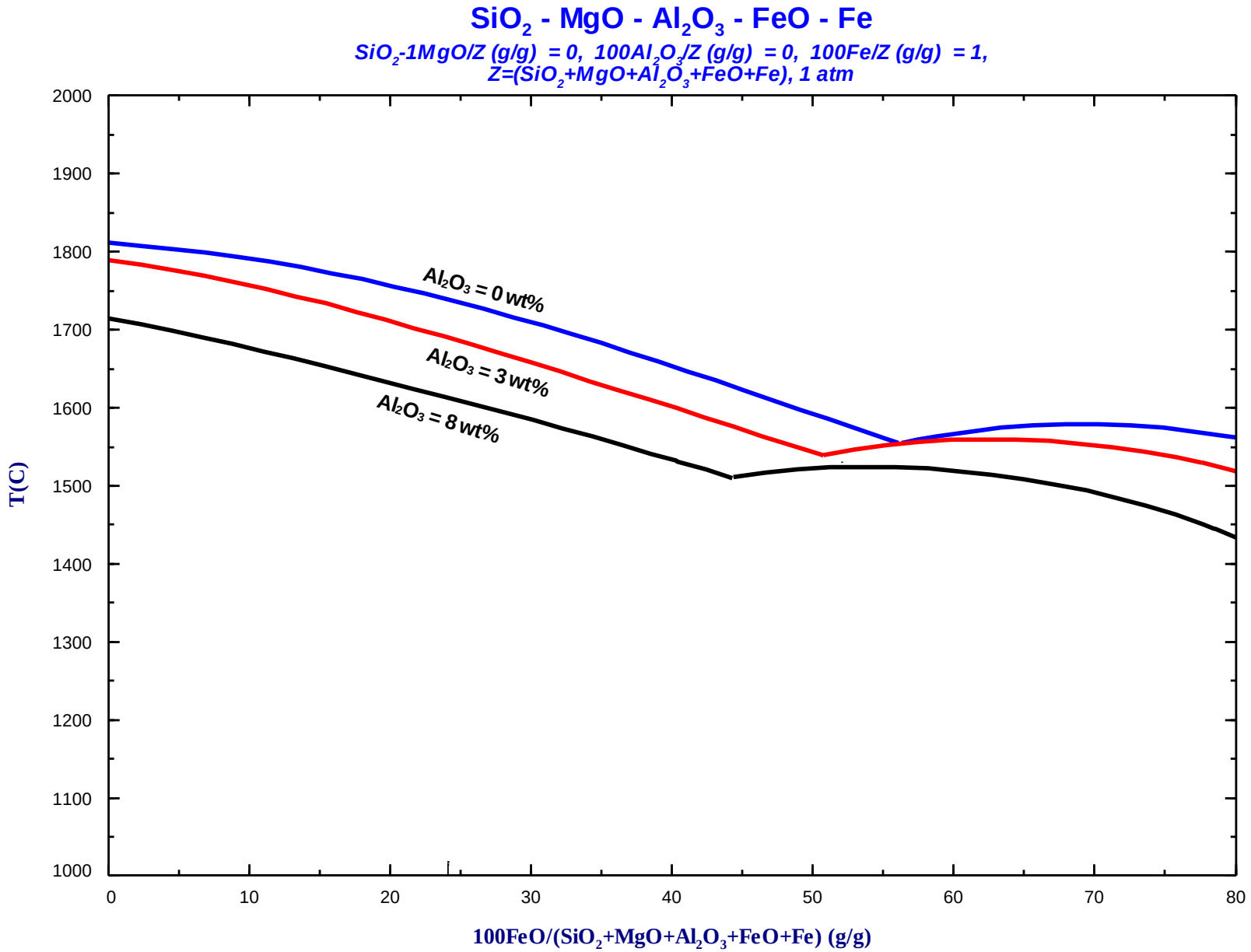
Phase diagram of SiO_2-MgO-Al_2O_3-FeO-Fe





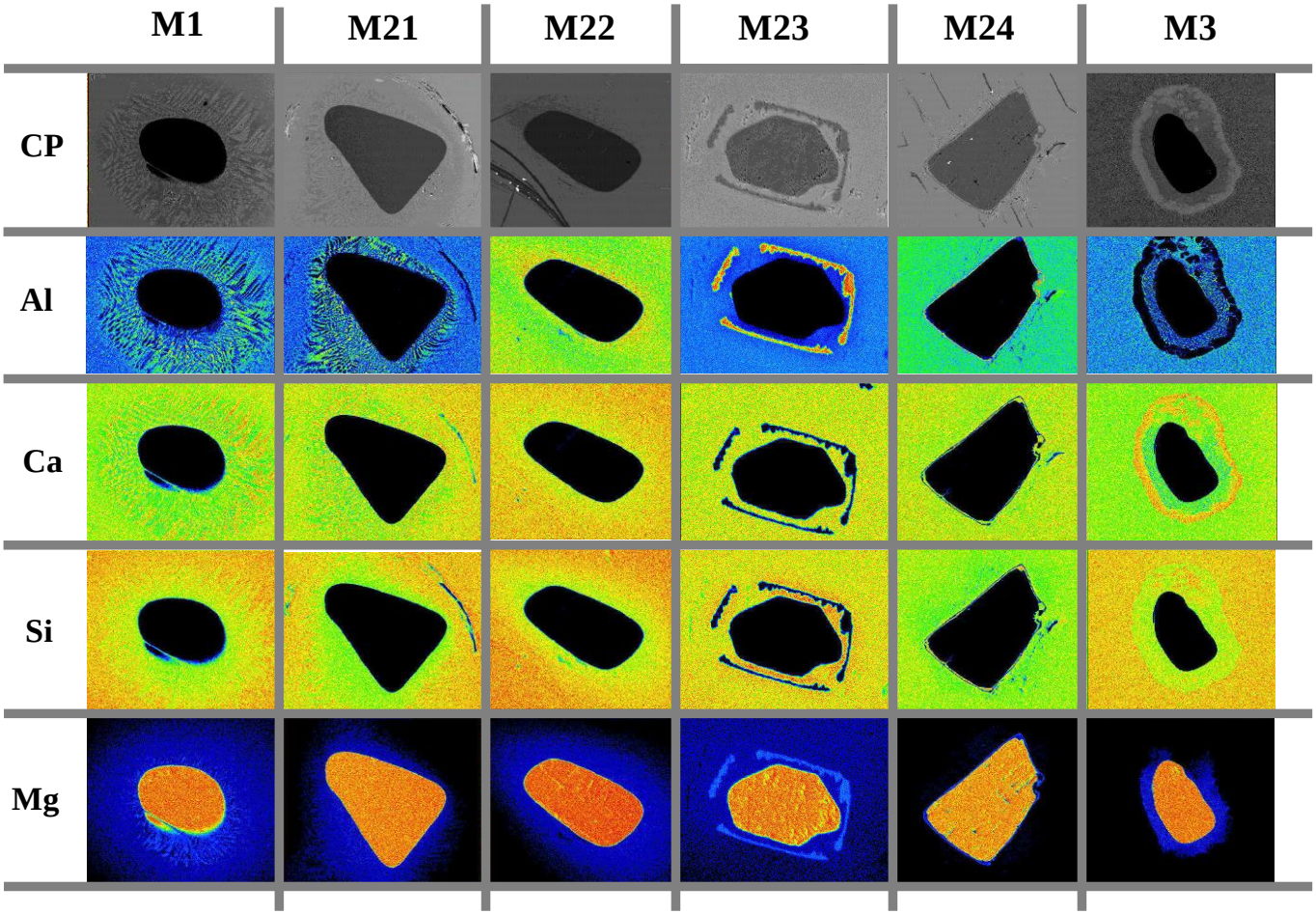
With change 0 to 8 wt% of Al_2O_3 at constant SiO_2/MgO=1 under Fe-saturation

Phase diagram of SiO_2-MgO-Al_2O_3-FeO-Fe



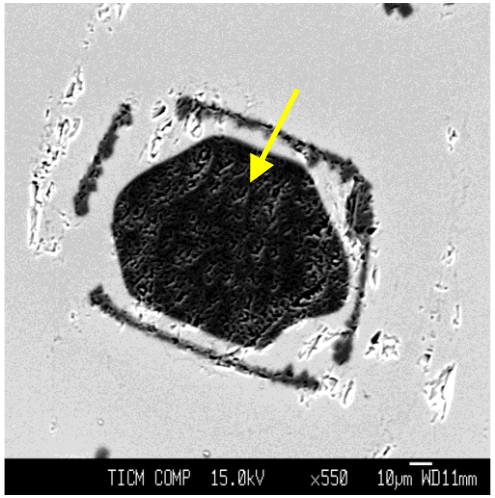
Dissolution of Inclusions into Molten Slags

Phase diagram between slag and inclusion to understand the inclusion dissolution mechanism

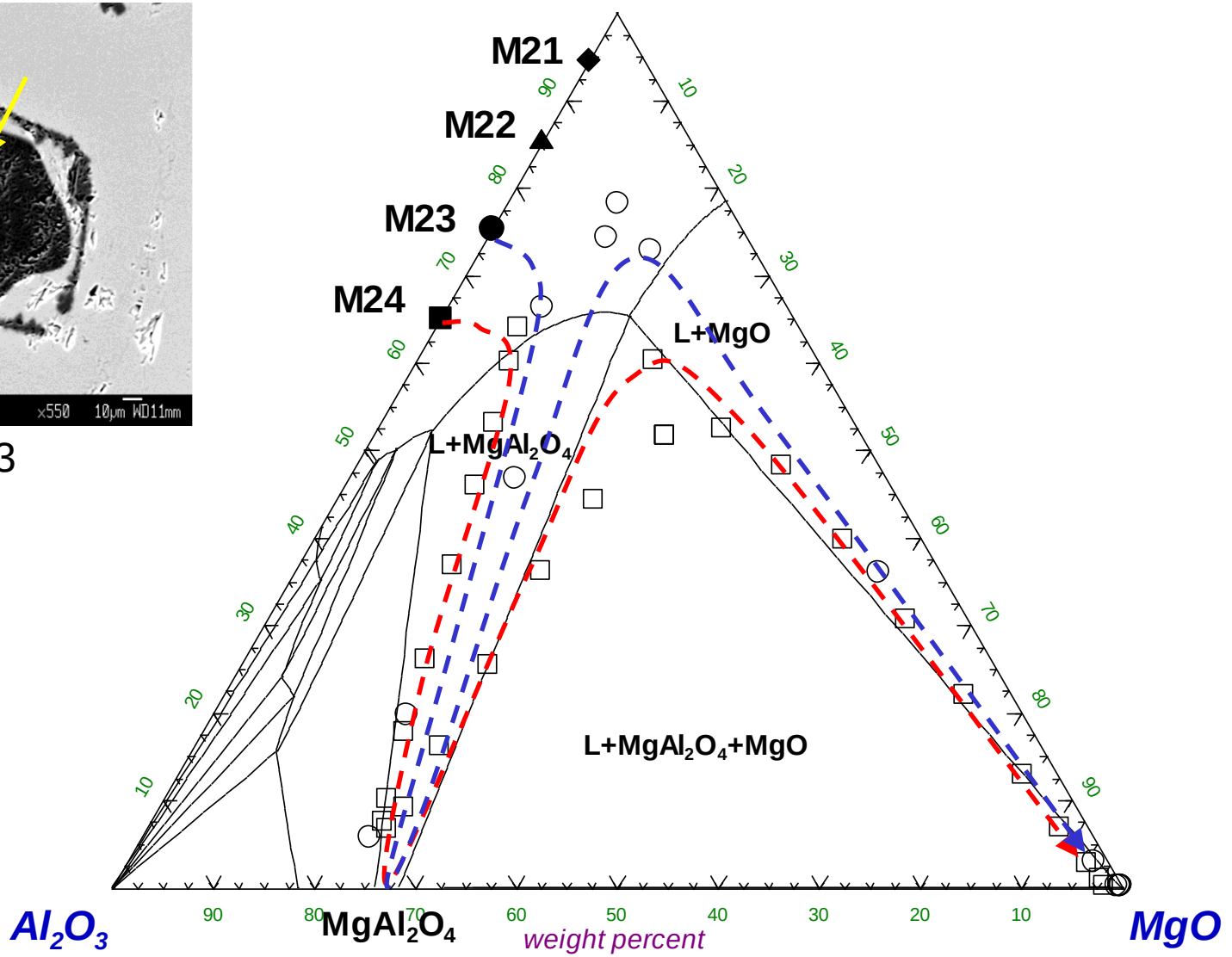


Park, Jung and Lee: ISIJ Inter. No. 11, 2006

Dissolution of Inclusions into Molten Slags

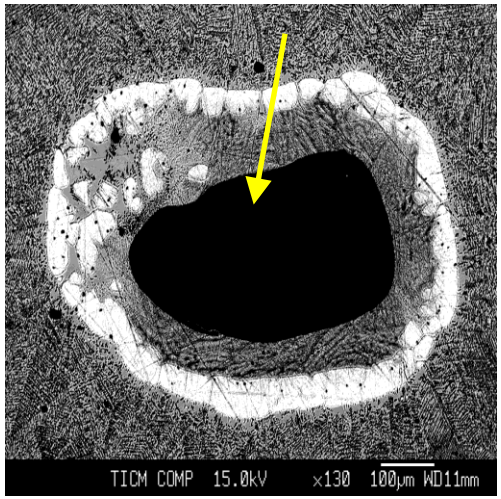


M23

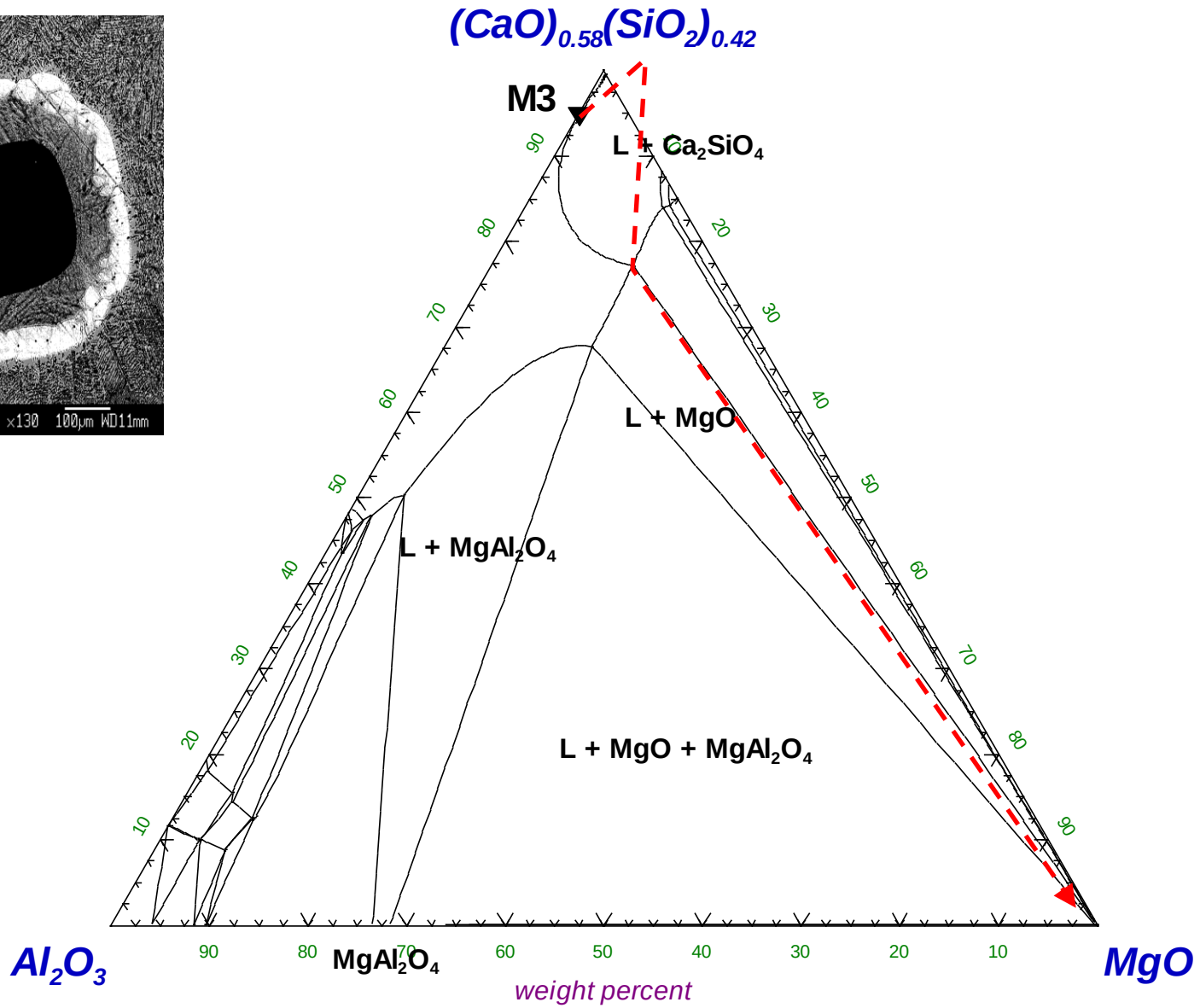


Park, Jung and Lee: ISIJ Inter. No. 11, 2006

Dissolution of Inclusions into Molten Slags



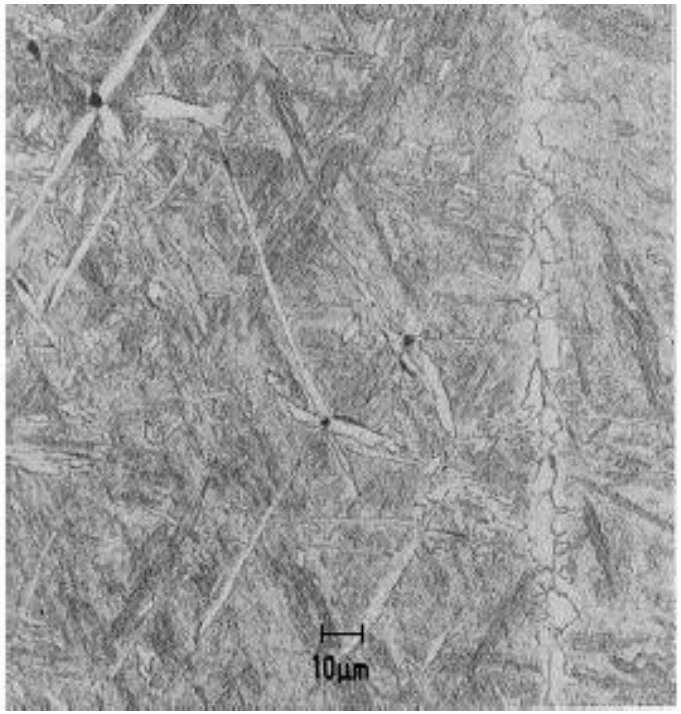
M3

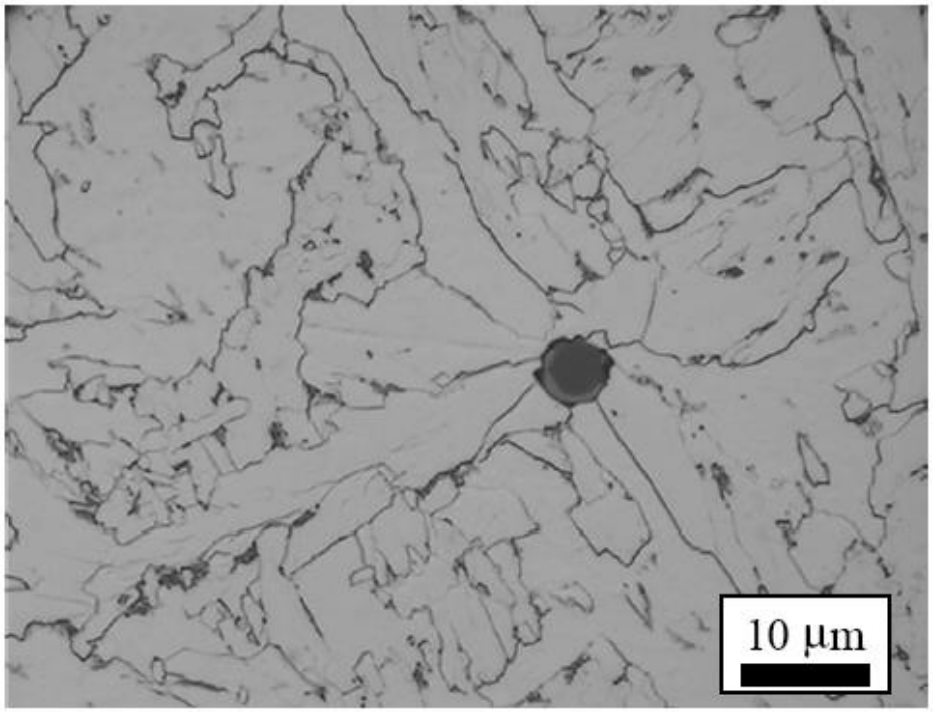


Park, Jung and Lee: ISIJ Inter. No. 11, 2006

Applications to Oxide metallurgy (Inclusion control)

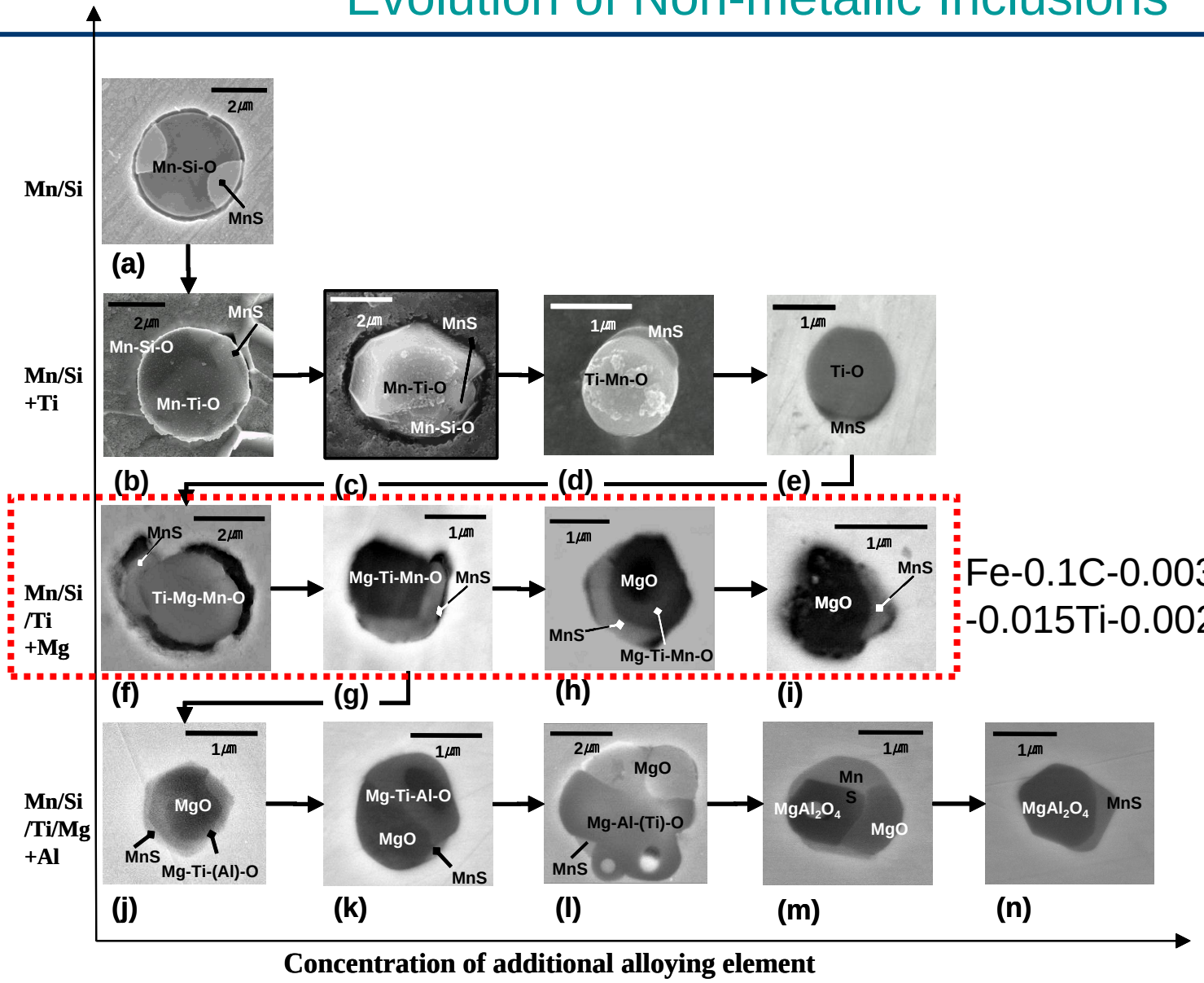
- Evolution of non-metallic inclusions: Formation of acicular ferrite -





- Non-metallic inclusions: nucleation sites for acicular ferrite
- Acicular ferrite: enhances the strength of steel

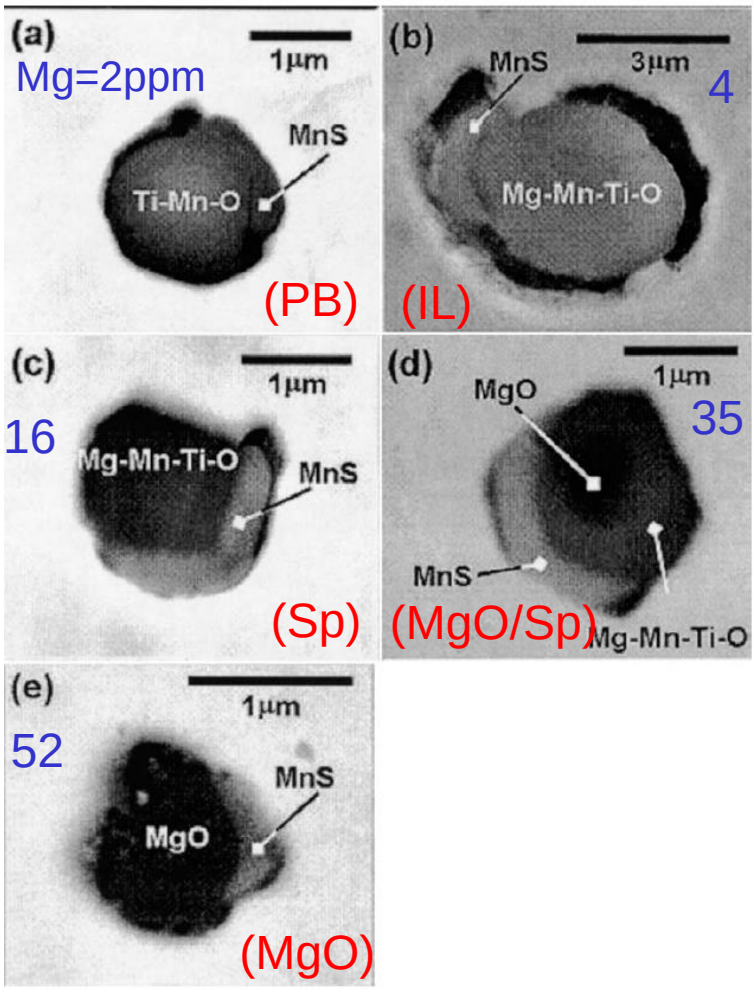
Evolution of Non-metallic Inclusions

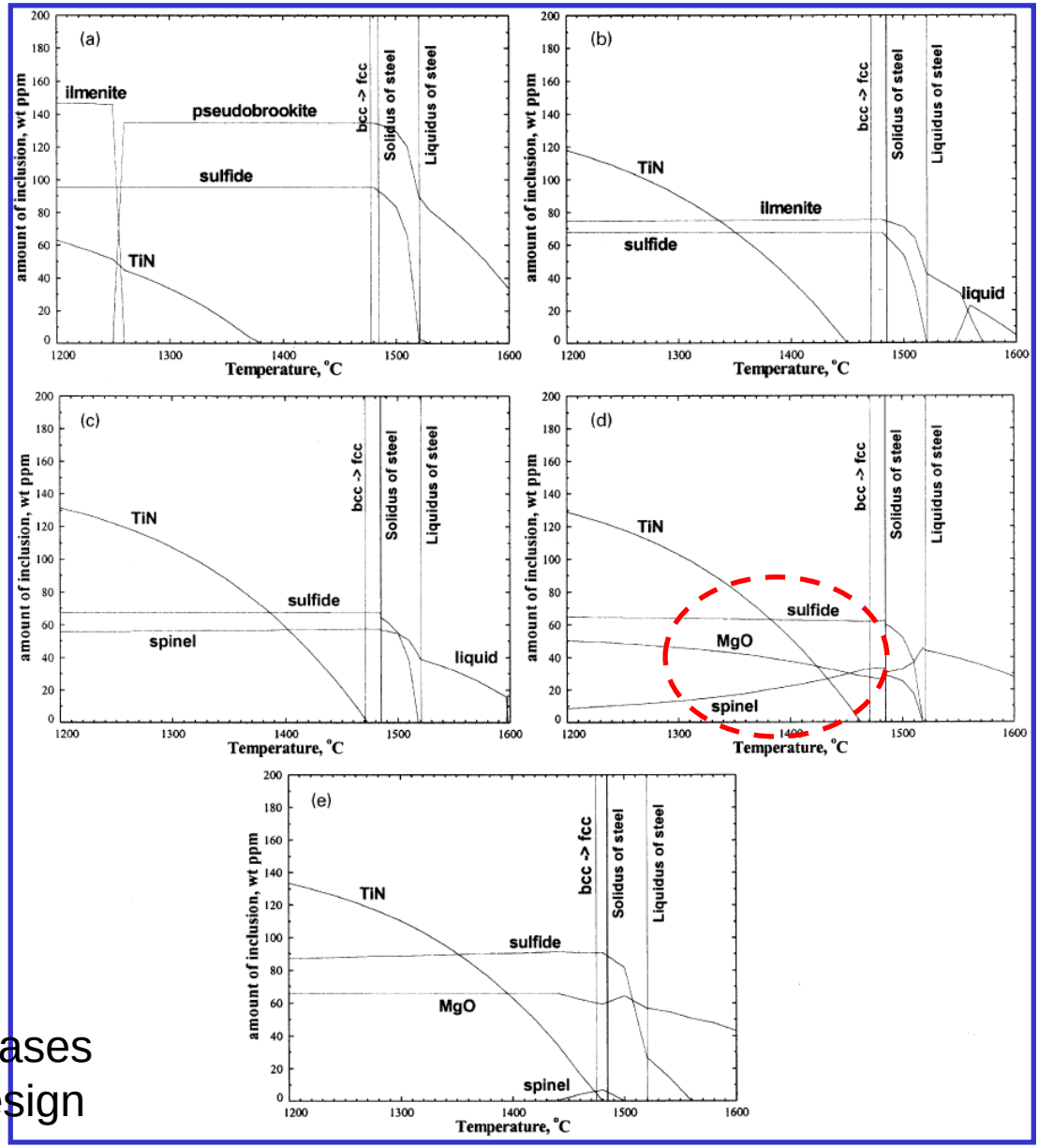


Fe-0.1C-0.0035S-1.45Mn-0.1Si -0.015Ti-0.0025O-0.03N+Mg

Morphologies of typical inclusions found in Fe-C-Mn-Si-O-S-Ti-Mg-Al-N

Evolution of Non-metallic Inclusions



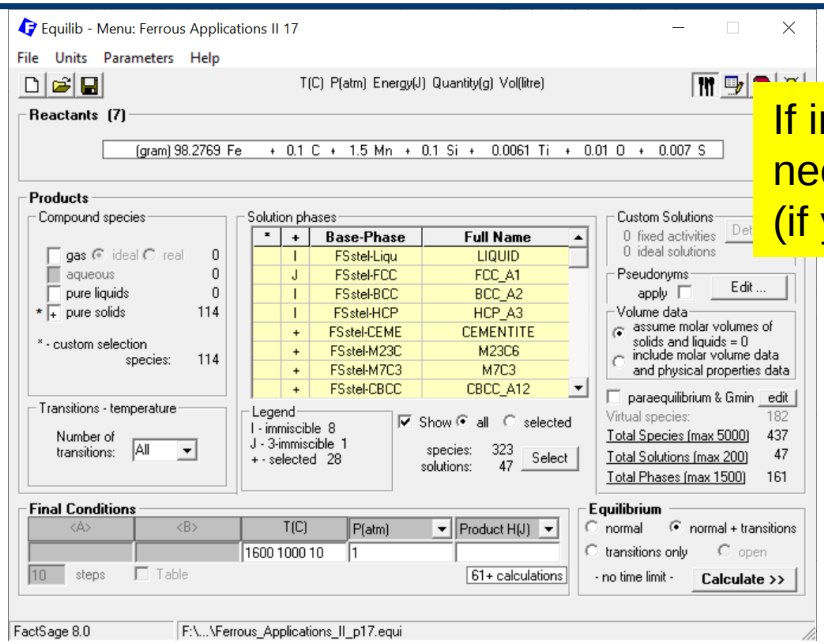


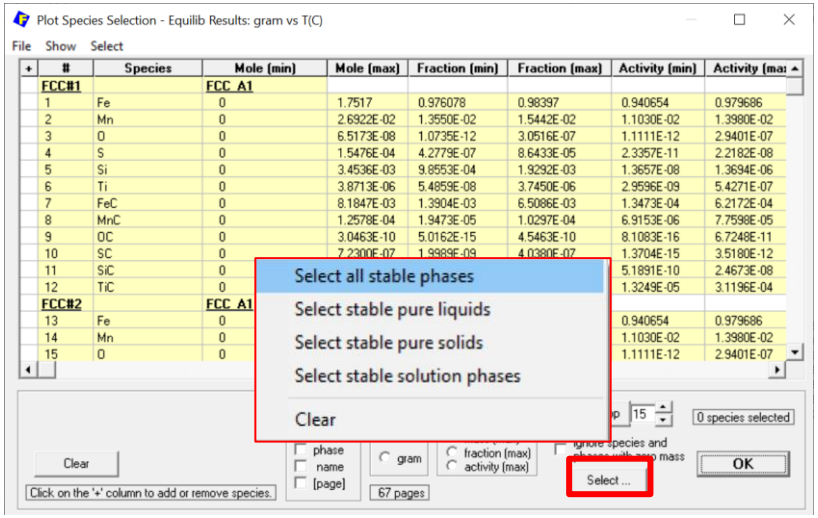
Thermodynamic Calculations

- Accurate prediction of inclusions phases
- Application to high strength steel design

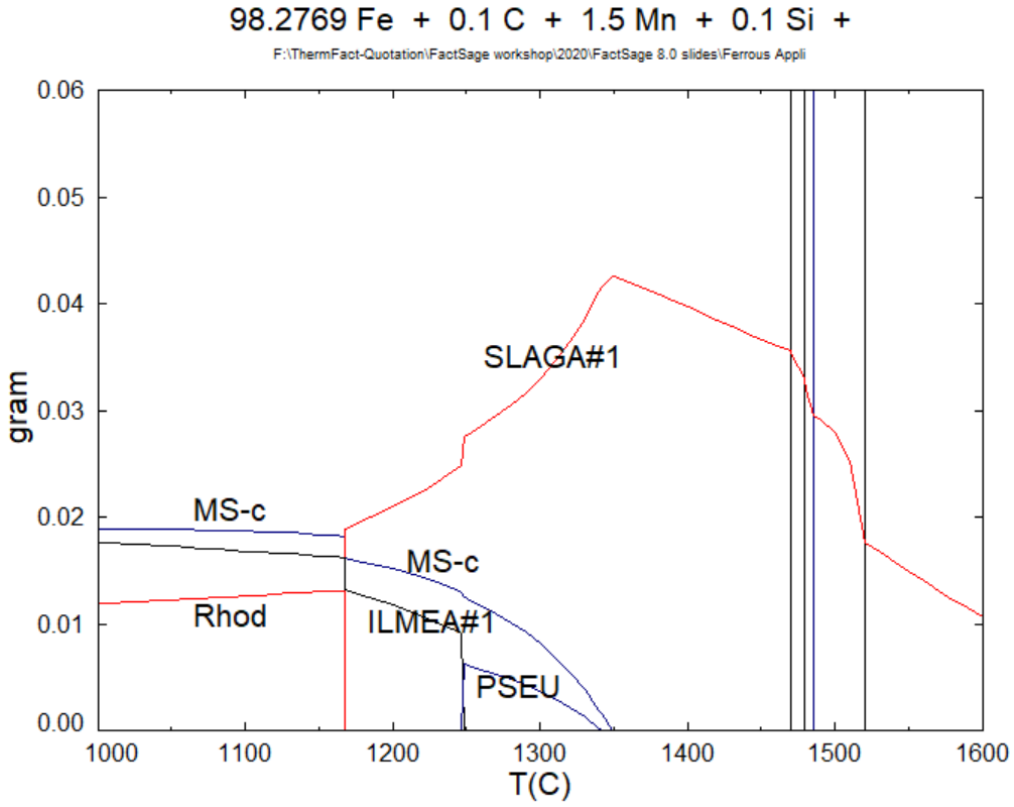
Inclusion evolution with temperature: Mn/Si/Ti steel

If inclusion evolution **in both liquid steel and solid steel** is needed, we recommend to use FToxid and FSStel database (if you want to use FTmisc-FeLq special caution is needed)



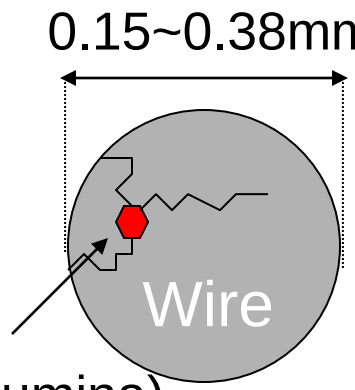


Select → “Select all stable phases”



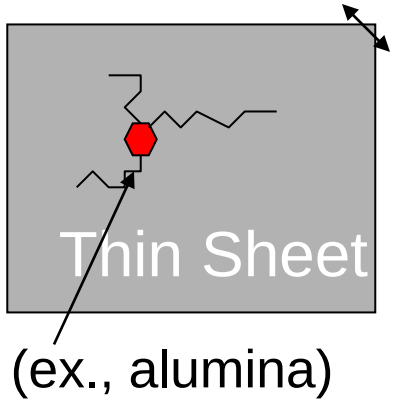
Application to Tire-Cord Steel (Mn/Si deoxidation)

Tire-Cord Steel



Crack Initiation

Fe-36%Ni Invar Steel

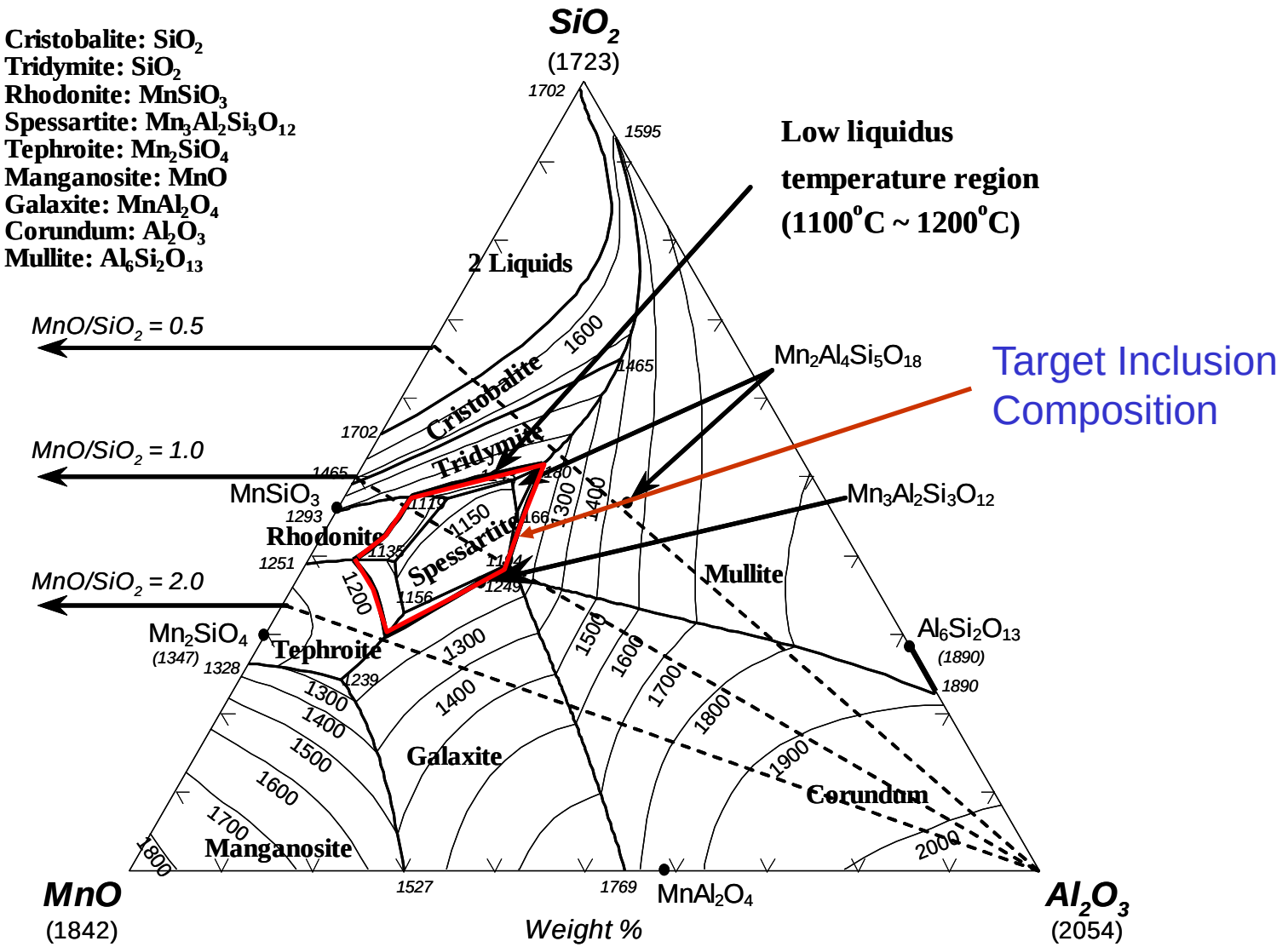


Crack Initiation
Surface Quality

- Undeformable Inclusion should be removed
- Liquid phase is desirable at process temperature (~1200°C)

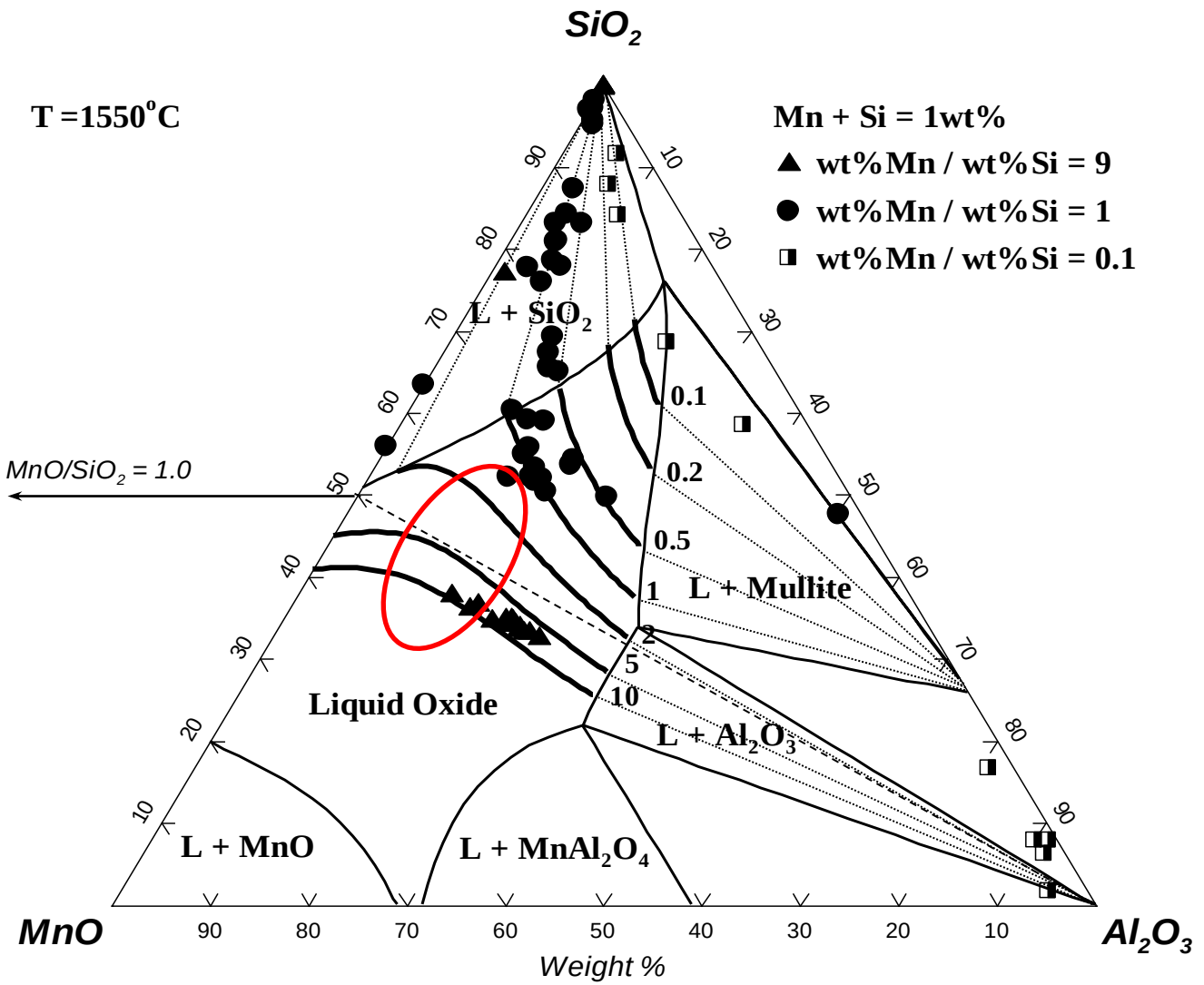
→ Mn/Si Deoxidation

MnO-Al_2O_3-SiO_2 Phase Diagram



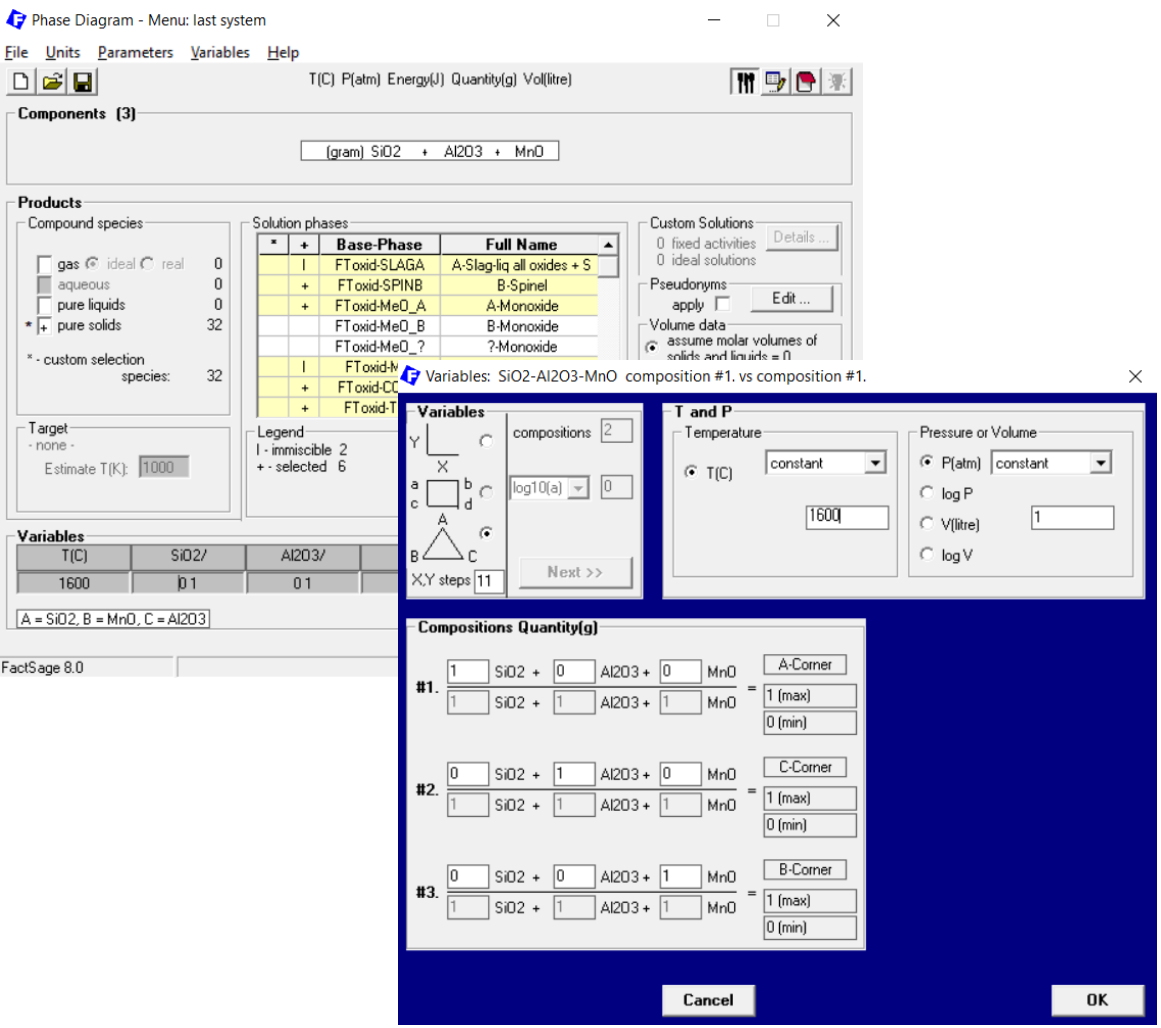
Jung et al., Metall. Mater. Trans. B, 2004, vol. 35B, pp. 259-268

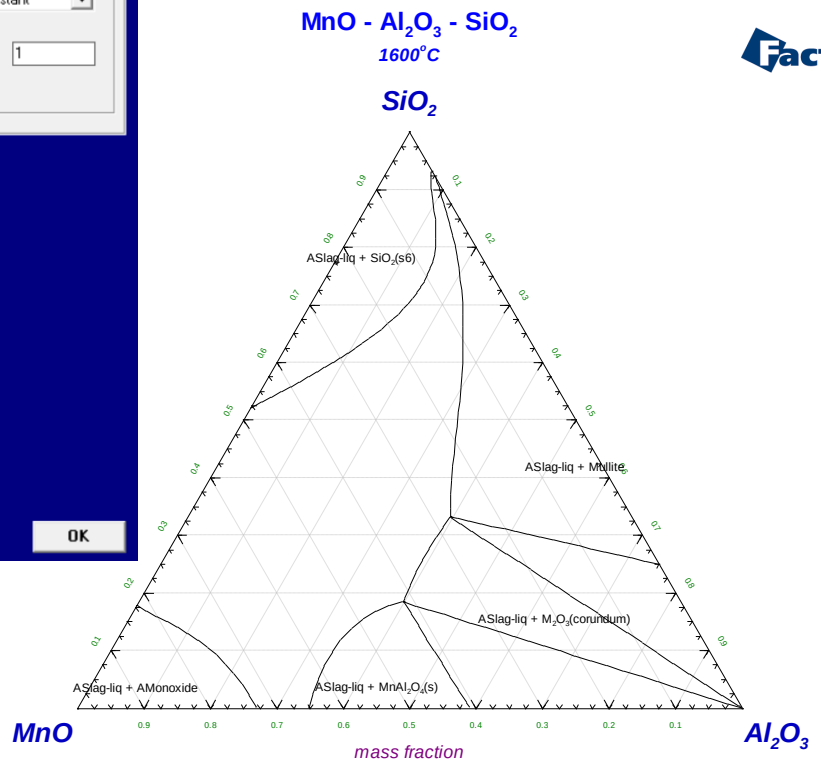
Inclusion composition with steel composition



Jung et al., Metall. Mater. Trans. B, 2004, vol. 35B, pp. 259-268
Kang and Lee, ISIJ Inter., 2004.

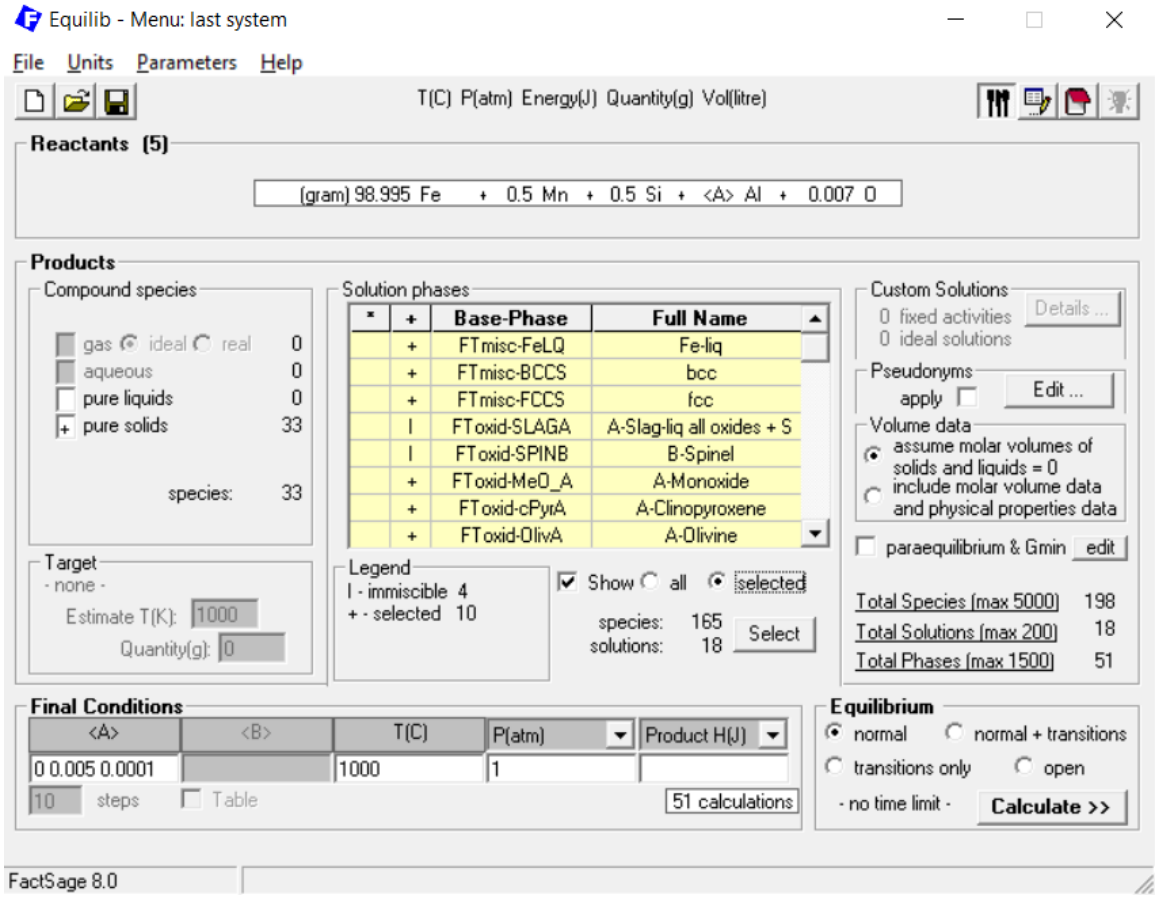
Inclusion calculation in Mn/Si deoxidation





Inclusion calculation in Mn/Si deoxidation

Calculation of the inclusion trajectory using Equilib



The compositions of Mn and Si are set based on the target Mn/Si ratio and Mn+Si content
Oxygen content should be controlled reasonably. If O is too high, Mn and Si will be largely changed from original target composition after rxn with oxygen.

Inclusion calculation in Mn/Si deoxidation

Equilib - Results A=0.001 (page 11/51)

Output Edit Show Pages Final Conditions

T(C) P(atm) Energy(J) Quantity(g) Vol(litre)

A=0 | A=1.00E-04 | A=0.0002 | A=0.0003 | A=0.0004 | A=0.0005 | A=0.0006 | A=0.0007 | A=0.0008
A=0.0018 | A=0.0019 | A=0.002 | A=0.0021 | A=0.0022 | A=0.0023 | A=0.0024
A=0.0009 | - A=0.001 - | A=0.0011 | A=0.0012 | A=0.0013 | A=0.0014 | A=0.0015 | A=0.0016 | A=0.0017

```
                                                              FactSage 8.0
(gram) 98.995 Fe  +  0.5 Mn  +  0.5 Si  +  <A> Al  +

(gram) 0.007 O  =

   99.998     gram  Fe-liq
   (99.998 gram, 1.7998 mol)
          (1600 C, 1 atm,      a=1.0000)
          ( 98.997      wt.% Fe
          + 2.2191E-04 wt.% Al
          + 0.49858     wt.% Mn
          + 4.5488E-03 wt.% O
          + 0.49882     wt.% Si
          + 6.3879E-05 wt.% Al1O
          + 1.3726E-04 wt.% Si1O
          + 3.7704E-04 wt.% Mn1O
          + 4.9534E-08 wt.% Al2O)

          System component          Amount/mol     Amount/gram    Mole fraction    Mass fraction
          Fe                        1.7727          98.995          0.98492          0.98997
          Mn                        9.0805E-03      0.49886         5.0452E-03       4.9888E-03
          Si                        1.7763E-02      0.49890         9.8696E-03       4.9891E-03
          Al                        9.7117E-06      2.6204E-04      5.3960E-06       2.6204E-06
          O                         2.9422E-04      4.7073E-03      1.6347E-04       4.7074E-05

+ 5.4382E-03 gram  Slag-liq#1
   (5.4382E-03 gram, 7.6652E-05 mol)
+ 0           gram  Slag-liq#2
          (1600 C, 1 atm,      a=1.0000)
          ( 25.640      wt.% Al2O3
          + 43.413      wt.% SiO2
          + 3.9764      wt.% FeO
          + 1.1443E-03 wt.% Fe2O3
          + 26.966      wt.% MnO
          + 4.1969E-03 wt.% Mn2O3)

          Site fraction of sublattice constituents:
          Al                        0.30279
          Si                        0.43499
          Fe2+                      3.3321E-02
          Fe3+                      8.6284E-06
          Mn2+                      0.22886
          Mn3+                      3.2009E-05
          ------------------------------------
          O                         1.0000
```

Mn + Si + Al + O → (Mn,Si,Al) oxide inclusion

After deoxidation, Mn ~ 0.5 and Si ~ 0.5

(Target steel composition: Mn/Si = 1 and Mn+Si = 1)

→ **Extraction of slag composition**

Spreadsheet - Equilib Page 1/51 : T(C) = 1600, P(atm) = 1

File Edit Show Select Stable

Selected: 6/185 | Spreadsheet Species | Pages: 1 – 51 [page]

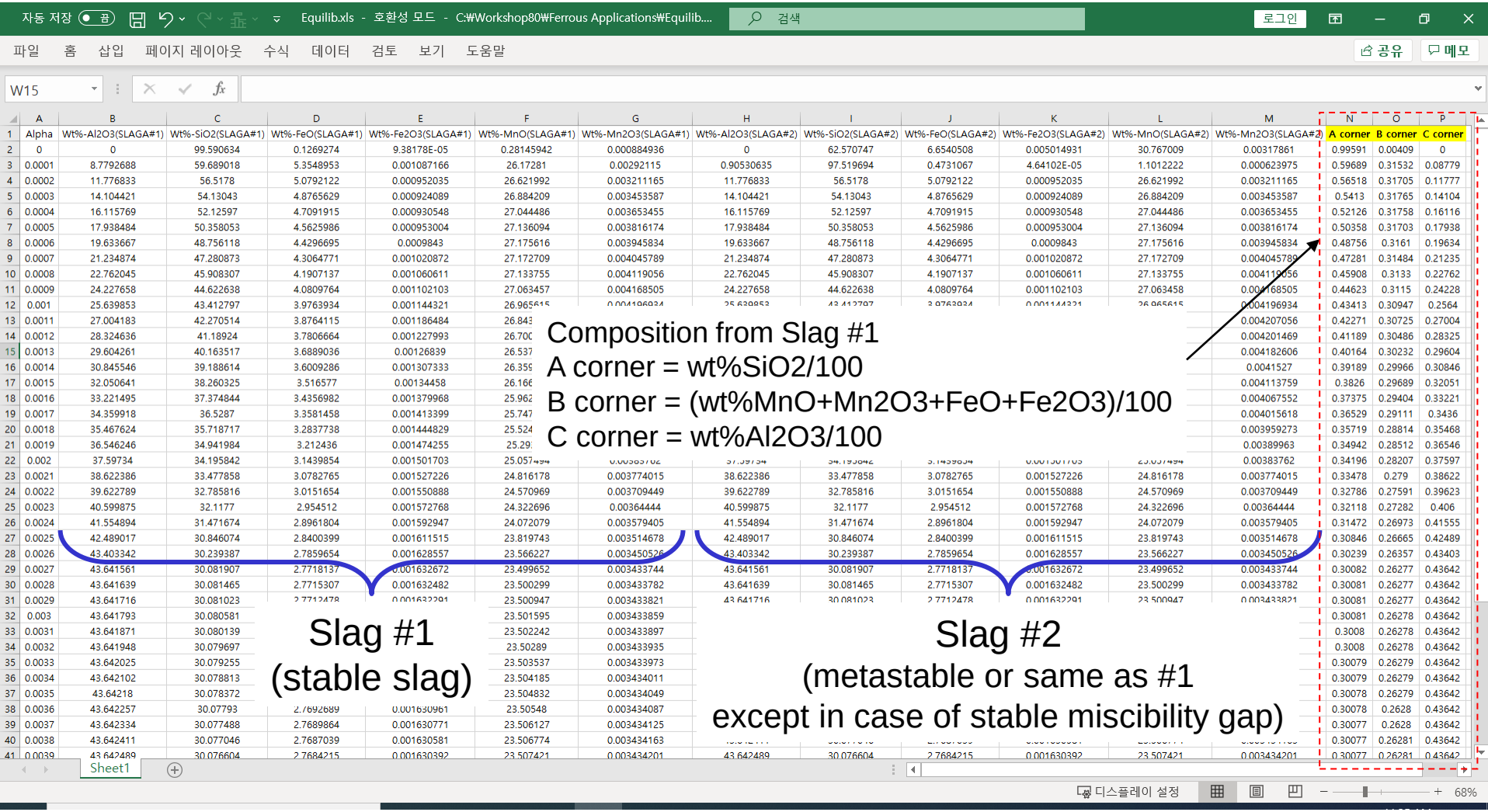
Page 1/51 : T(C) = 1600, P(atm) = 1

+	Code	Species	Data	Phase	T	V	Activity	Minimum	Maximum
	46	Fe:Va(BCCS)	FTmisc	FTmisc-BCCS			0.9546	0.9546 [1]	0.9547 [27]
	47	Mn:Va(BCCS)	FTmisc	FTmisc-BCCS			4.2376E-03	4.2273E-03 [27]	4.2394E-03 [51]
	48	Fe:Va(FCCS)	FTmisc	FTmisc-FCCS			0.9469	0.9469 [1]	0.9470 [27]
	49	Mn:Va(FCCS)	FTmisc	FTmisc-FCCS			4.0246E-03	4.0148E-03 [27]	4.0263E-03 [51]
+	50	Al2O3(SLAGA)	FToxid	FToxid-SLAGA#				0 [1]	0.2308 [51]
+	51	SiO2(SLAGA)	FToxid	FToxid-SLAGA#			0.9628	0.2550 [51]	0.9628 [1]
+	52	FeO(SLAGA)	FToxid	FToxid-SLAGA#			2.6267E-02	1.3509E-02 [51]	2.6267E-02 [1]
+	53	Fe2O3(SLAGA)	FToxid	FToxid-SLAGA#			3.3986E-08	4.6227E-09 [51]	3.3986E-08 [1]
+	54	MnO(SLAGA)	FToxid	FToxid-SLAGA#			3.8735E-02	1.9928E-02 [51]	3.8735E-02 [1]
+	55	Mn2O3(SLAGA)	FToxid	FToxid-SLAGA#			1.0321E-08	1.4048E-09 [51]	1.0321E-08 [1]
	56	Fe3O4(SPINB)	FToxid	FToxid-SPINB#			2.0314E-09	1.4210E-10 [51]	2.0314E-09 [1]
	57	Fe3O4[1-](SPINB)	FToxid	FToxid-SPINB#			3.1323E-10	3.1323E-10 [1]	1.1148E-07 [8]
	58	Fe3O4[1+](SPINB)	FToxid	FToxid-SPINB#			6.8466E-09	4.5641E-13 [51]	6.8466E-09 [1]
	59	Fe3O4[2-](SPINB)	FToxid	FToxid-SPINB#			3.3630E-11	3.3630E-11 [1]	1.2051E-05 [11]
	60	Fe1O4[5-](SPINB)	FToxid	FToxid-SPINB#			3.0706E-23	3.0706E-23 [1]	1.5756E-08 [12]
	61	Fe1O4[6-](SPINB)	FToxid	FToxid-SPINB#			3.2971E-24	3.2971E-24 [1]	1.9180E-06 [12]
	62	Fe1Al2O4(SPINB)	FToxid	FToxid-SPINB#				0 [1]	1.5976E-02 [28]
	63	Al3O4[1+](SPINB)	FToxid	FToxid-SPINB#				0 [1]	0.3866 [51]

'+' denotes all the Species Properties as defined in the Spreadsheet Setup.

Select All | Clear | OK

Inclusion calculation in Mn/Si deoxidation



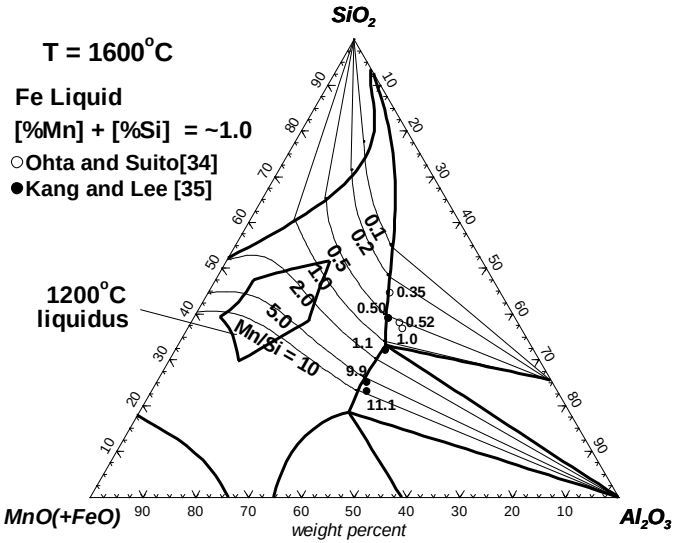
Alpha	Wt%-Al2O3(SLAGA#1)	Wt%-SiO2(SLAGA#1)	Wt%-FeO(SLAGA#1)	Wt%-Fe2O3(SLAGA#1)	Wt%-MnO(SLAGA#1)	Wt%-Mn2O3(SLAGA#1)	Wt%-Al2O3(SLAGA#2)	Wt%-SiO2(SLAGA#2)	Wt%-FeO(SLAGA#2)	Wt%-Fe2O3(SLAGA#2)	Wt%-MnO(SLAGA#2)	Wt%-Mn2O3(SLAGA#2)	A corner	B corner	C corner
0	0	99.590634	0.1269274	9.38178E-05	0.28145942	0.000884936	0	62.570747	6.6540508	0.005014931	30.767009	0.00317861	0.99591	0.00409	0
0.0001	8.7792688	59.689018	5.3548953	0.001087166	26.17281	0.00292115	0.90530635	97.519694	0.4731067	4.64102E-05	1.1012222	0.000623975	0.59689	0.31532	0.08779
0.0002	11.776833	56.5178	5.0792122	0.000952035	26.621992	0.003211165	11.776833	56.5178	5.0792122	0.000952035	26.621992	0.003211165	0.56518	0.31705	0.11777
0.0003	14.104421	54.13043	4.8765629	0.000924089	26.884209	0.003453587	14.104421	54.13043	4.8765629	0.000924089	26.884209	0.003453587	0.5413	0.31765	0.14104
0.0004	16.115769	52.12597	4.7091915	0.000930548	27.044486	0.003653455	16.115769	52.12597	4.7091915	0.000930548	27.044486	0.003653455	0.52126	0.31758	0.16116
0.0005	17.938484	50.358053	4.5625986	0.000953004	27.136094	0.003816174	17.938484	50.358053	4.5625986	0.000953004	27.136094	0.003816174	0.50358	0.31703	0.17938
0.0006	19.633667	48.756118	4.4296695	0.0009843	27.175616	0.003945834	19.633667	48.756118	4.4296695	0.0009843	27.175616	0.003945834	0.48756	0.3161	0.19634
0.0007	21.234874	47.280873	4.3064771	0.001020872	27.172709	0.004045789	21.234874	47.280873	4.3064771	0.001020872	27.172709	0.004045789	0.47281	0.31484	0.21235
0.0008	22.762045	45.908307	4.1907137	0.001060611	27.133755	0.004119056	22.762045	45.908307	4.1907137	0.001060611	27.133755	0.004119056	0.45908	0.3133	0.22762
0.0009	24.227658	44.622638	4.0809764	0.001102103	27.063457	0.004168505	24.227658	44.622638	4.0809764	0.001102103	27.063458	0.004168505	0.44623	0.3115	0.24228
0.001	25.639853	43.412797	3.9763934	0.001144321	26.965615	0.004196934	25.639853	43.412797	3.9763934	0.001144321	26.965615	0.004196934	0.43413	0.30947	0.2564
0.0011	27.004183	42.270514	3.8764115	0.001186484	26.843							0.004207056	0.42271	0.30725	0.27004
0.0012	28.324636	41.18924	3.7806664	0.001227993	26.700							0.004201469	0.41189	0.30486	0.28325
0.0013	29.604261	40.163517	3.6889036	0.00126839	26.537							0.004182606	0.40164	0.30232	0.29604
0.0014	30.845546	39.188614	3.6009286	0.001307333	26.359							0.0041527	0.39189	0.29966	0.30846
0.0015	32.050641	38.260325	3.516577	0.00134458	26.166							0.004113759	0.3826	0.29689	0.32051
0.0016	33.221495	37.374844	3.4356982	0.001379968	25.962							0.004067552	0.37375	0.29404	0.33221
0.0017	34.359918	36.5287	3.3581458	0.001413399	25.747							0.004015618	0.36529	0.29111	0.3436
0.0018	35.467624	35.718717	3.2837738	0.001444829	25.524							0.003959273	0.35719	0.28814	0.35468
0.0019	36.546246	34.941984	3.212436	0.001474255	25.29							0.00389963	0.34942	0.28512	0.36546
0.002	37.59734	34.195842	3.1439854	0.001501703	25.057							0.00383762	0.34196	0.28207	0.37597
0.0021	38.622386	33.477858	3.0782765	0.001527226	24.816178	0.003774015	38.622386	33.477858	3.0782765	0.001527226	24.816178	0.003774015	0.33478	0.279	0.38622
0.0022	39.622789	32.785816	3.0151654	0.001550888	24.570969	0.003709449	39.622789	32.785816	3.0151654	0.001550888	24.570969	0.003709449	0.32786	0.27591	0.39623
0.0023	40.599875	32.1177	2.954512	0.001572768	24.322696	0.00364444	40.599875	32.1177	2.954512	0.001572768	24.322696	0.00364444	0.32118	0.27282	0.406
0.0024	41.554894	31.471674	2.8961804	0.001592947	24.072079	0.003579405	41.554894	31.471674	2.8961804	0.001592947	24.072079	0.003579405	0.31472	0.26973	0.41555
0.0025	42.489017	30.846074	2.8400399	0.001611515	23.819743	0.003514678	42.489017	30.846074	2.8400399	0.001611515	23.819743	0.003514678	0.30846	0.26665	0.42489
0.0026	43.403342	30.239387	2.7859654	0.001628557	23.566227	0.003450526	43.403342	30.239387	2.7859654	0.001628557	23.566227	0.003450526	0.30239	0.26357	0.43403
0.0027	43.641561	30.081907	2.7718137	0.001632672	23.499652	0.003433744	43.641561	30.081907	2.7718137	0.001632672	23.499652	0.003433744	0.30082	0.26277	0.43642
0.0028	43.641639	30.081465	2.7715307	0.001632482	23.500299	0.003433782	43.641639	30.081465	2.7715307	0.001632482	23.500299	0.003433782	0.30081	0.26277	0.43642
0.0029	43.641716	30.081023	2.7712478	0.001632291	23.500947	0.003433821	43.641716	30.081023	2.7712478	0.001632291	23.500947	0.003433821	0.30081	0.26277	0.43642
0.003	43.641793	30.080581	2.7709619	0.001632101	23.501595	0.003433859							0.30081	0.26278	0.43642
0.0031	43.641871	30.080139	2.7706759	0.001631911	23.502242	0.003433897							0.3008	0.26278	0.43642
0.0032	43.641948	30.079697	2.7703899	0.001631721	23.50289	0.003433935							0.3008	0.26278	0.43642
0.0033	43.642025	30.079255	2.770104	0.001631531	23.503537	0.003433973							0.30079	0.26279	0.43642
0.0034	43.642102	30.078813	2.769818	0.001631341	23.504185	0.003434011							0.30079	0.26279	0.43642
0.0035	43.64218	30.078372	2.769532	0.001631151	23.504832	0.003434049							0.30078	0.26279	0.43642
0.0036	43.642257	30.07793	2.7692689	0.001630961	23.50548	0.003434087							0.30078	0.2628	0.43642
0.0037	43.642334	30.077488	2.7689864	0.001630771	23.506127	0.003434125							0.30077	0.2628	0.43642
0.0038	43.642411	30.077046	2.7687039	0.001630581	23.506774	0.003434163							0.30077	0.26281	0.43642
0.0039	43.642489	30.076604	2.7684215	0.001630392	23.507421	0.003434201	43.642489	30.076604	2.7684215	0.001630392	23.507421	0.003434201	0.30077	0.26281	0.43642

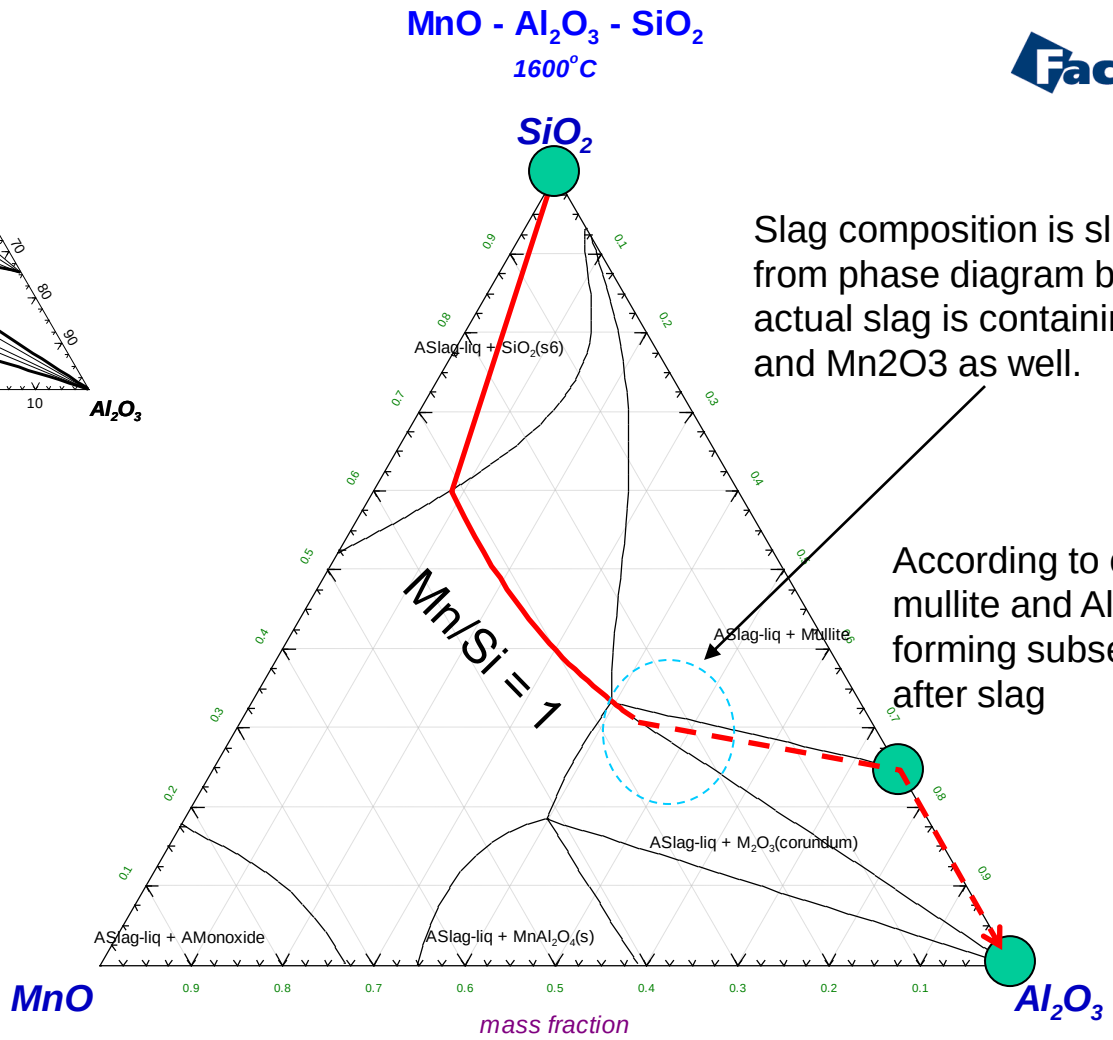
Composition from Slag #1
A corner = wt%SiO2/100
B corner = (wt%MnO+Mn2O3+FeO+Fe2O3)/100
C corner = wt%Al2O3/100

Slag #1
(stable slag)

Slag #2
(metastable or same as #1
except in case of stable miscibility gap)

Inclusion calculation in Mn/Si deoxidation

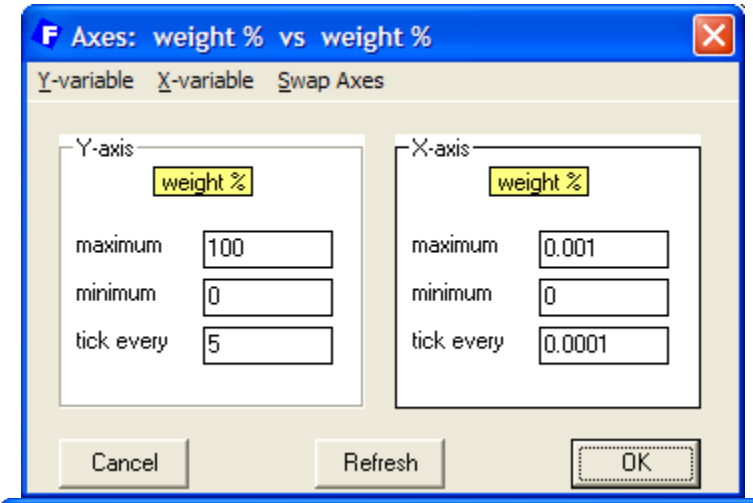


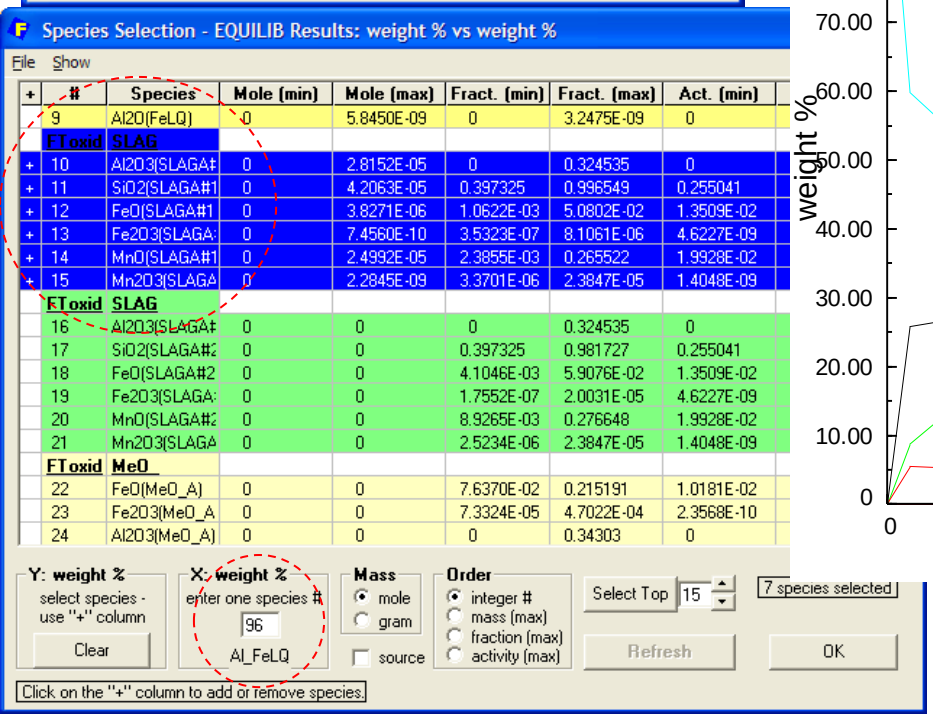


Slag composition is slightly off from phase diagram because the actual slag is containing Fe_tO and Mn2O3 as well.

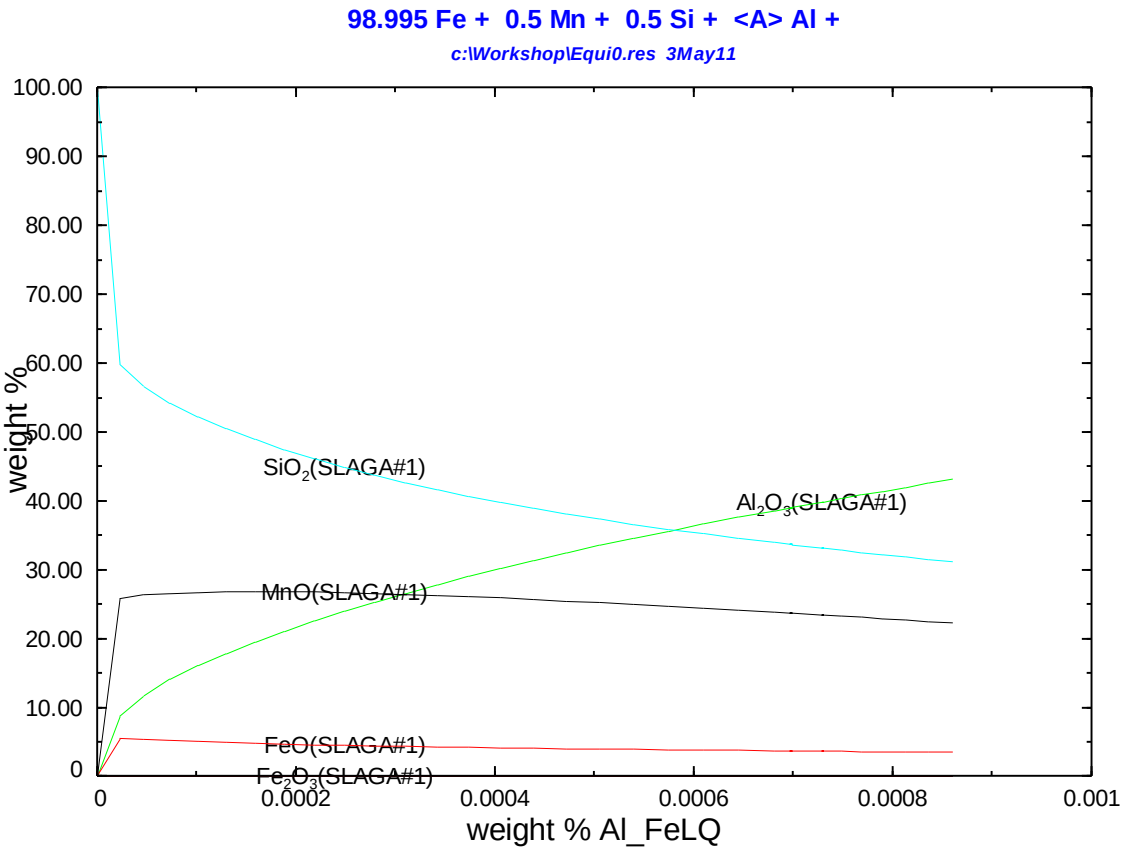
According to calculations, mullite and Al2O3 are forming subsequently after slag

Inclusion calculation in Mn/Si deoxidation



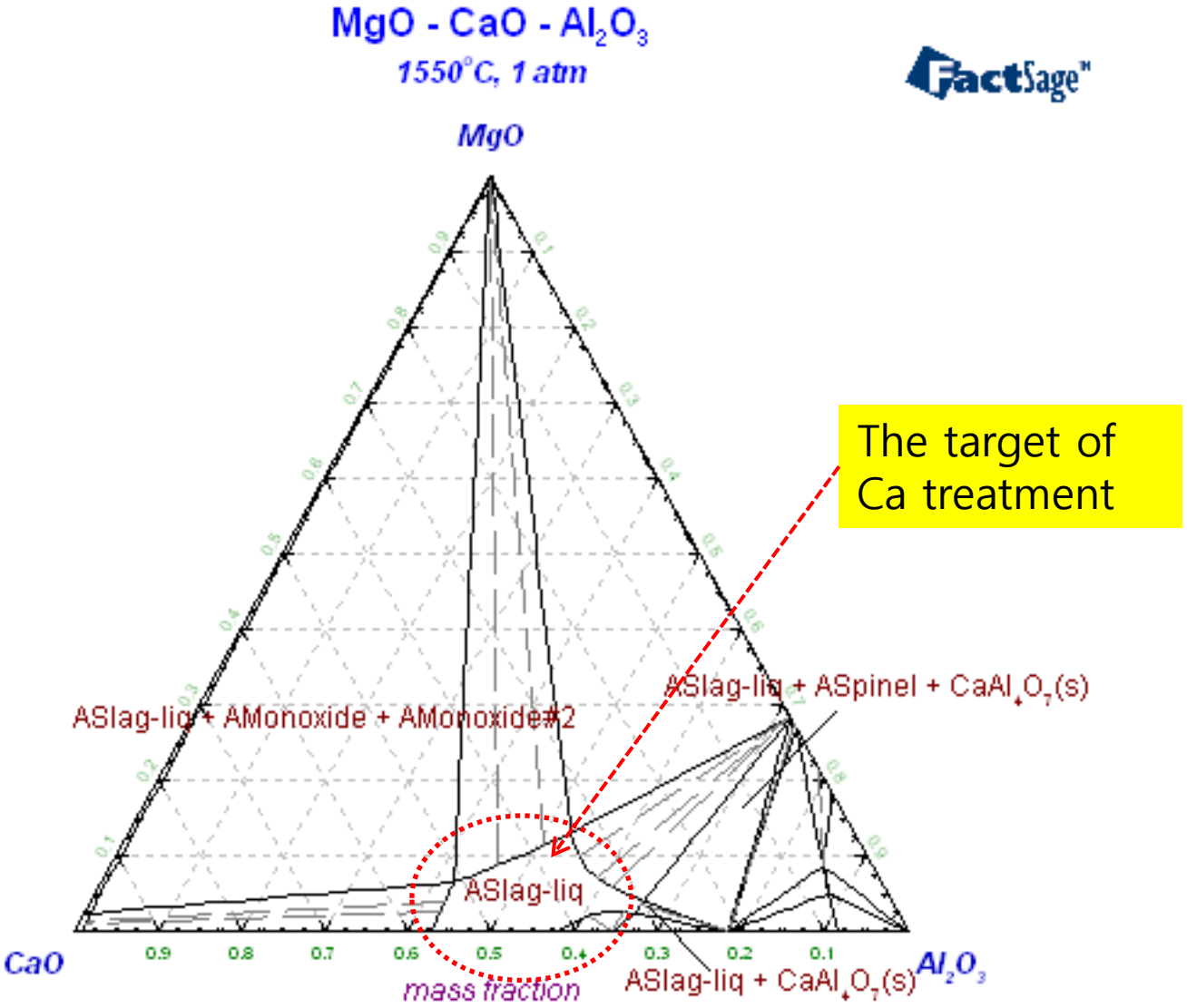


Soluble Al vs. Inclusion composition



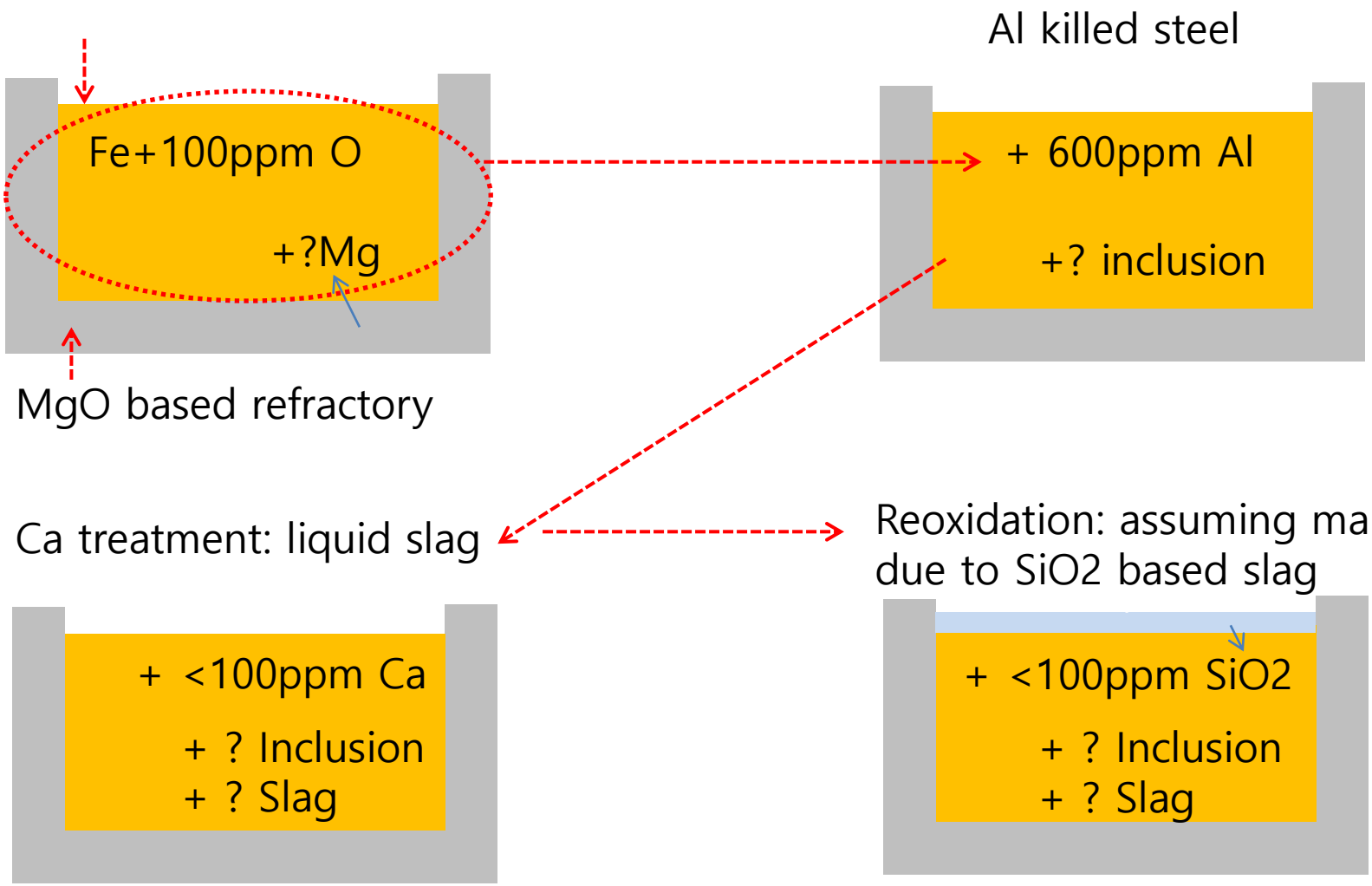
Re-oxidation and inclusion modification in the tundish – Ca-treated steel

Reoxidation and inclusion modification in the tundish

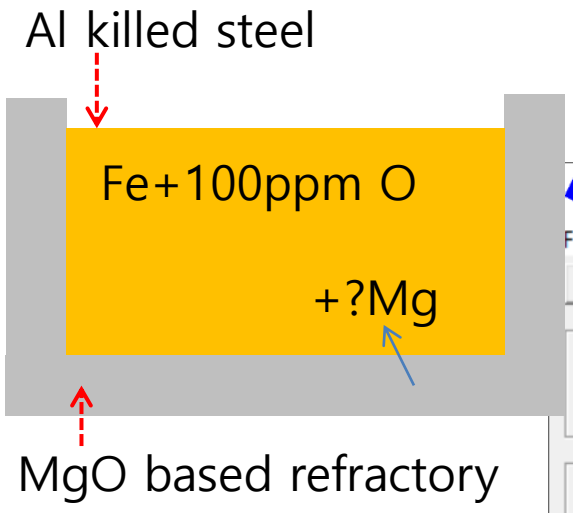


Reoxidation and inclusion modification in the tundish

At 1550°C



Reoxidation and inclusion modification in the tundish



Databases: FACTPS + FTOxid + FTMisc

Equilib - Menu: last system

File Units Parameters Help

T(C) P(atm) Energy(J) Quantity(g) Vol(litre)

Reactants (3)

(gram) 99.09 Fe + 0.01 O + MgO

Products

Compound species

gas ideal real 8
aqueous 0
pure liquids 0
* pure solids 7

* - custom selection species: 15

Solution phases

*	+	Base-Phase	Full Name
	+	FTmisc-FeLQ	Fe-liq
	I	FToxid-SLAGA	A-Slag-liq all oxides + S
	+	FToxid-SPINA	A-Spinel
	+	FToxid-MeO_A	A-Monoxide

Custom Solutions
0 fixed activities
0 ideal solutions
Details ...

Pseudonyms
apply
Edit ...

Volume data
assume molar volumes of solids and liquids = 0
include molar volume data and physical properties data

paraequilibrium & Gmin edit

Virtual species: 6
Total Species (max 5000) 40
Total Solutions (max 200) 5
Total Phases (max 1500) 13

Target
- none -
Estimate T(K): 1000
Quantity(g): 0

Legend
I - immiscible 1
+ - selected 3

Show all selected
species: 25
solutions: 5
Select

Final Conditions

<A>	<B>	T(C)	P(atm)	Product H(J)
		1550	1	

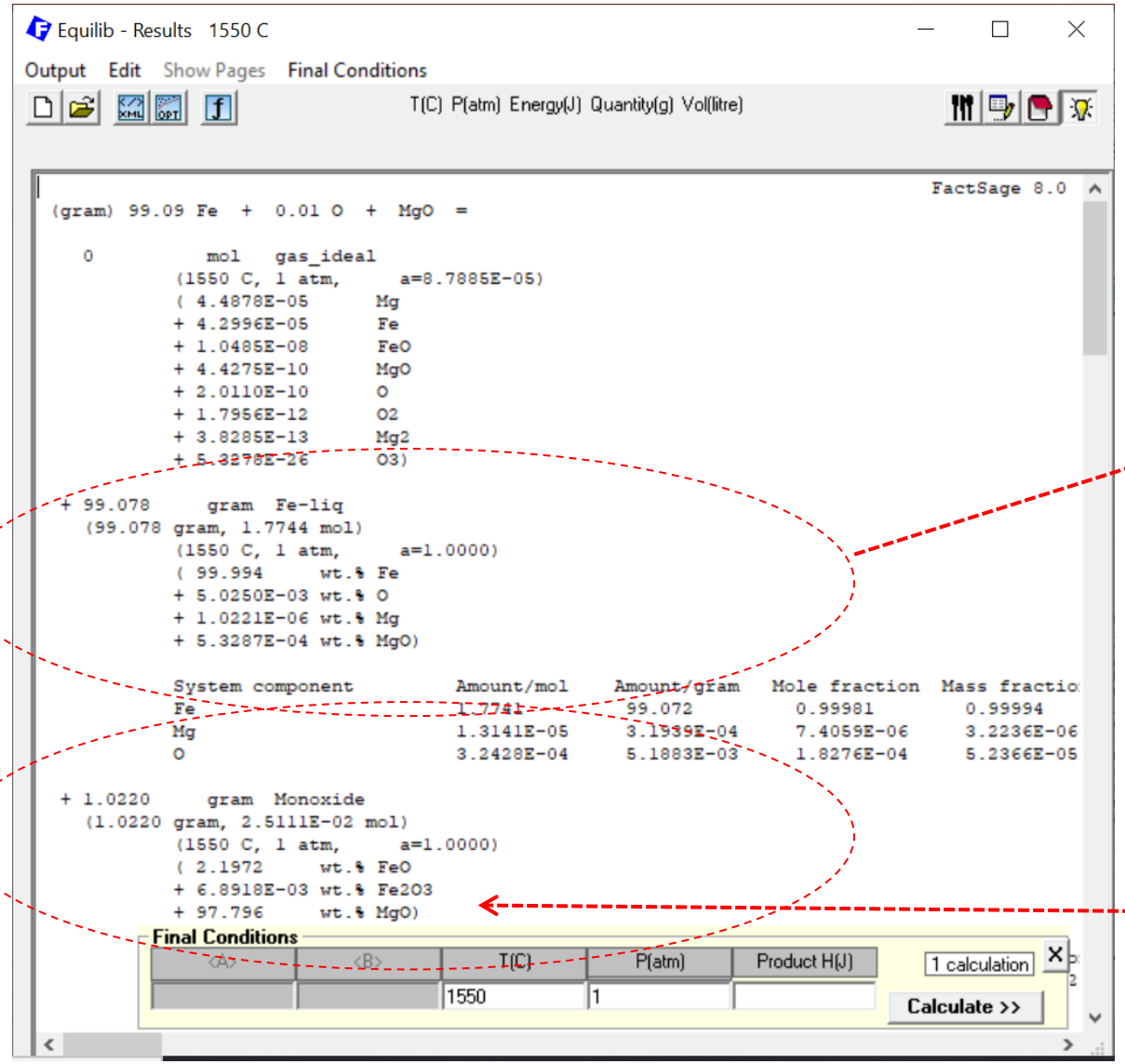
10 steps Table 1 calculation

Equilibrium

normal normal + transitions
transitions only open
- no time limit - Calculate >>

FactSage 8.0

Reoxidation and inclusion modification in the tundish



Only save liquid Fe
as stream file for next step
Stream name: "Ex4-1(a)"

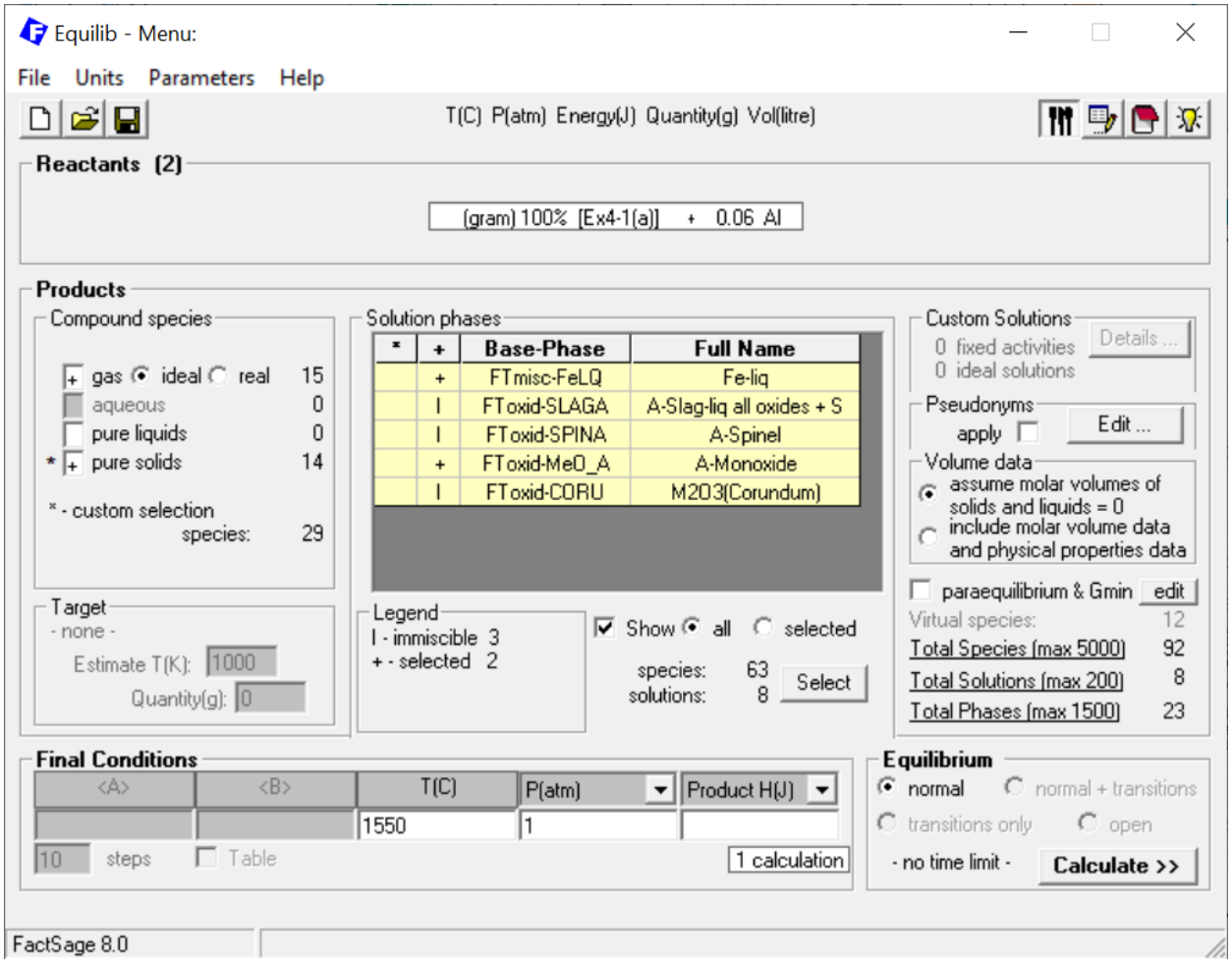
MgO based
refractory

Reoxidation and inclusion modification in the tundish

Al killed steel

+ 600ppm Al

+? inclusion



Reoxidation and inclusion modification in the tundish

Equilib - Results 1550 C

Output Edit Show Pages Final Conditions

T(C) P(atm) Energy(J) Quantity(g) Vol(litre)

```
+ 99.127     gram  Fe-liq
  (99.127 gram, 1.7761 mol)
          (1550 C, 1 atm,      a=1.0000)
          ( 99.945     wt.% Fe
          + 5.4869E-02 wt.% Al
          + 9.5372E-05 wt.% O
          + 2.6380E-06 wt.% Mg
          + 2.5692E-05 wt.% MgO
          + 3.7713E-04 wt.% AlO
          + 7.7107E-05 wt.% Al2O)

          System component         Amount/mol    Amount/gram   Mole fraction  Mass fractio
          Fe                       1.7741         99.072         0.99885        0.99945
          Al                       2.0267E-03     5.4684E-02     1.1411E-03     5.5165E-04
          Mg                       7.3947E-07     1.7973E-05     4.1634E-07     1.8131E-07
          O                        1.6331E-05     2.6129E-04     9.1949E-06     2.6359E-06

+ 7.8073E-03 gram  M2O3(Corundum)#1
  (7.8073E-03 gram, 7.6571E-05 mol)
+ 0           gram  M2O3(Corundum)#2
          (1550 C, 1 atm,      a=1.0000)
          (100.000     wt.% Al2O3
          + 7.7599E-06 wt.% Fe2O3)

          System component         Amount/mol    Amount/gram   Mole fraction  Mass fractio
          Fe                       7.5877E-12     4.2374E-10     1.9819E-08     5.4274E-08
          Al                       1.5314E-04     4.1320E-03     0.40000        0.52925
          O                        2.2971E-04     3.6753E-03     0.60000        0.47075

+ 2.7380E-03 gram  Spinel#1
  (2.7380E-03 gram, 1.9559E-05 mol)
+ 0           gram  Spinel#2
          (1550 C, 1 atm,      a=1.0000)
          ( 9.1657E-09 wt.% Fe3O4
          + 1.1370E-09 wt.% Fe3O4[1-]
          + 1.1017E-12 wt.% Fe
          + 9.4593E-06 wt.% Fe
          + 3.8893E-07 wt.% Fe
```

Only 55 ppm soluble Al

Only 2.6 ppm soluble O

Alumina inclusion which can cause later nozzle clogging

Formation of spinel inclusion which is bad for steel quality

Stream name: "Ex4-1(b)"

Save all phases as stream file for next step
(assumption: all inclusions stay without any floatation removal)

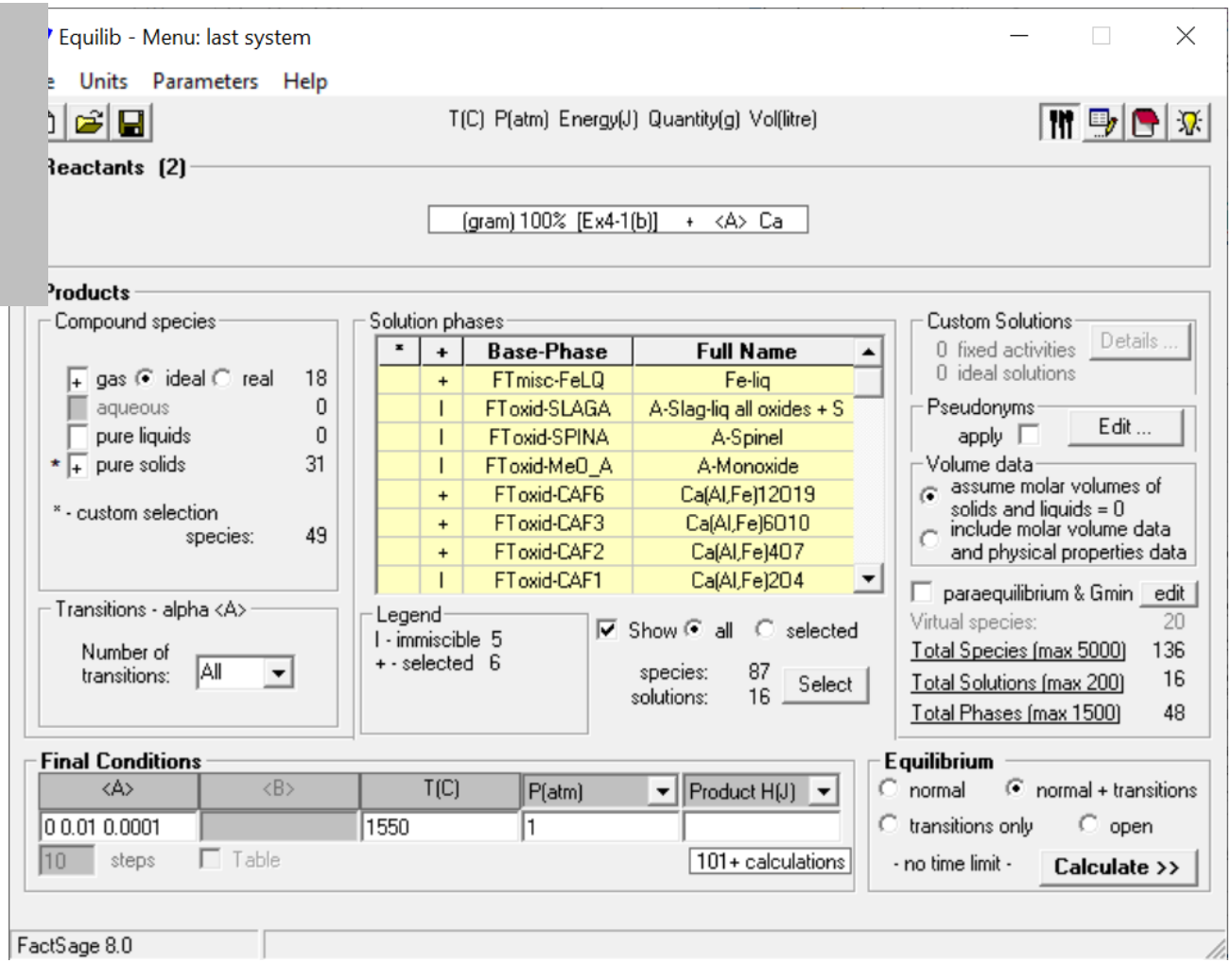
Reoxidation and inclusion modification in the tundish

Ca treatment: liquid slag

+ <100ppm Ca

+ ? Inclusion

+ ? Slag



Reoxidation and inclusion modification in the tundish

Equilib - Results A=0.0034 (page 50/117)

Output Edit Show Pages Final Conditions

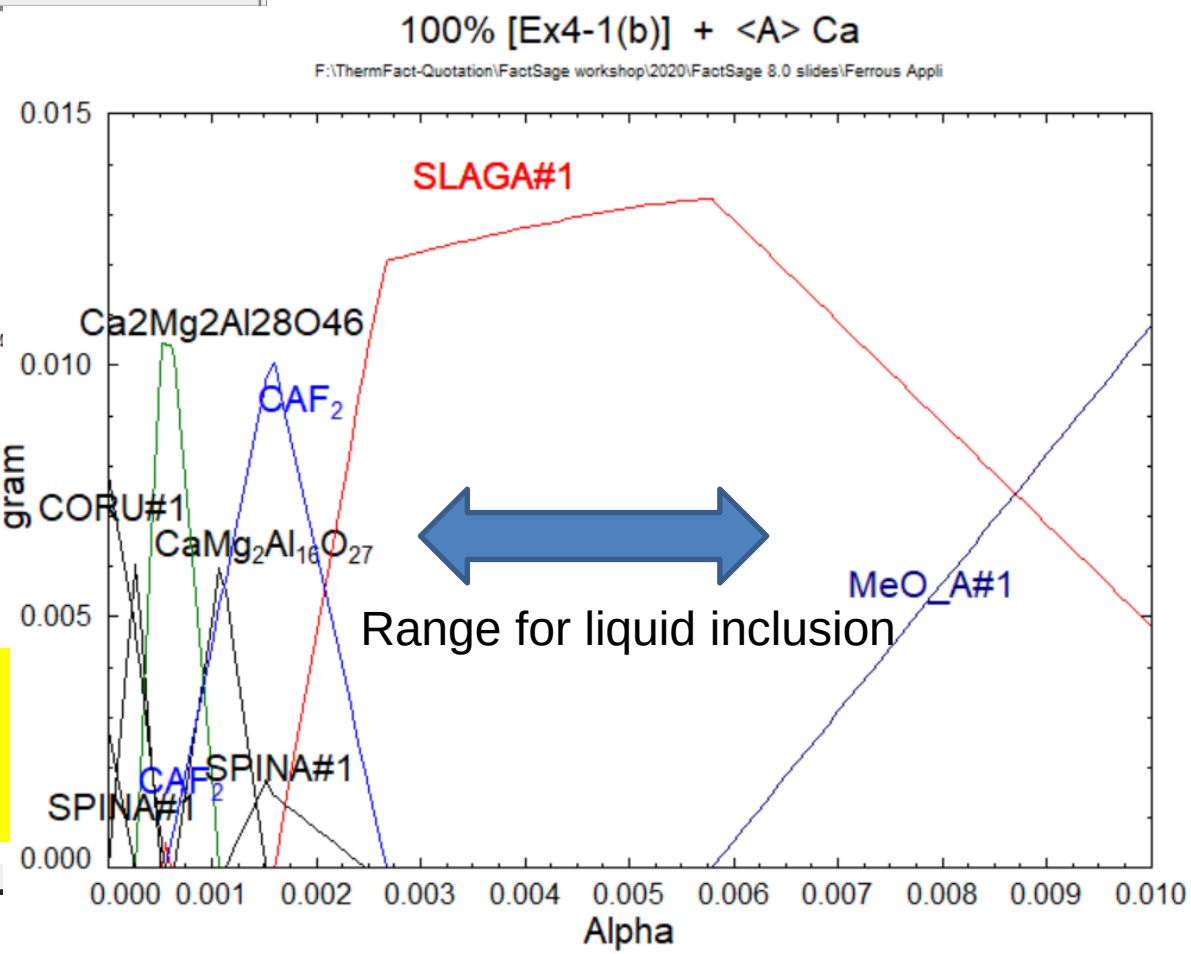
T(C) P(atm) Energy(J) Quantity(g) Vol(litre)

A=0.0021 | A=0.0022 | A=0.0023 | A=0.0024 | A=0.0025 | A=0.0025 | A=0.0026 | A=0.0027 | A=0.0027
A=0.0014 | A=0.0015 | A=0.0015 | A=0.0016 | A=0.0016 | A=0.0017 | A=0.0018 | A=0.0019 | A=0.002
A=0.0028 | A=0.0029 | A=0.003 | A=0.0031 | A=0.0032 | A=0.0033 | - A=0.0034 -

```
+ 99.129     gram  Fe-liq
  (99.129 gram, 1.7761 mol)
          (1550 C, 1 atm,     a=1.0000)
          ( 99.943     wt.% Fe
          + 5.6396E-02 wt.% Al
          + 1.0837E-07 wt.% Ca
          + 4.8319E-05 wt.% O
          + 2.2296E-05 wt.% Mg
          + 1.0997E-04 wt.% MgO
          + 1.4651E-04 wt.% CaO
          + 1.9640E-04 wt.% AlO
          + 4.1276E-05 wt.% Al2O)

          System component        Amount/mol    Amount/gram   M
          Fe                      1.7741        99.072
          Ca                      2.5926E-06    1.0391E-04
          Al                      2.0777E-03    5.6059E-02
          Mg                      3.6140E-06    8.7839E-05
          O                       1.3403E-05    2.1444E-04

+ 1.2443E-02 gram  Slag-liq#1
  (1.2443E-02 gram, 1.6481E-04 mol)
+ 0           gram  Slag-liq#2
          (1550 C, 1 atm,     a=1.0000)
          ( 59.844     wt.% Al2O3
          + 37.064     wt.% CaO

          Fe3+                    2.5781E-07
```

Save all phases at <A> = 0.004 as stream file for next step

Stream name: "Ex4-1(c)"



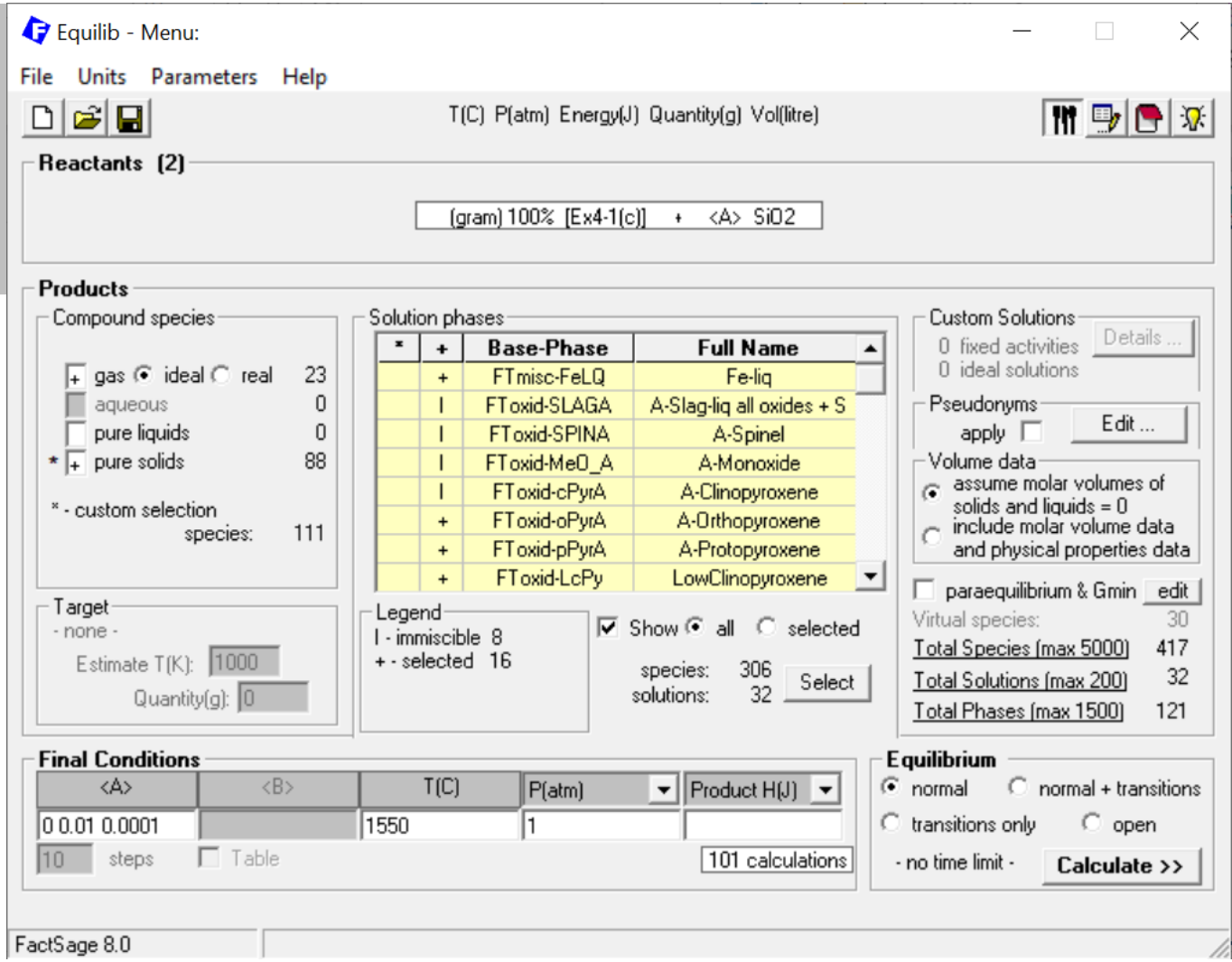
Reoxidation and inclusion modification in the tundish

Reoxidation: assuming mainly due to SiO2 based slag

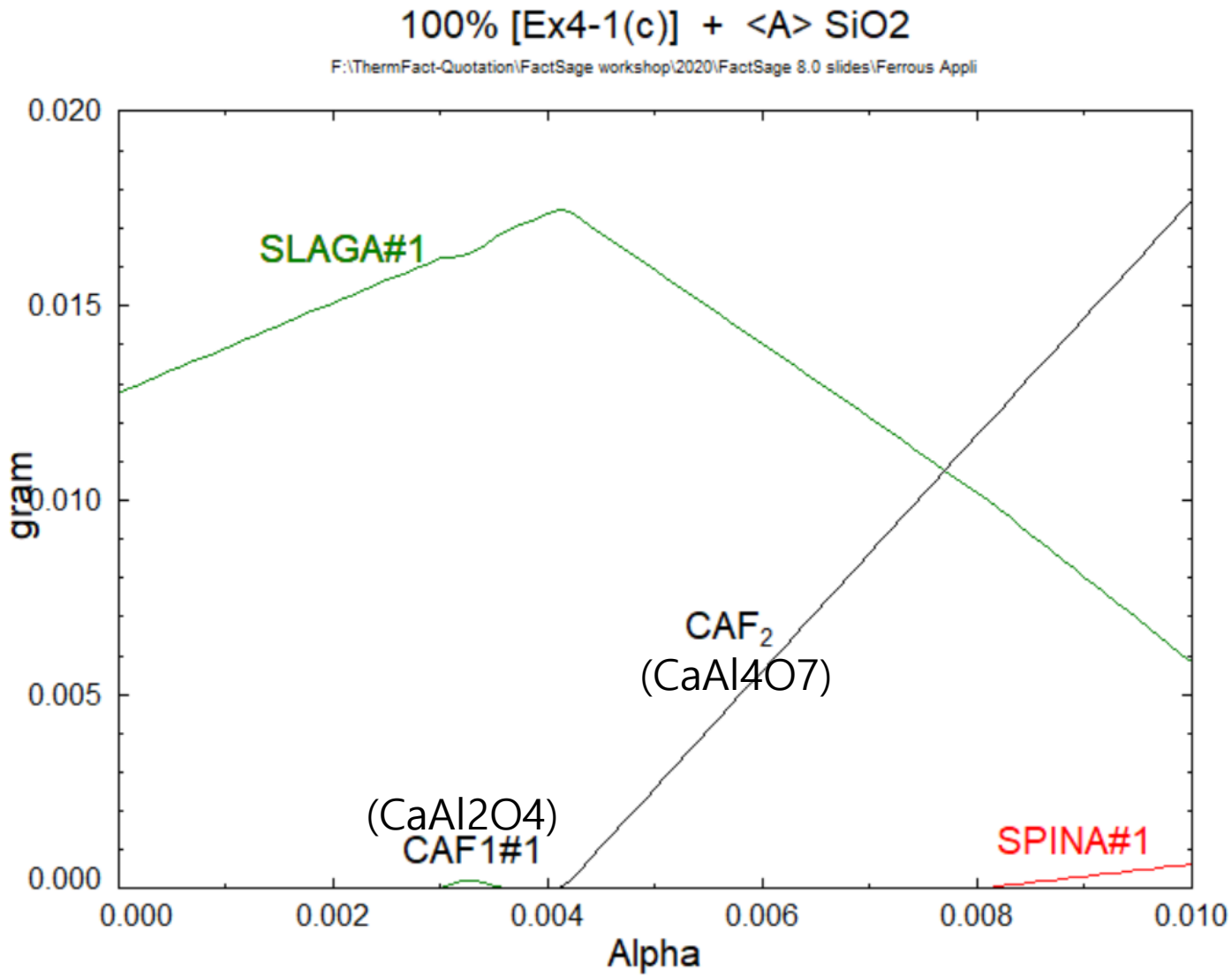
+ <100ppm SiO2

+ ? Inclusion

+ ? Slag



Reoxidation and inclusion modification in the tundish

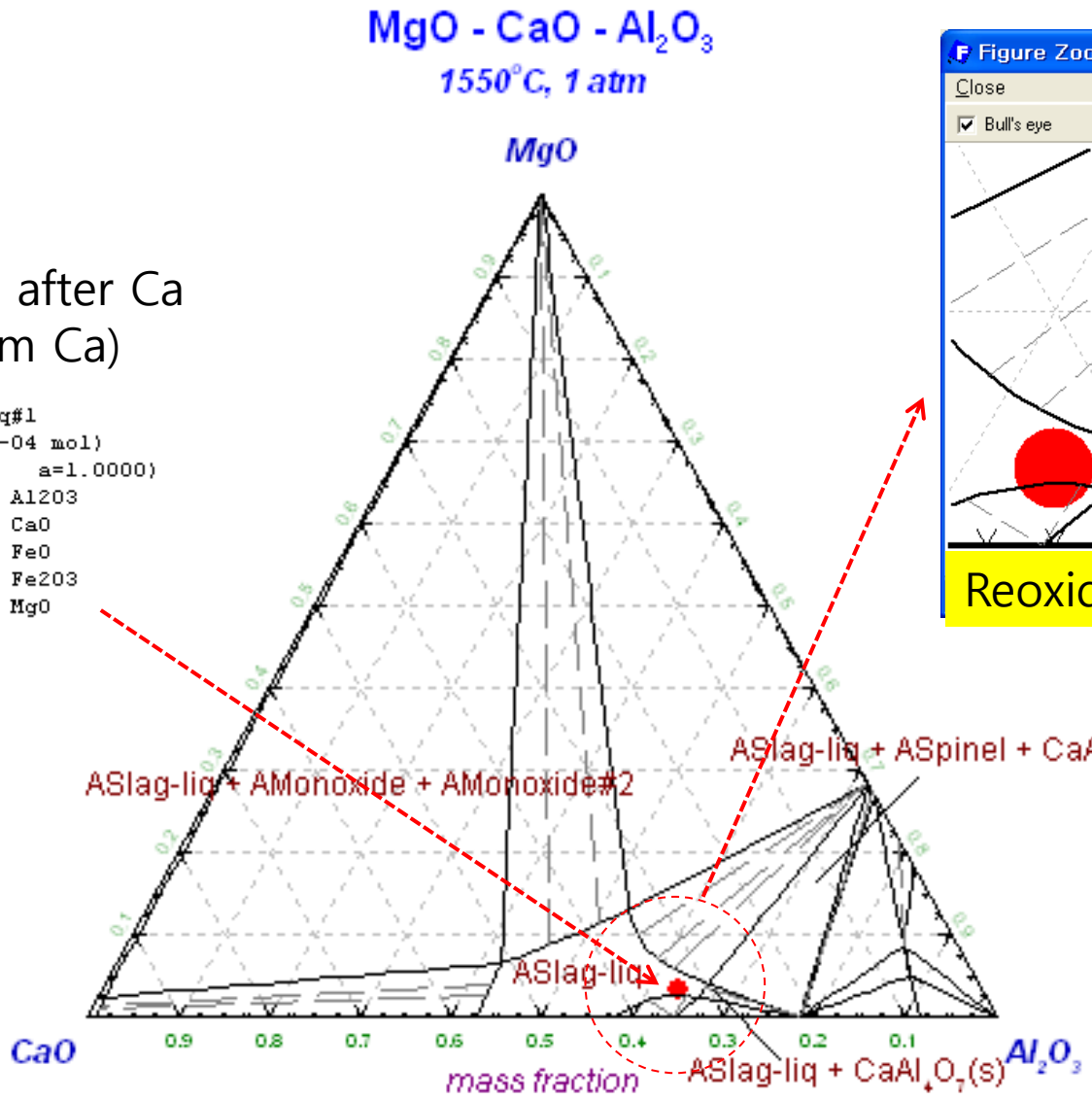


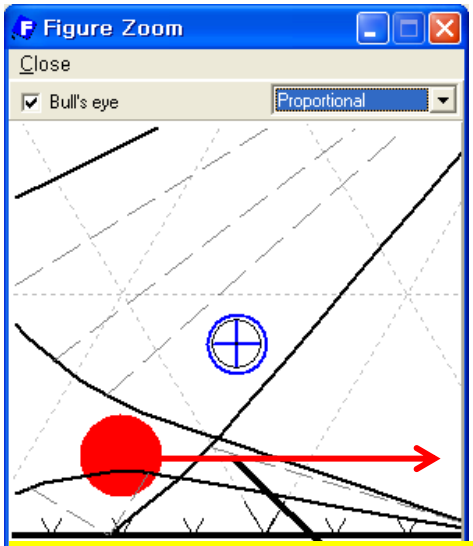
In this condition,
SiO2 is reduced by Al during the reoxidation

Reoxidation and inclusion modification in the tundish

Slag composition after Ca treatment (30 ppm Ca)

```
+ 1.2284E-02 gram  ASlag-liq#1
  (1.2284E-02 gram, 1.5945E-04 mol)
          (1550 C, 1 atm,      a=1.0000)
          ( 63.328      wt.% Al2O3
          + 33.369      wt.% CaO
          + 6.3444E-03 wt.% FeO
          + 3.9494E-05 wt.% Fe2O3
          + 3.2969      wt.% MgO
```





Reoxidation direction

Inclusion diagram: Fe-Al-O, Al deoxidation

Phase Diagram - Menu: Ferrous Applications II p39

File Units Parameters Variables Help

T(C) P(atm) Energy(J) Quantity(g) Vol(litre)

Components (3)

(gram) Fe + Al + O

Products

Compound species

gas ideal real 0
aqueous 0
pure liquids 0
pure solids 0
species: 0

Solution phases

*	+	Base-Phase	Full Name
	+	FTmisc-FeLQ	Fe-liq
	I	FToxid-SLAGA	A-Slag-liq all oxides + S
	I	FToxid-SPINA	A-Spinel
	+	FToxid-MeO_A	A-Monoxide
	I	FToxid-CORU	M2O3(Corundum)

Custom Solutions
0 fixed activities
0 ideal solutions
Details ...

Pseudonyms
Edit ...

Target
- none -
Estimate T(K): 1000

Legend
I - immiscible 3
+ - selected 2

Show all selected
species: 42
solutions: 8
Select

Variables

T(C)	Al/(Fe+Al+O)	O/(Fe+Al+O)		
1600	0 0.01	0 0.001		

O/(Fe+Al+O) vs Al/(Fe+Al+O)

FactSage 8.0 C:\...\Ferrous_Applications_II_p39.phas

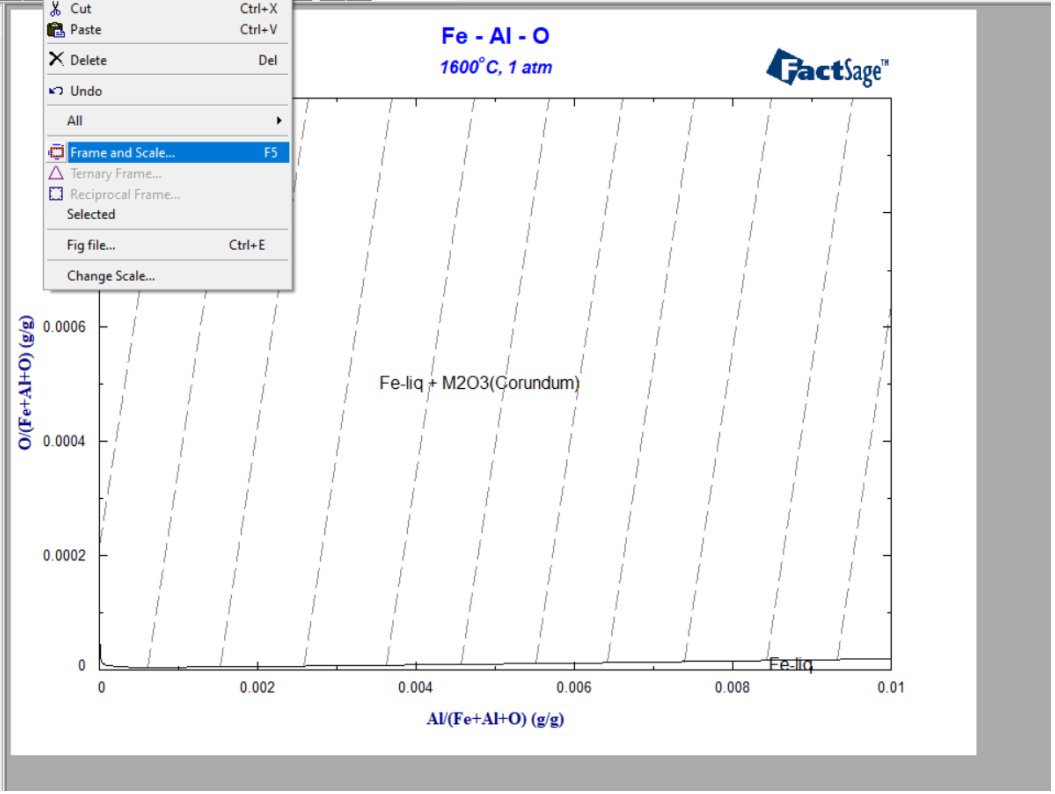
(1): draw rectangular diagram

Figure User : FactSage Workshop

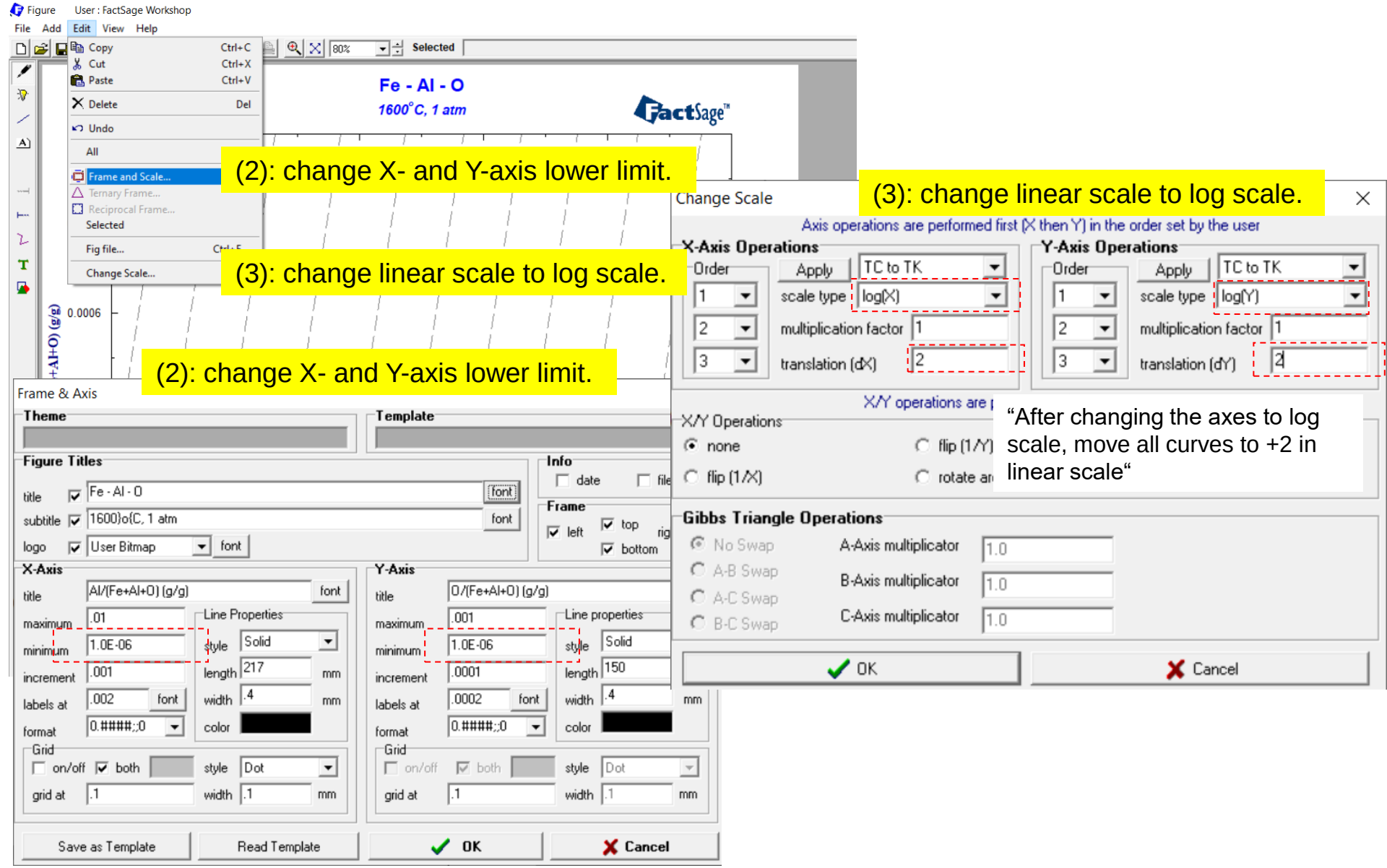
File Add Edit View Help

Copy Ctrl+C
Cut Ctrl+X
Paste Ctrl+V
Delete Del
Undo
All
Frame and Scale... F5
Ternary Frame...
Reciprocal Frame...
Selected
Fig file... Ctrl+E
Change Scale...

80% Selected



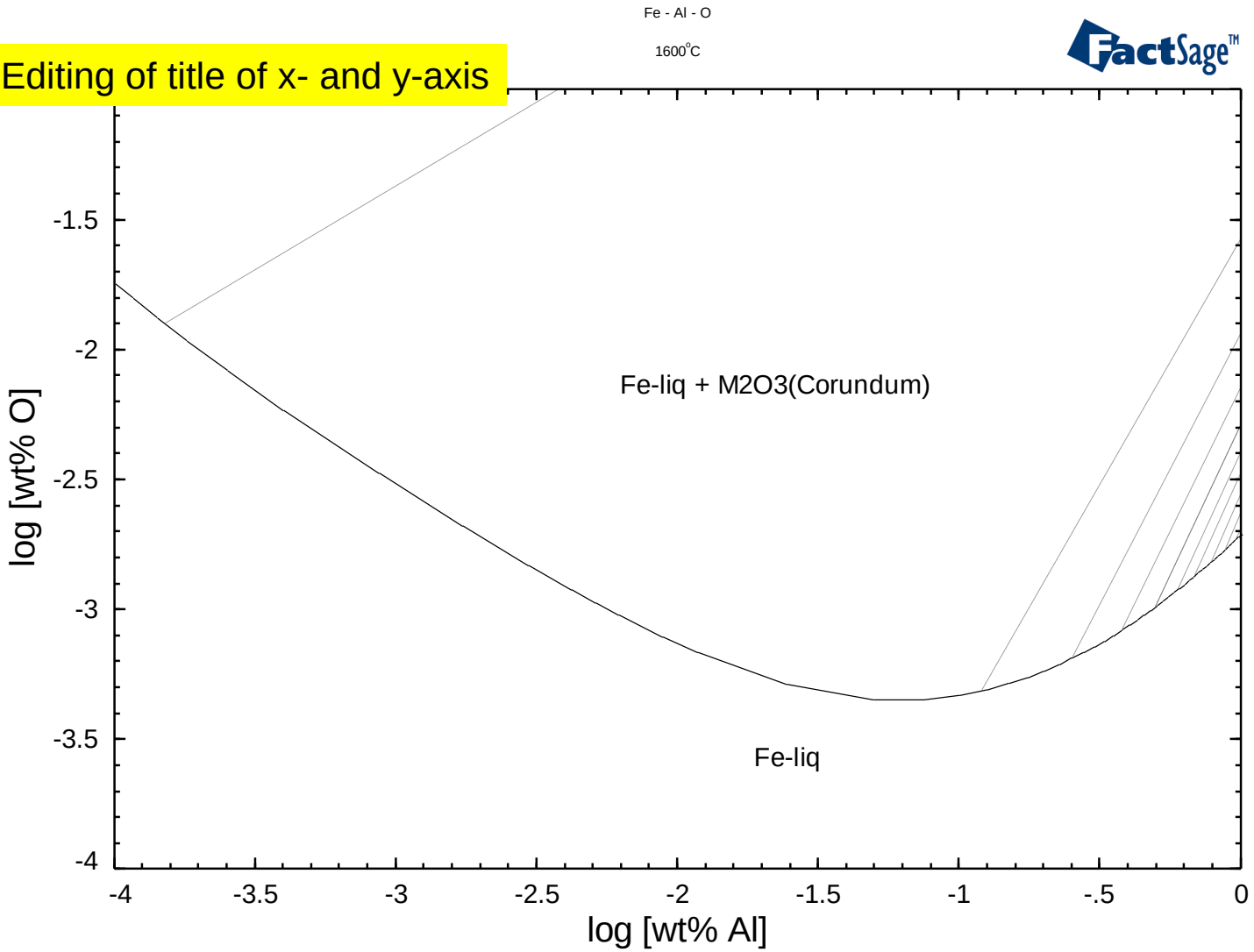
Inclusion diagram: Fe-Al-O, Al deoxidation



"After changing the axes to log scale, move all curves to +2 in linear scale"

Inclusion diagram: Fe-Al-O, Al deoxidation

(4) Editing of title of x- and y-axis

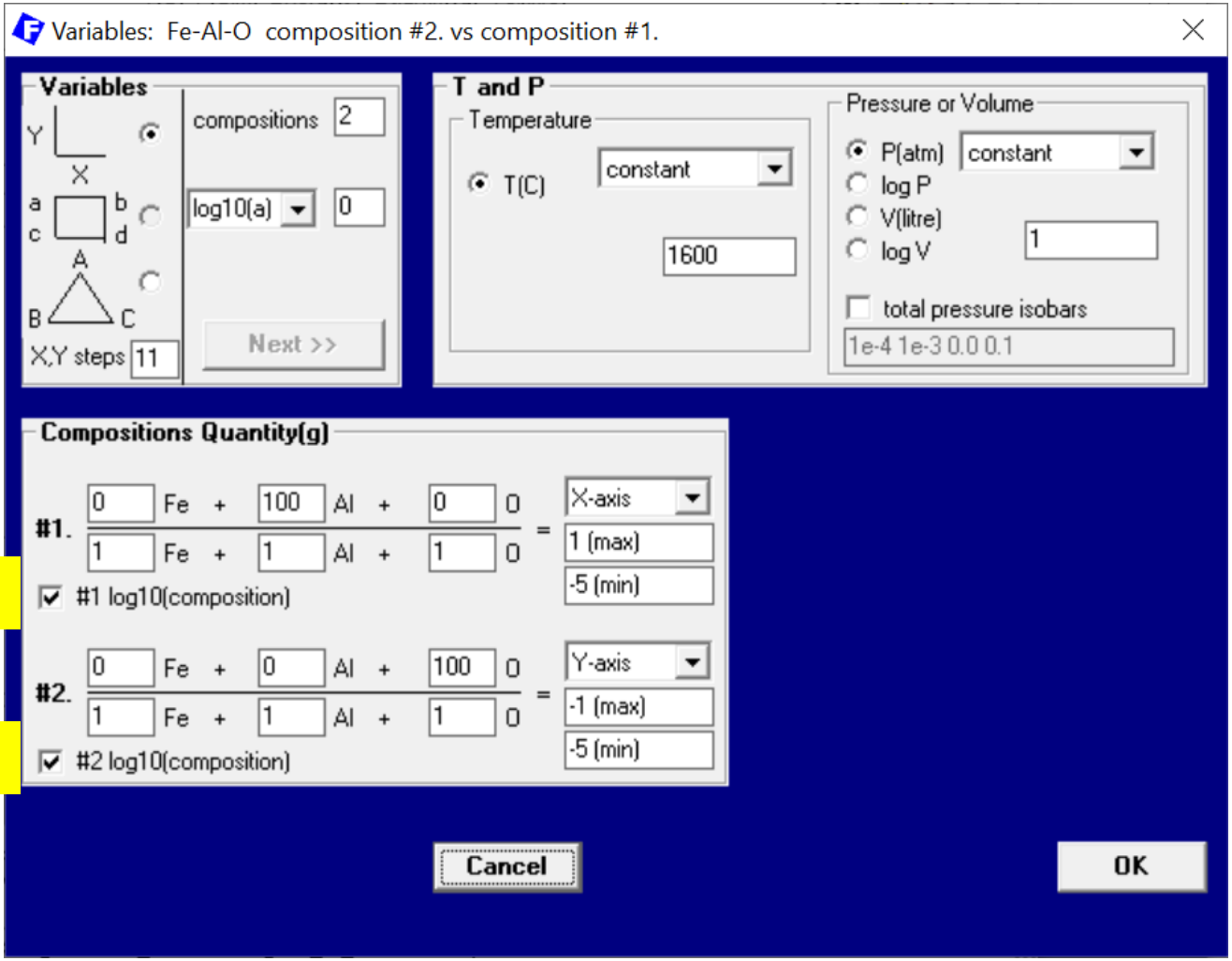


Inclusion diagram: Fe-Al-O, Al deoxidation

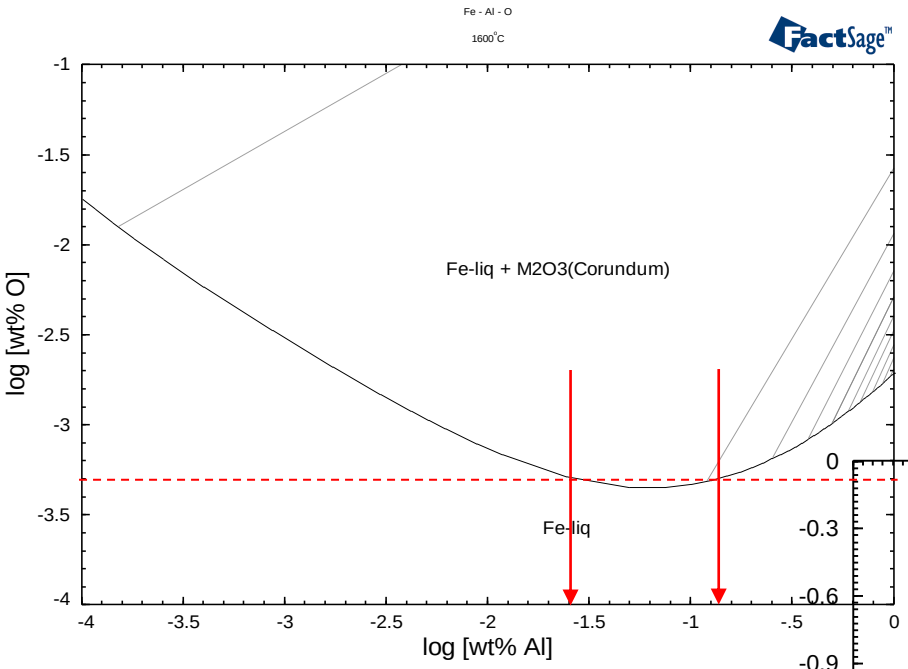
New way to set the axis in log scale
→ log – log diagram or log – linear scale diagram can be calculated now

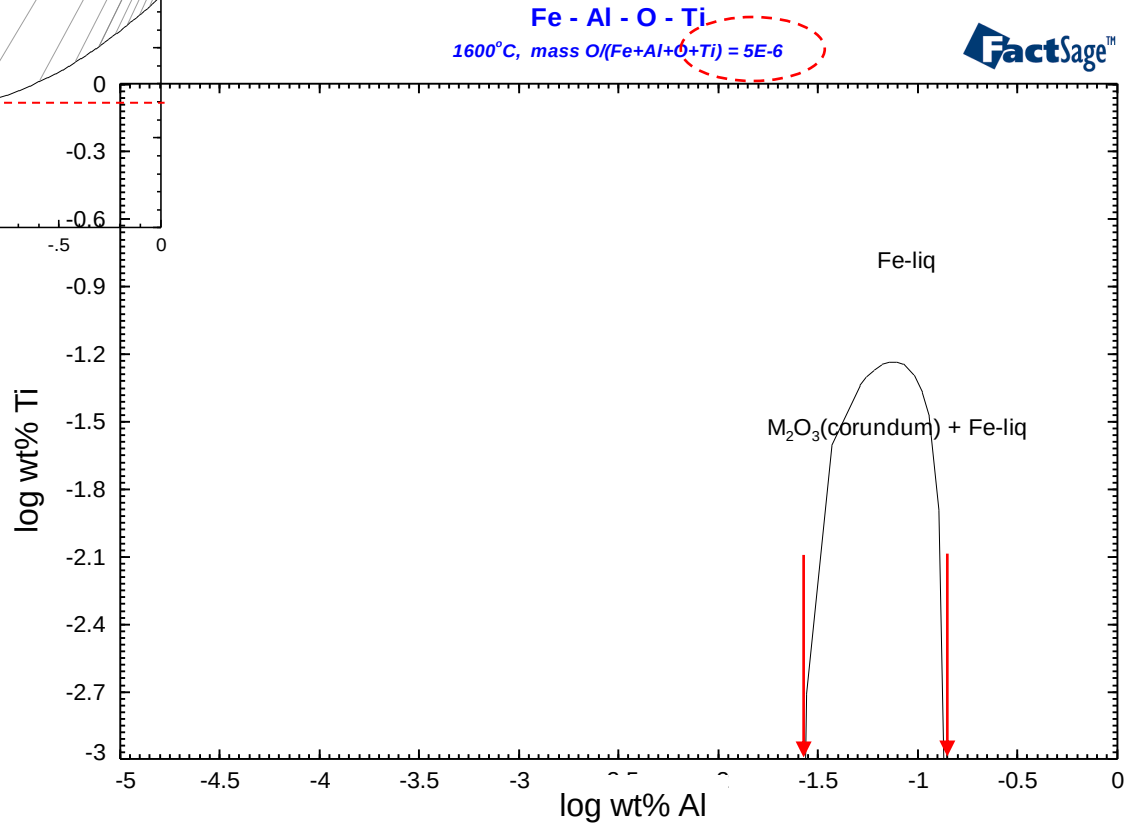
Log scale →

Log scale →

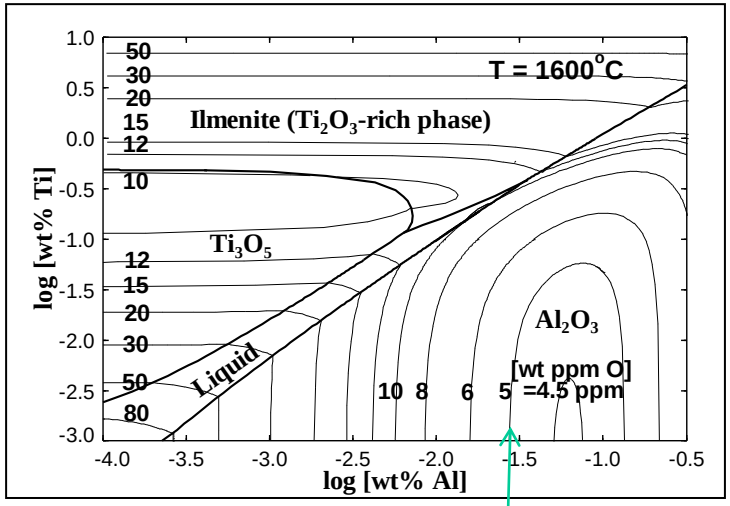


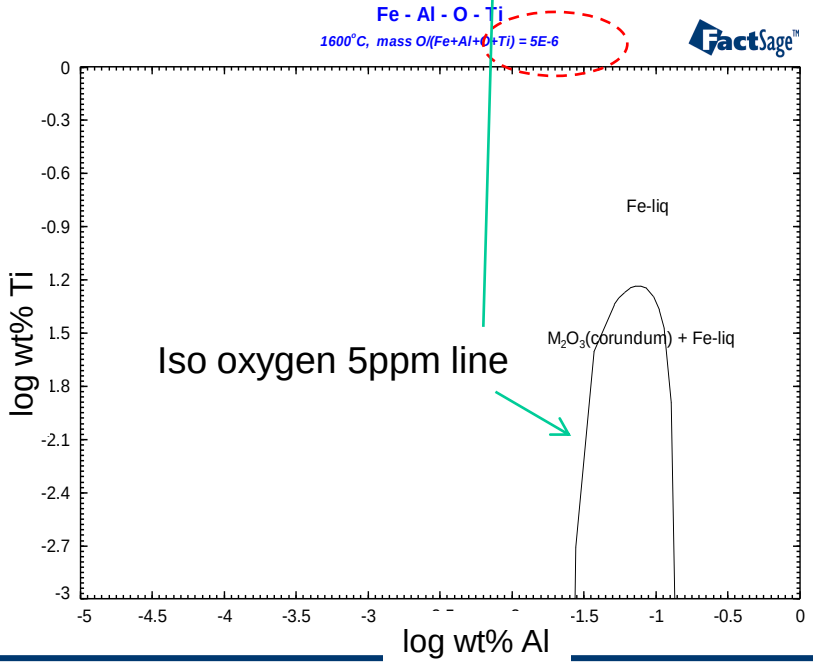
Inclusion diagram: Fe-Al-Ti-O, Al/Ti deoxidation



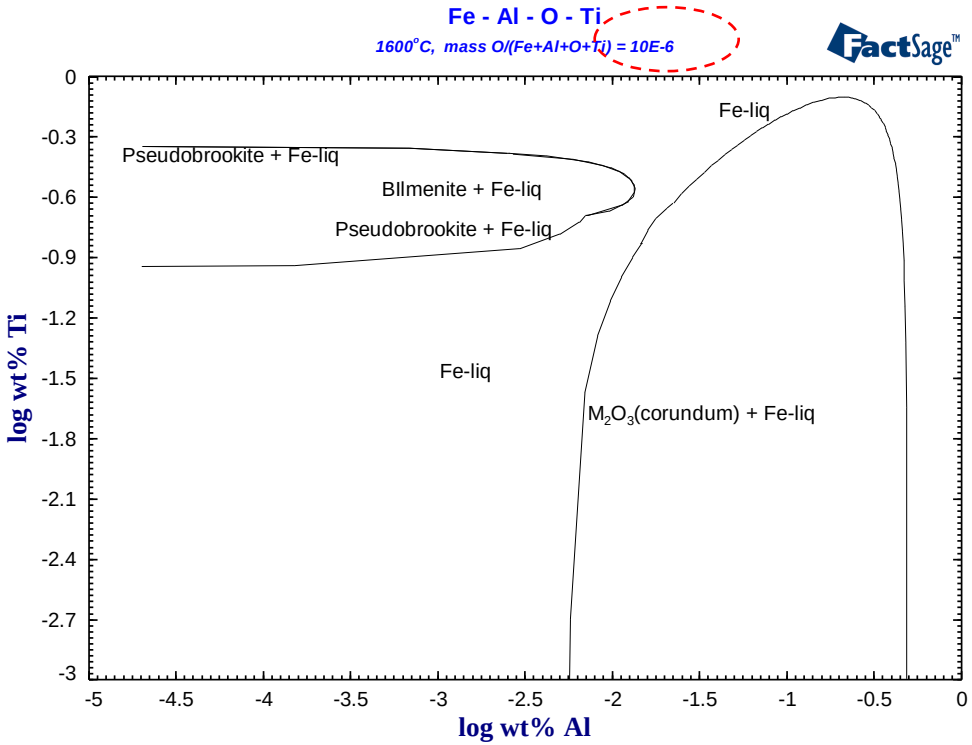


Inclusion diagram: Fe-Al-Ti-O, Al/Ti deoxidation





Iso oxygen 5ppm line



1) Change oxygen content and calculate similar diagram
2) Superimpose all the diagram together
3) Calculate the phase boundaries from Equilib (or simply connect boundaries in the calculated diagram)

Inclusion after Mn/Si deoxidation

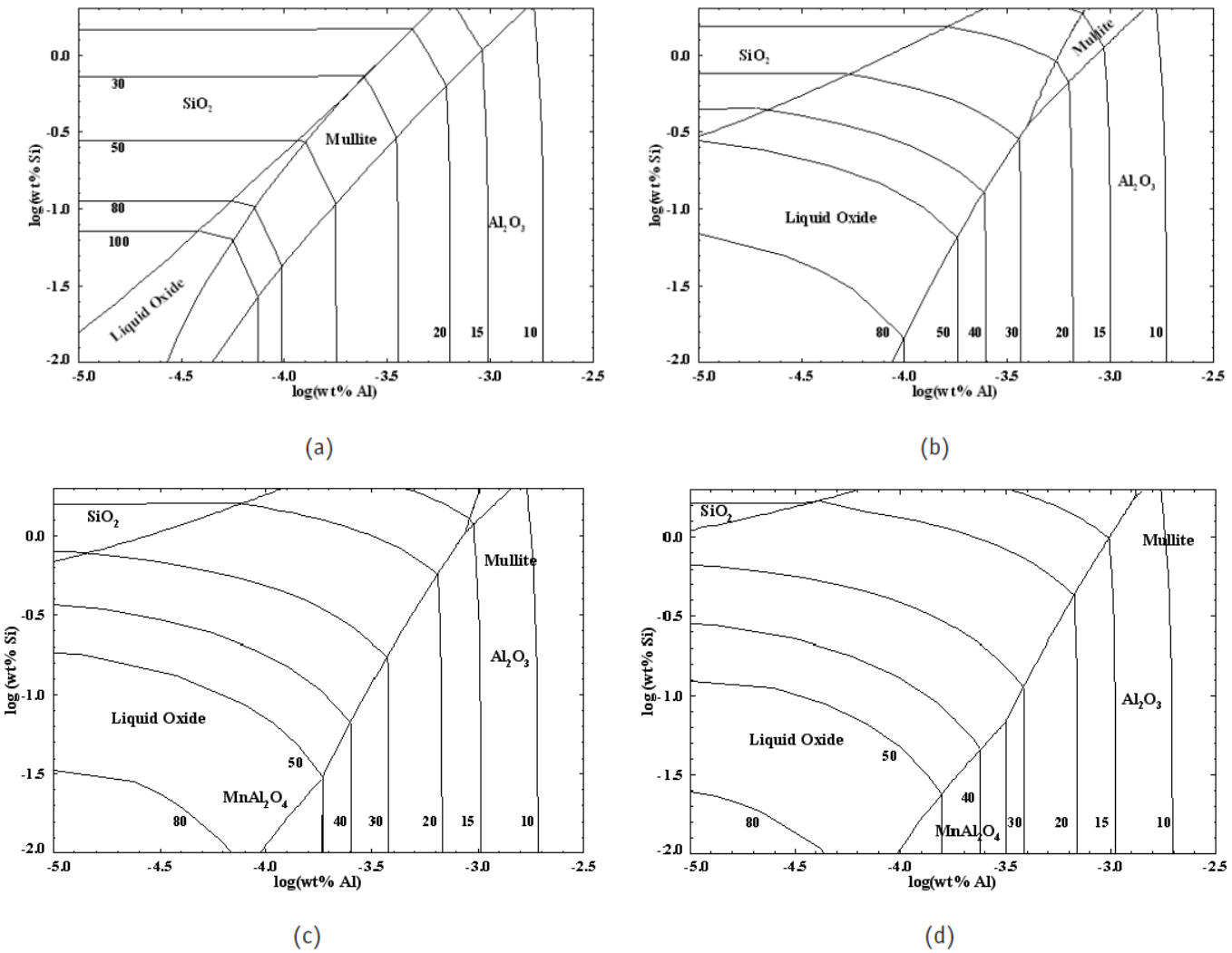
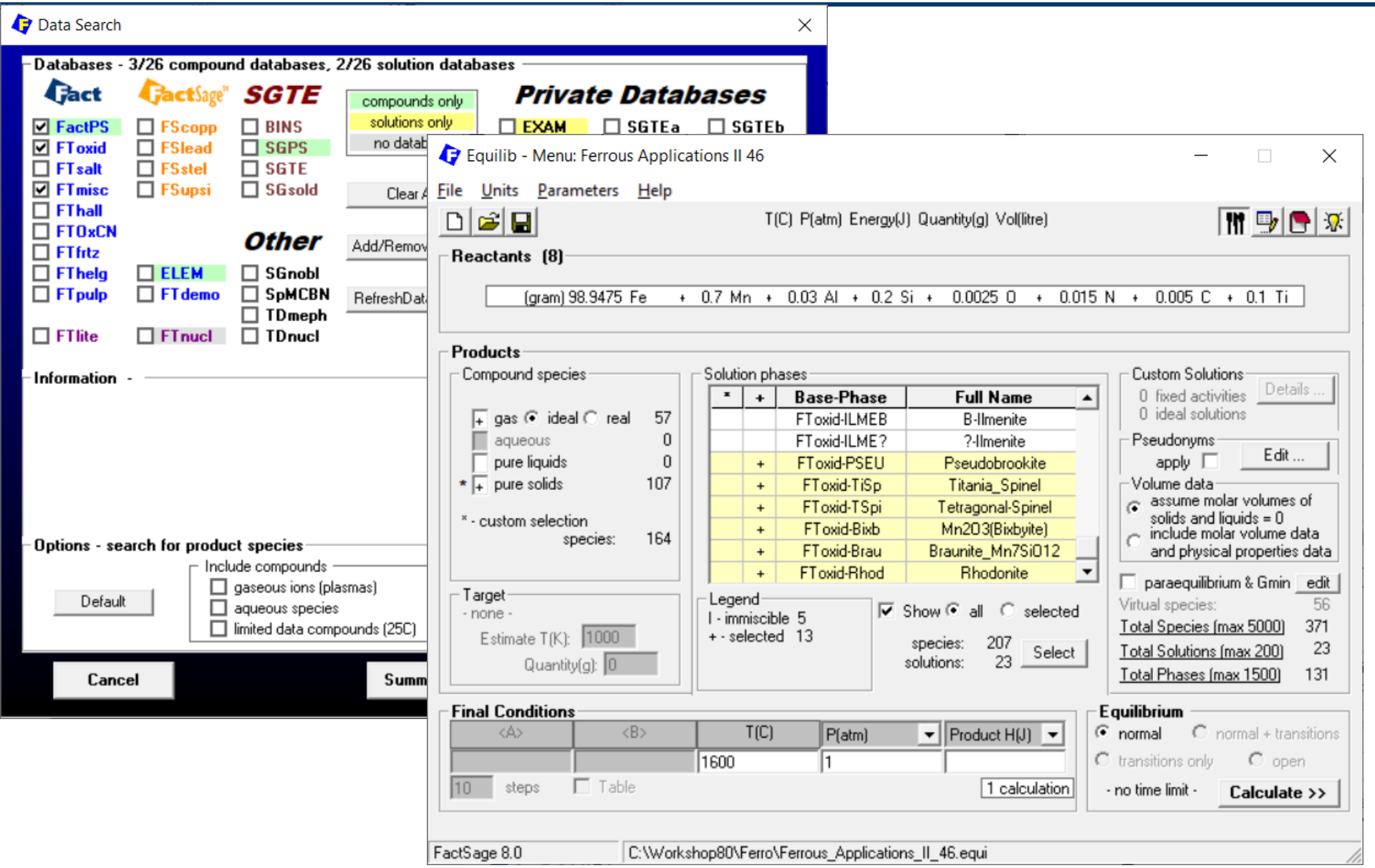


Figure 11: Calculated inclusion stability diagrams in the Fe-Mn-Si-Al-O system at 1550°C for (a) mass% Mn = 0, (b) mass% Mn = 0.5, (c) mass% Mn = 1.0 and (d) mass% Mn = 1.5. Numbers adjacent to each line represent equilibrium oxygen contents (in ppm) in liquid steel [23].

Al killed Ti bearing steel



Al killed Ti bearing steel

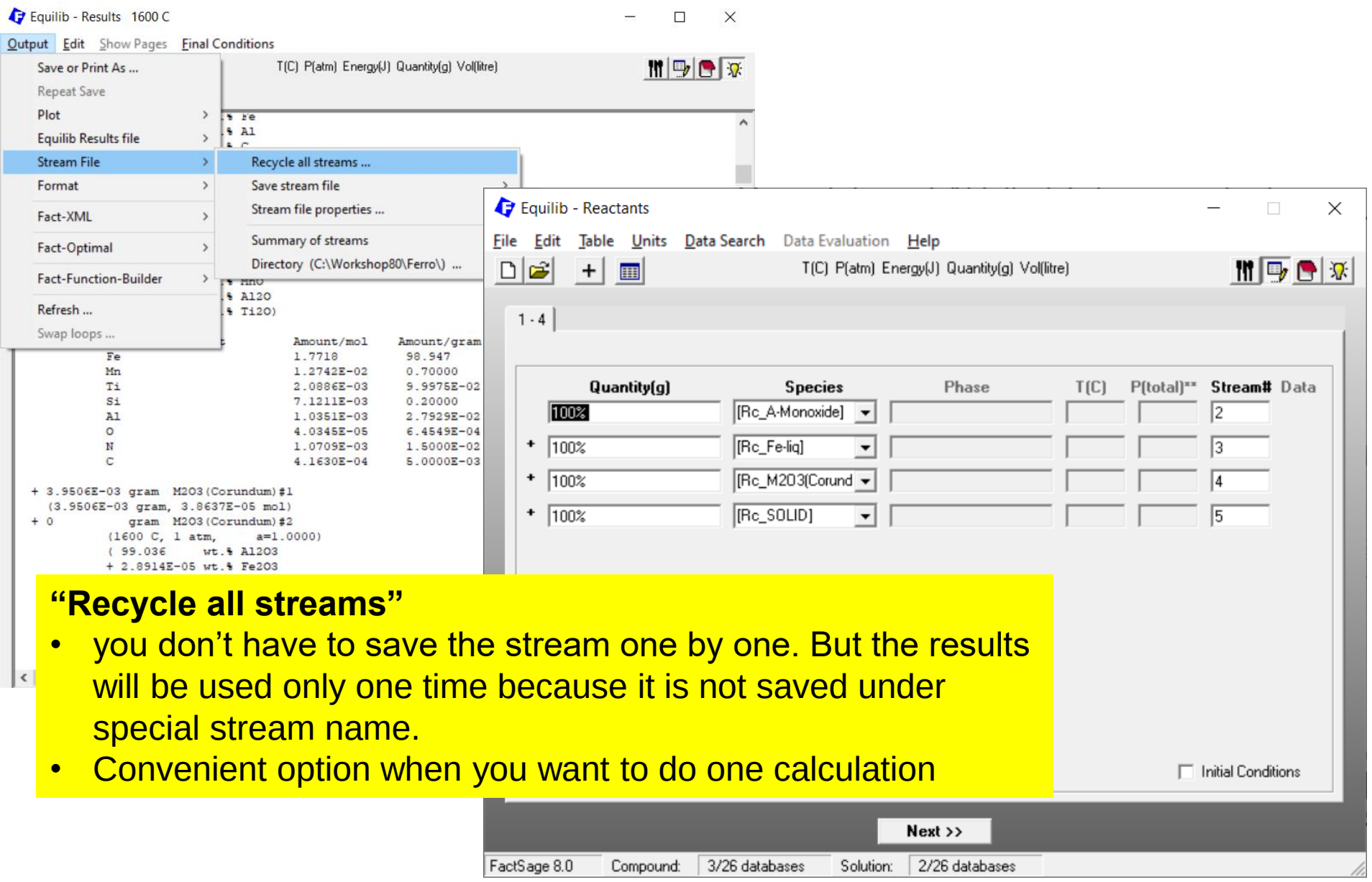
Equilib - Results 1600 C

Output Edit Show Pages Final Conditions

T(C) P(atm) Energy(J) Quantity(g) Vol(litre)

```
          + 1.5906E-40      Fe(CO)5
          + 2.8722E-45      N2O4
          + 3.6814E-55      N2O5)

+ 99.996     gram  Fe-liq
  (99.996 gram, 1.7963 mol)
          (1600 C, 1 atm,     a=1.0000)
          ( 98.951     wt.% Fe
          + 2.7583E-02 wt.% Al
          + 5.0002E-03 wt.% C
          + 0.70000    wt.% Mn
          + 1.5001E-02 wt.% N
          + 2.9406E-04 wt.% O
          + 0.20001    wt.% Si
          + 9.9530E-02 wt.% Ti
          + 4.9668E-04 wt.% AlO
          + 5.7546E-04 wt.% TiO
          + 3.3327E-06 wt.% SiO
          + 3.4562E-05 wt.% MnO
          + 4.6211E-05 wt.% Al2O
          + 1.9820E-05 wt.% Ti2O)

          System component         Amount/mol    Amount/gram   Mole fraction  Mass fraction
          Fe                       1.7718         98.947         0.98635        0.98951
          Mn                       1.2742E-02     0.70000        7.0931E-03     7.0003E-03
          Ti                       2.0886E-03     9.9975E-02     1.1627E-03     9.9979E-04
          Si                       7.1211E-03     0.20000        3.9642E-03     2.0001E-03
          Al                       1.0351E-03     2.7929E-02     5.7624E-04     2.7930E-04
          O                        4.0345E-05     6.4549E-04     2.2459E-05     6.4552E-06
          N                        1.0709E-03     1.5000E-02     5.9617E-04     1.5001E-04
          C                        4.1630E-04     5.0000E-03     2.3175E-04     5.0002E-05

+ 3.9506E-03 gram  M2O3(Corundum)#1
  (3.9506E-03 gram, 3.8637E-05 mol)
+ 0          gram  M2O3(Corundum)#2
          (1600 C, 1 atm,     a=1.0000)
          ( 99.036     wt.% Al2O3
```

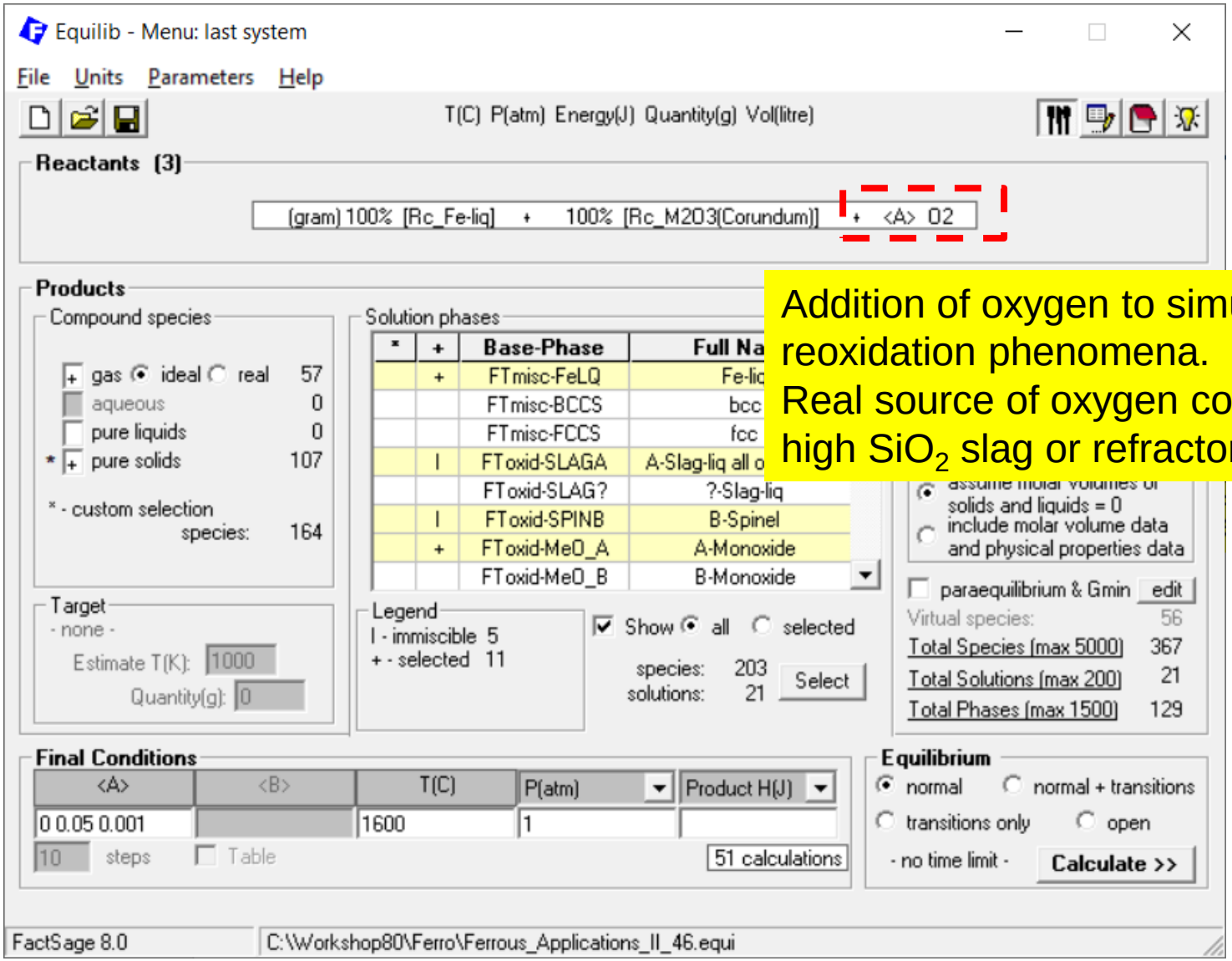
Reoxidation of Al killed Ti bearing steel



"Recycle all streams"

- you don't have to save the stream one by one. But the results will be used only one time because it is not saved under special stream name.
- Convenient option when you want to do one calculation

Reoxidation of Al killed Ti bearing steel

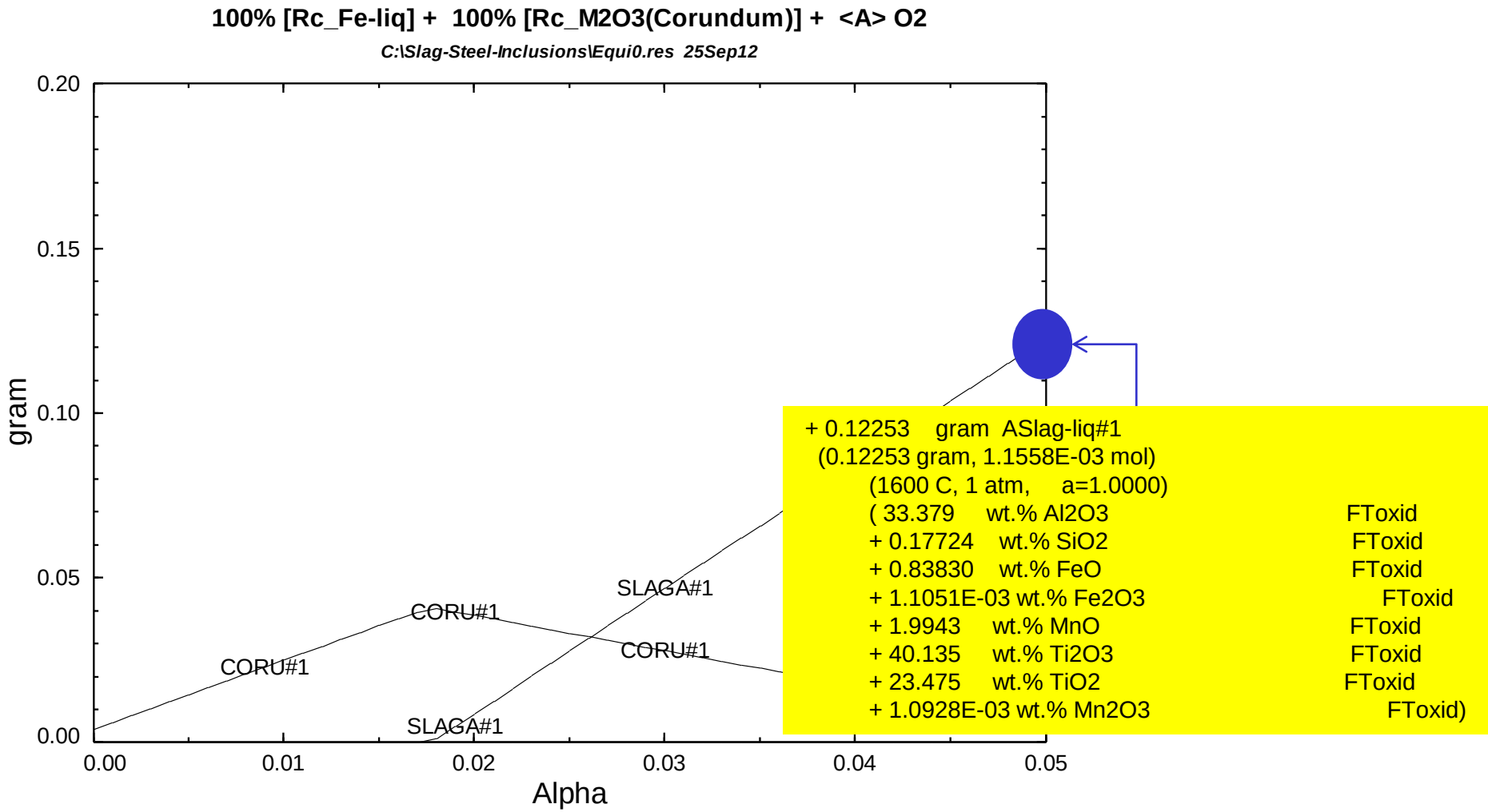


Addition of oxygen to simulation reoxidation phenomena.
Real source of oxygen could be high SiO_2 slag or refractories

Reoxidation of Al killed Ti bearing steel

This calculation shows that mixed inclusion of Al2O3(s) and liquid (Al2O3-TiO2-Ti2O3) can be formed by the reoxidation of Al-killed Ti bearing steel.

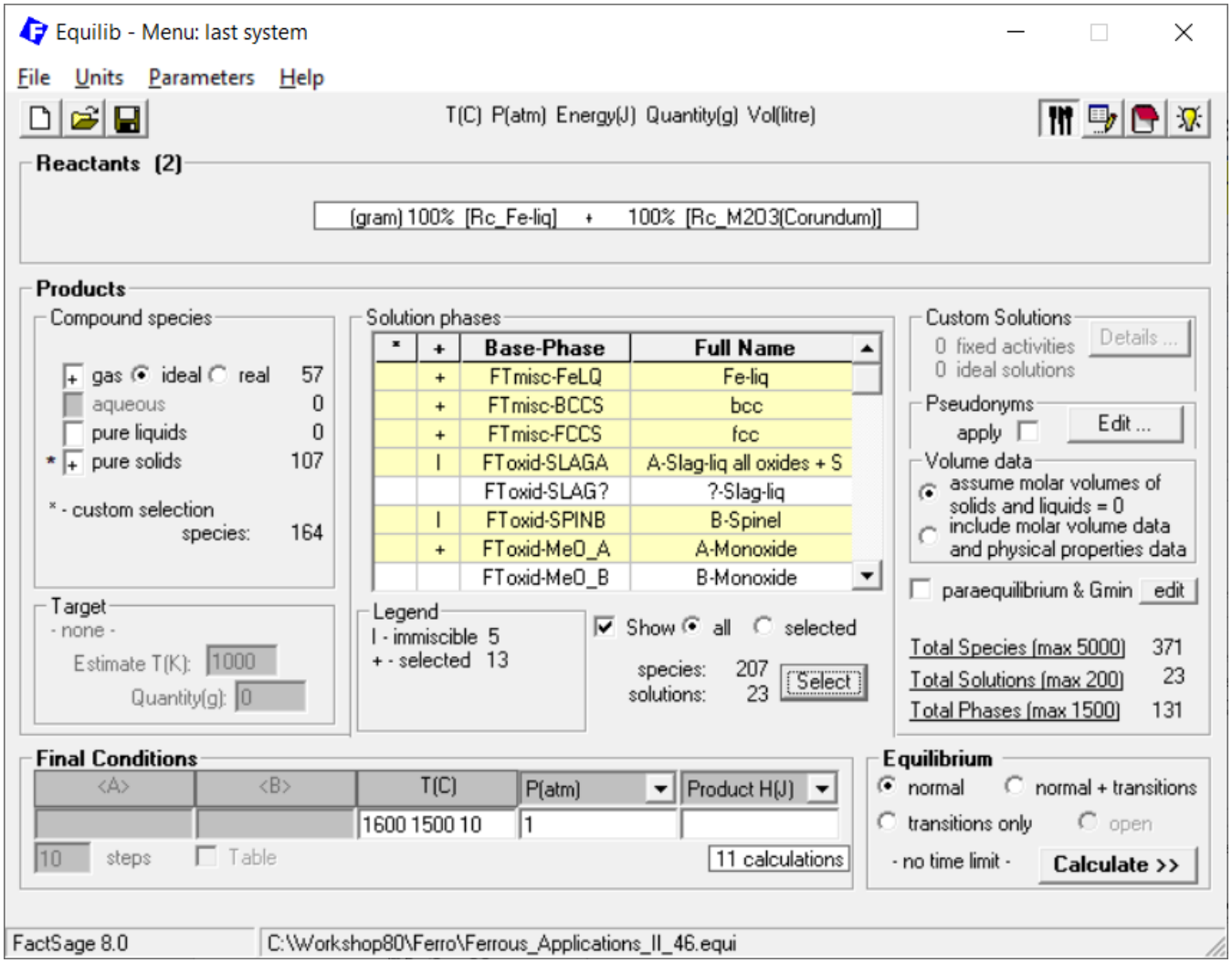
→ Nozzle clogging.



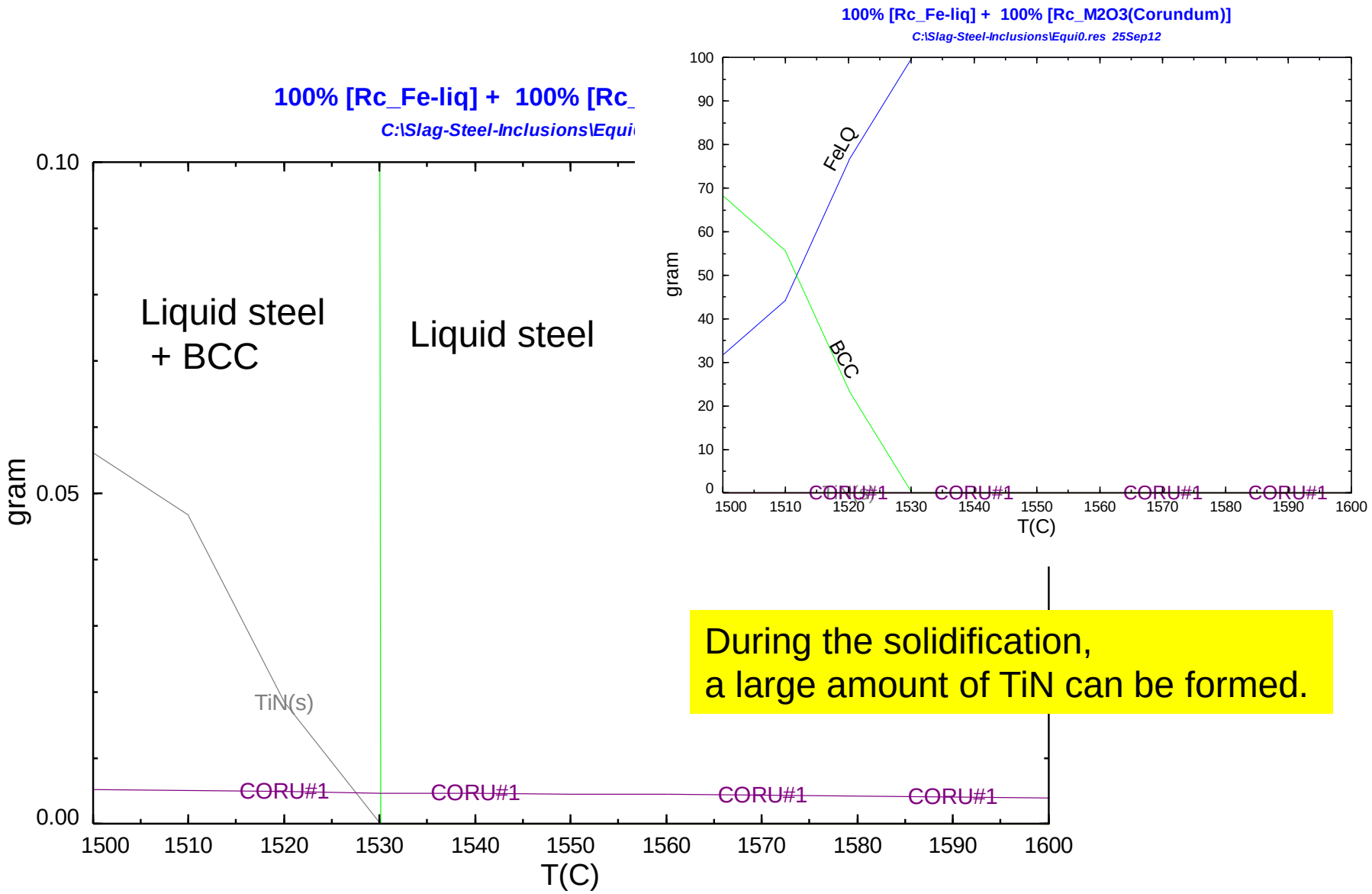
TiN formation in Al killed and Ti bearing steel

Original steel composition at 1600C: high N and high Ti → may form TiN

(gram) 98.9475 Fe + 0.7 Mn + 0.03 Al + 0.2 Si + 0.0025 O + 0.015 N + 0.005 C + 0.1 Ti



TiN formation in Al killed and Ti bearing steel



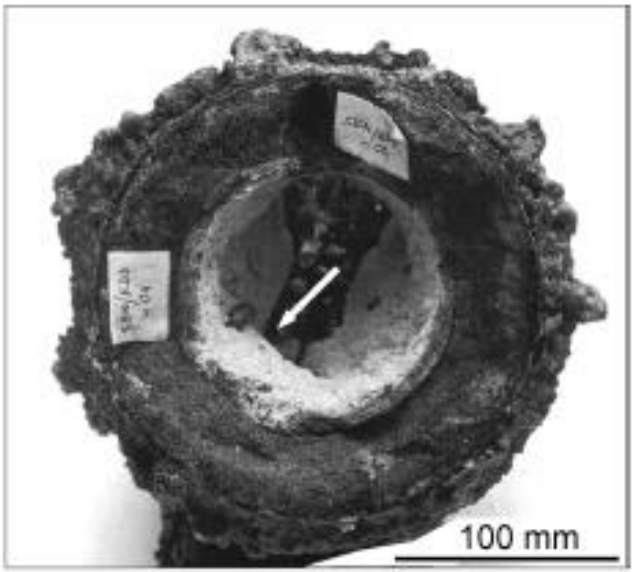
During the solidification,
a large amount of TiN can be formed.

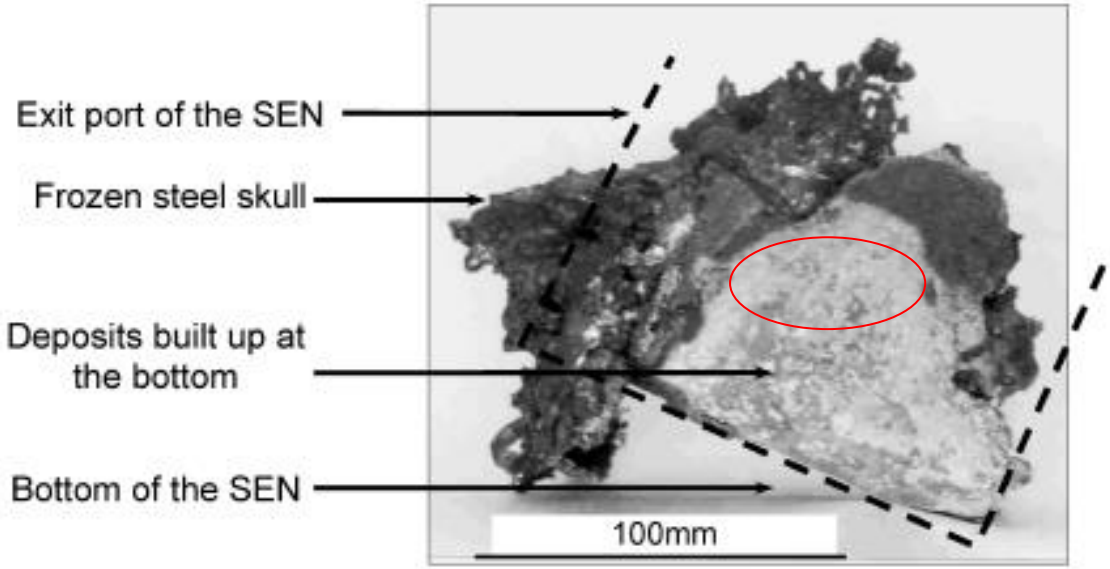
Nozzle Clogging in Ti-bearing Al-killed steel

- Kawashima *et al., CAMP-ISIJ (1991*)
  - Liquid Al-Ti-O (reoxidization) attached to Al_2O_3 inclusions
- Basu *et al*. *ISIJ Int. (2004)*

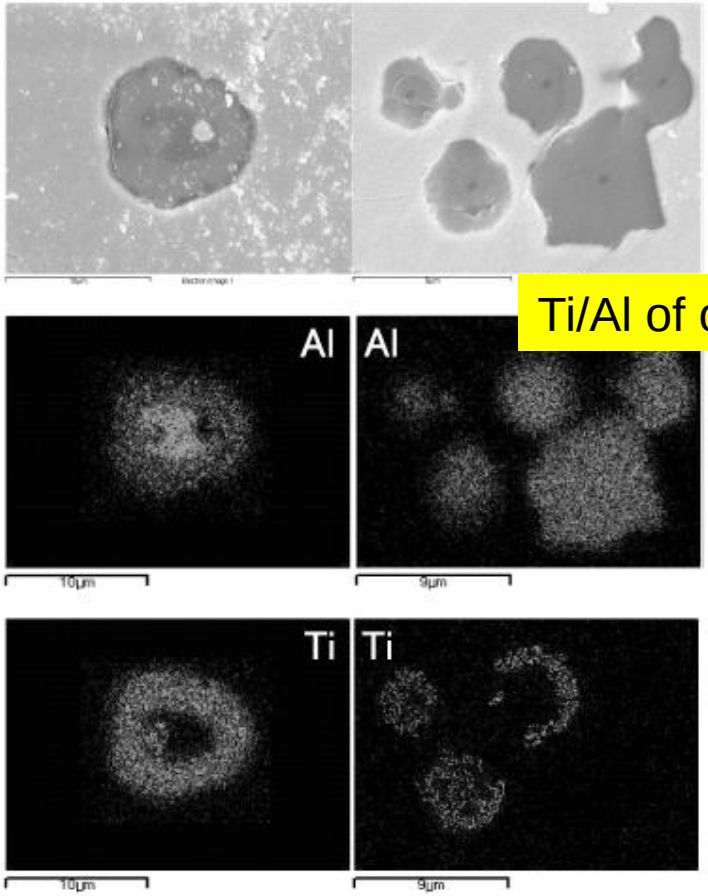
  Significant difference of nozzle clogging of Ti-bearing steel from and Ti-free steel is the existence of the Al-Ti-O inclusions covering Al_2O_3 core oxides.

  Reoxidation in tundish (high SiO_2 slags) causes the nozzle clogging.

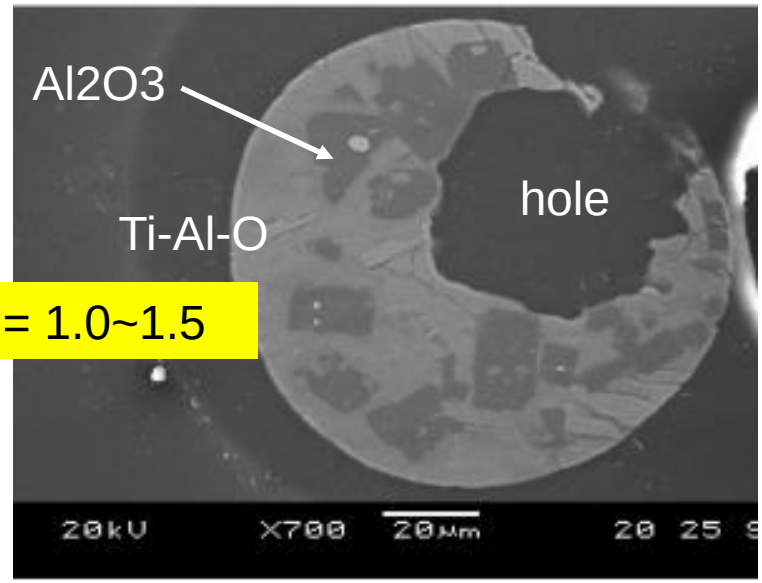




Inclusions generated by Reoxidation process

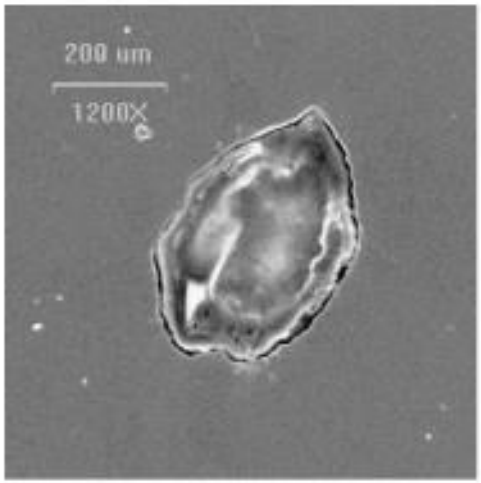


Ti/Al of outer layer = 1.0~1.5



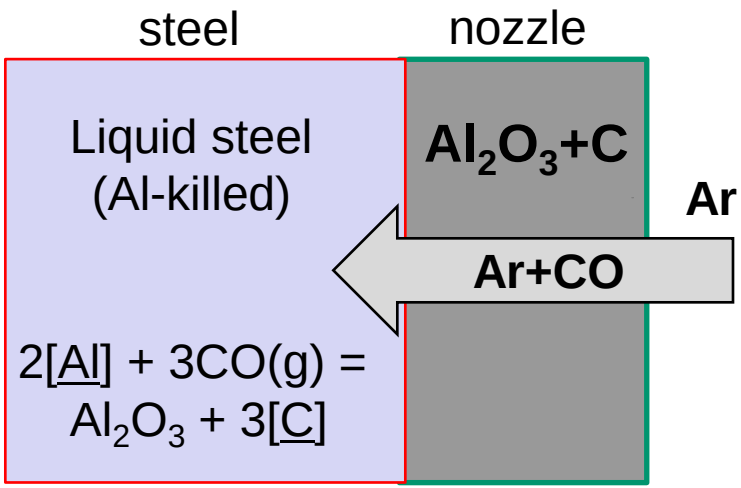
RH process after Ti addition (POSCO)
Doo et al. (2007)

Reoxidation in Tundish
(high SiO2 slags)
Park et al. (2004)

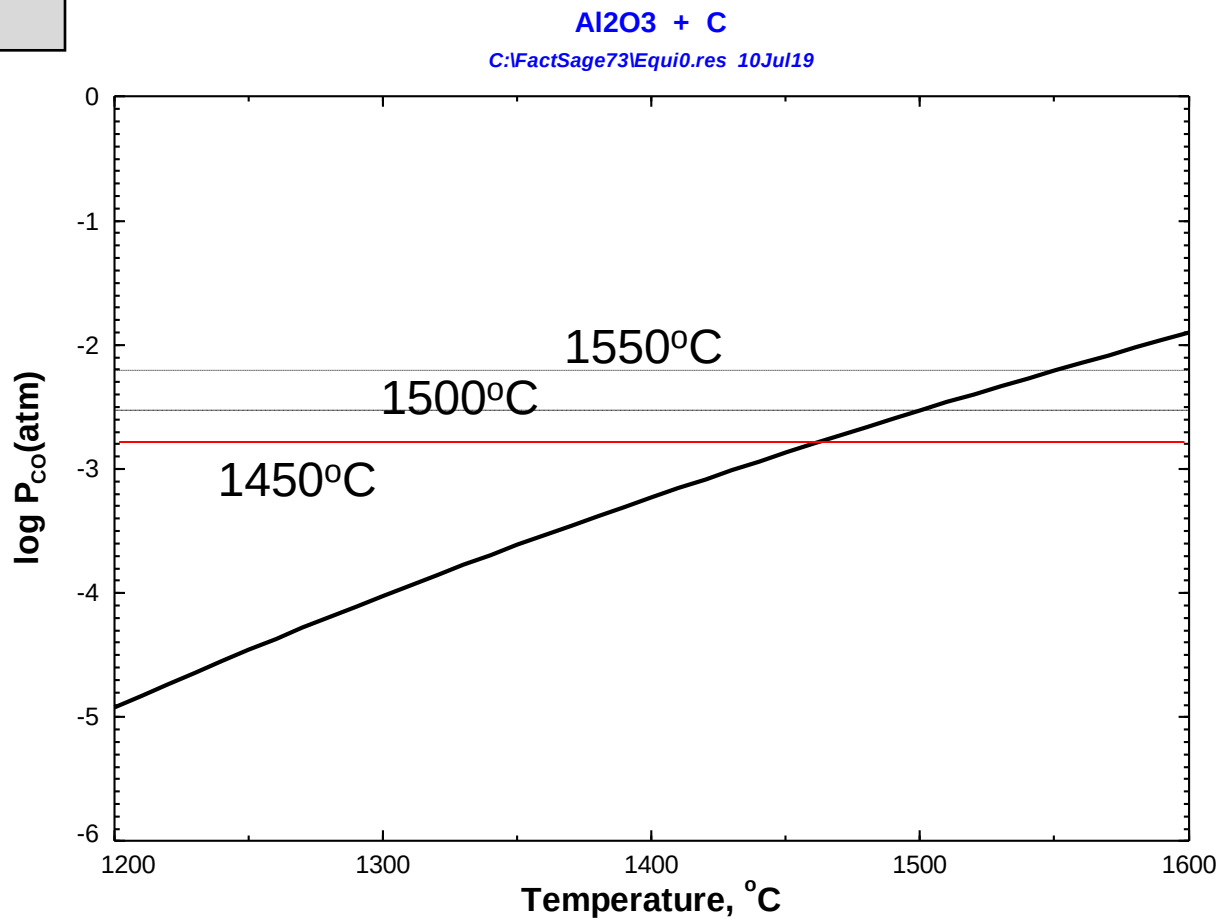


Reoxidation in Tundish
Basu *et al. (2004)*

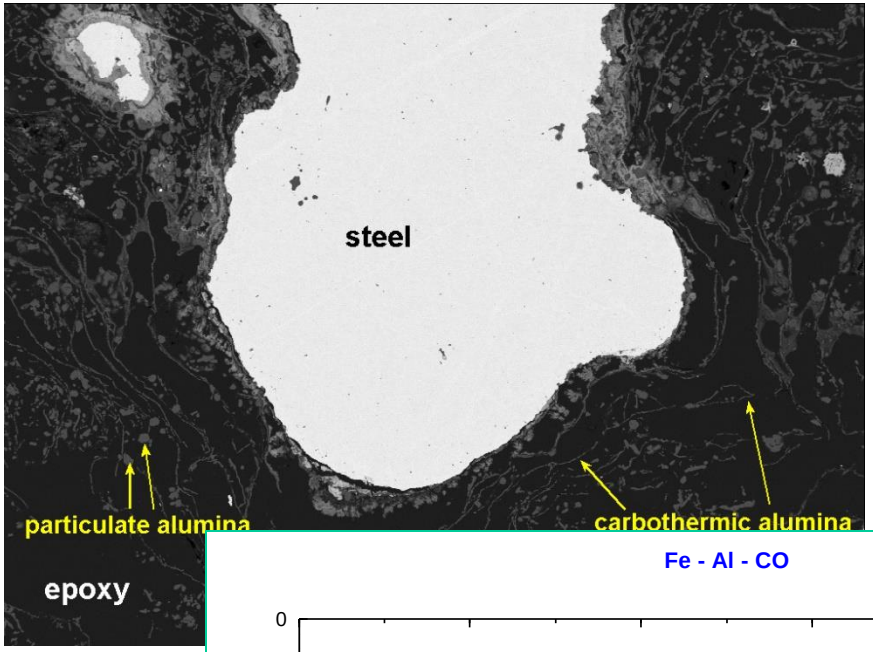
Reoxidation of steel by CO gas



$2Al_2O_3+9C = Al_4C_3+6CO(g)$



Reoxidation of steel by CO gas



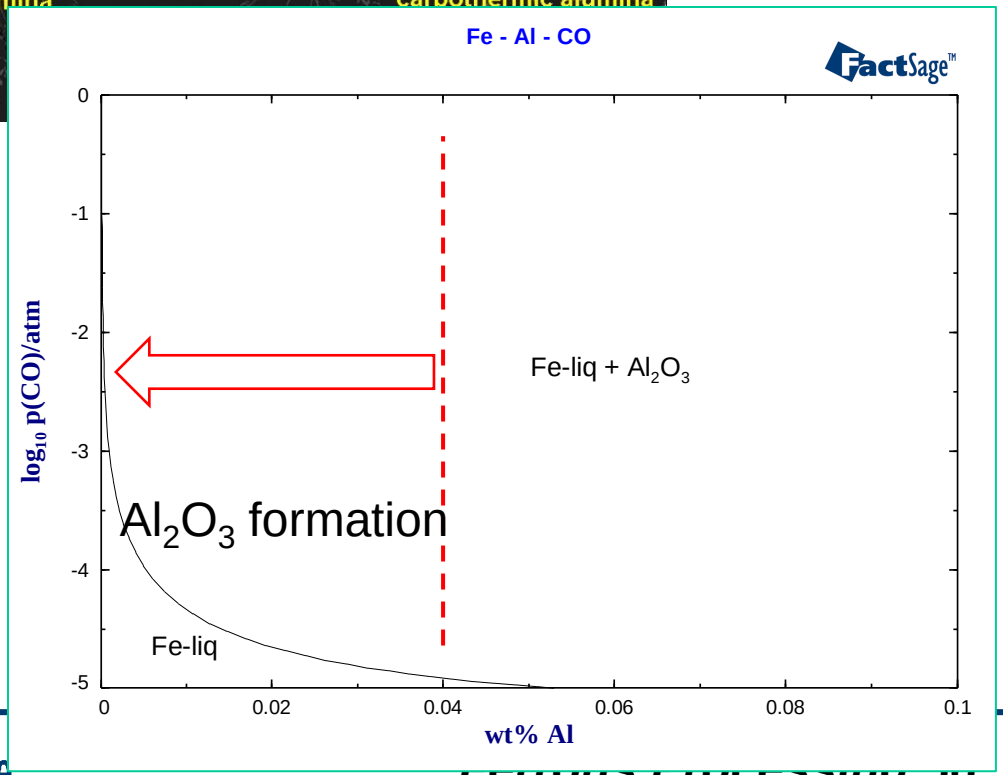
Al_2O_3+C

Liquid steel
(Al-killed)

Ar+CO

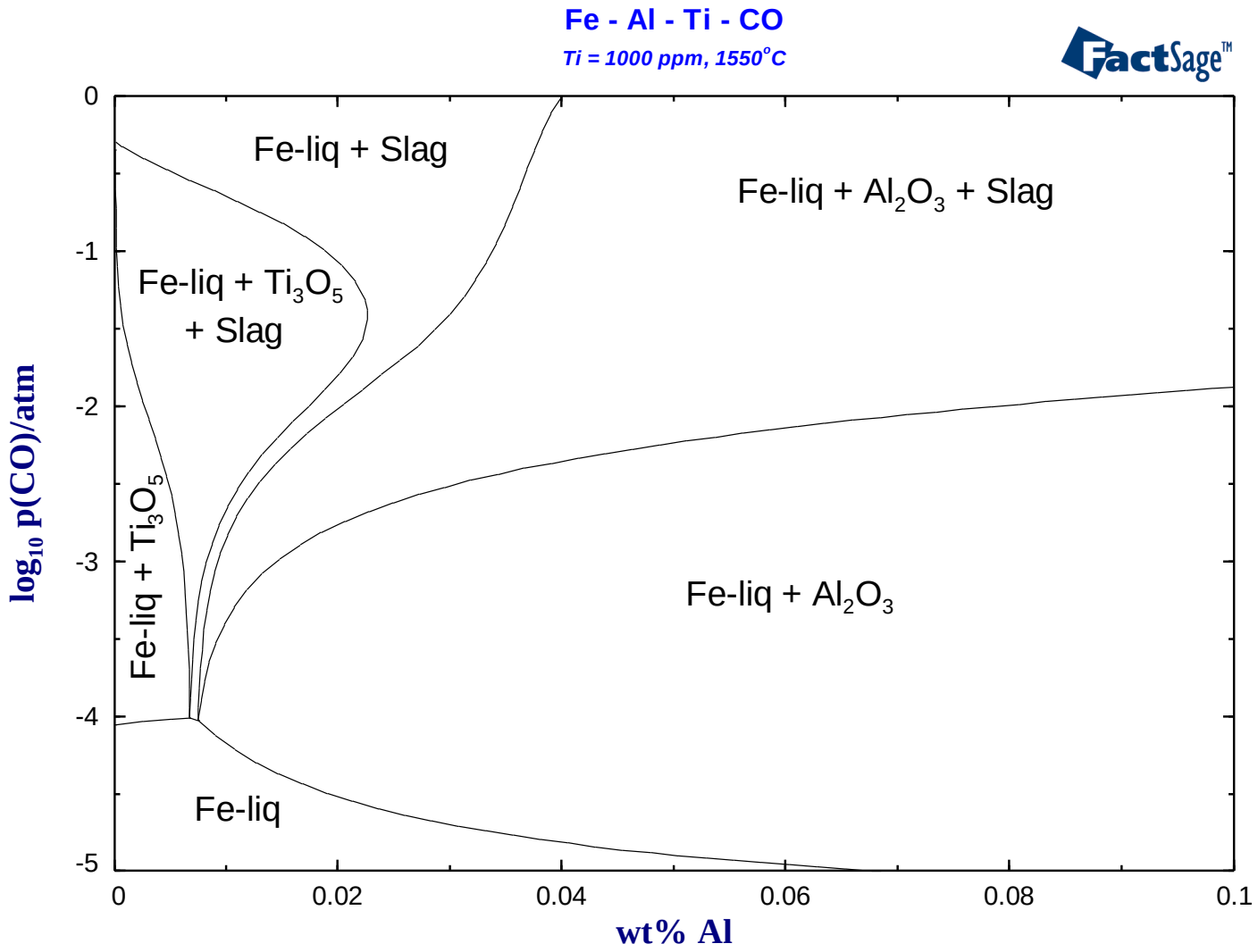
Ar gas

$2[\underline{Al}] + 3CO(g) = Al_2O_3 + 3[\underline{C}]$



$2Al_2O_3+9C = Al_4C_3+6CO(g)$

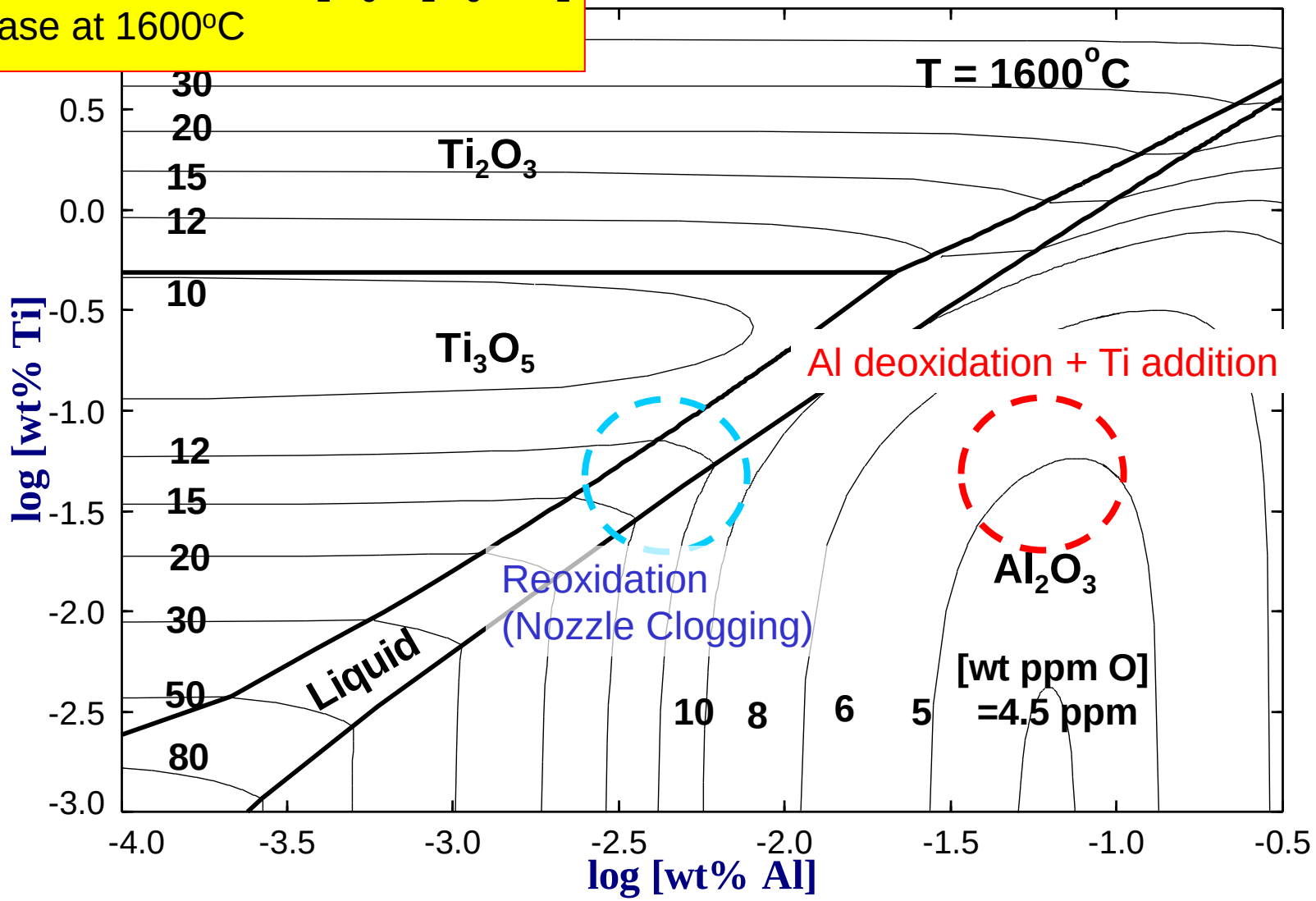
Reoxidation of steel by CO gas



Reoxidation of steel by CO gas through ceramic nozzle to form slag(Al-Ti-O) and Al_2O_3

Newly calculated Inclusion diagram of Fe-Al-Ti-O system

Existence of Liquid Al_2O_3-Ti_2O_3-TiO_2 phase at 1600°C

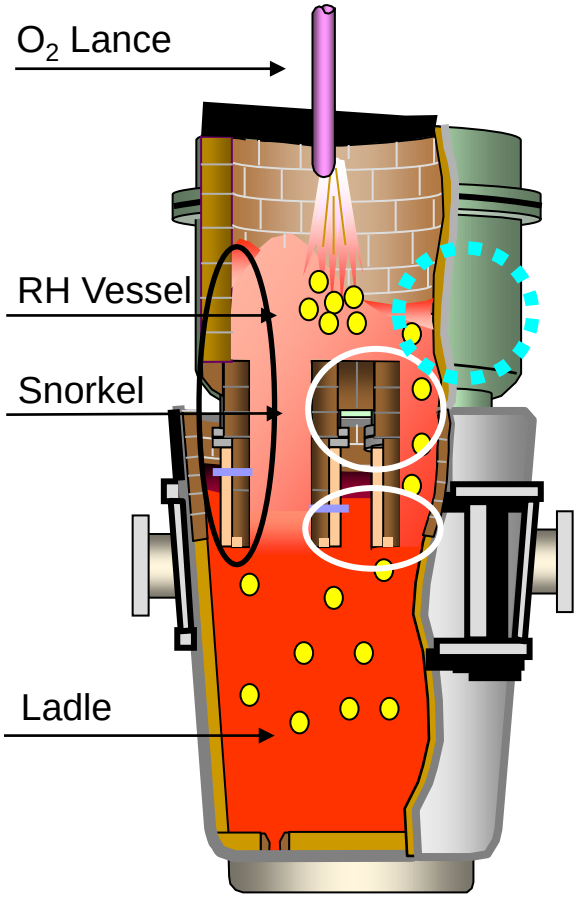


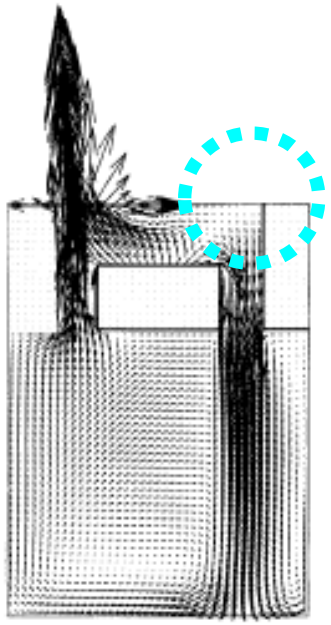
RH Vessel Refractory

RH OB

- ***High amount of oxygen blowing***
- ***Increase of Ferro-alloy (Al, Si, Mn, etc) addition***

→ More severe local corrosion of RH vessel refractory



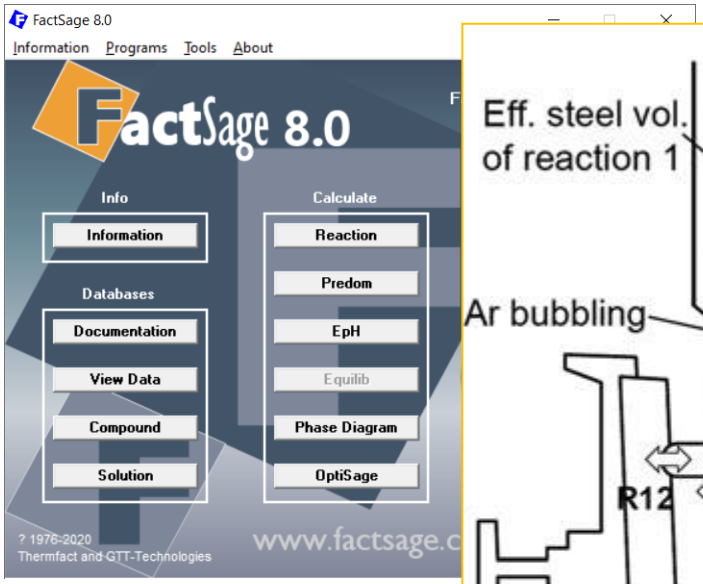


Flow pattern in RH CFD model

Normal corrosion

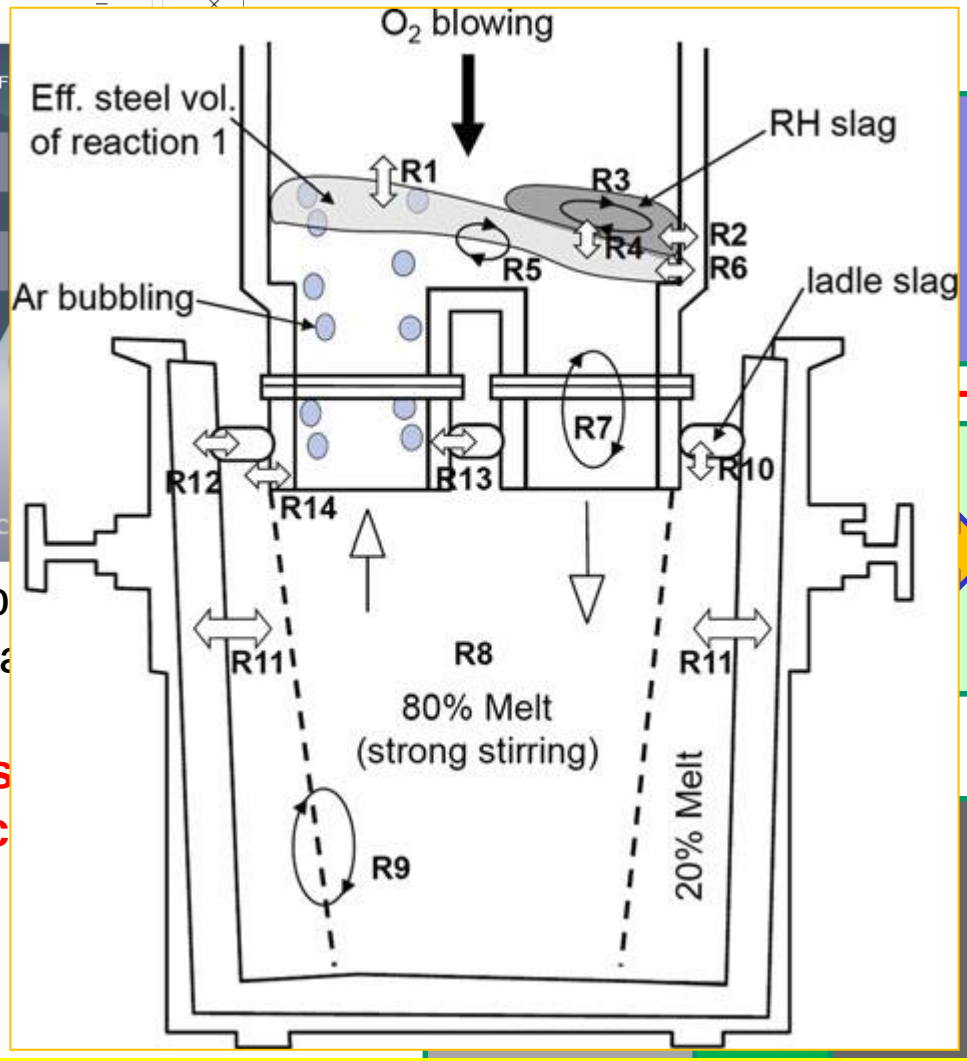
Abnormally severe corrosion

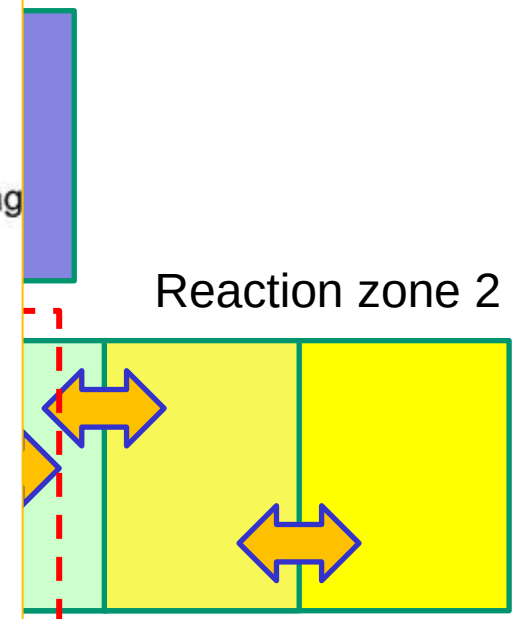
Concept for RH process simulation modeling



Quite enough thermo
(gas, molten steel, sla

**Write kinetic proces
input/output to Exc**





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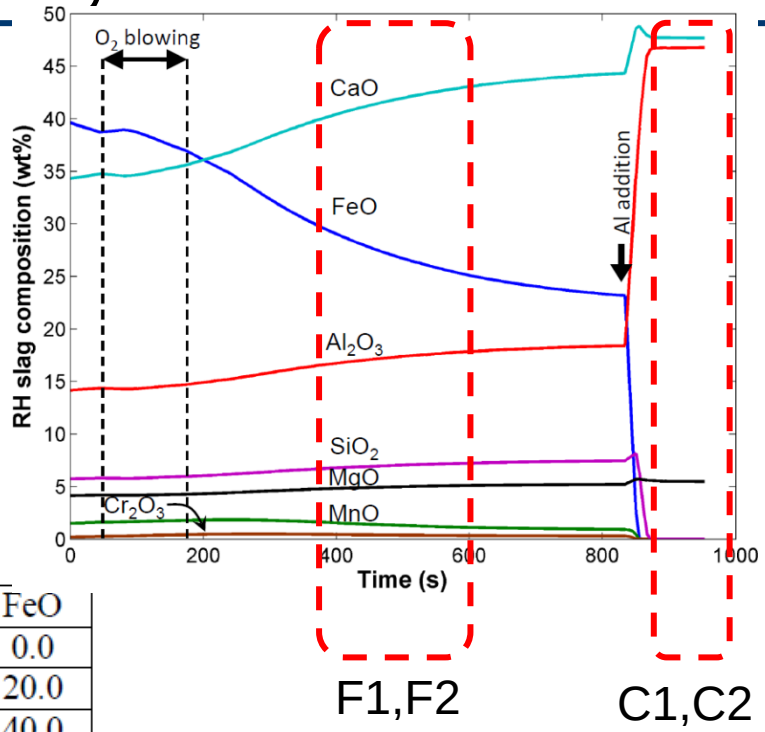
Van Ende et al: 'A Kinetic Model for the Ruhrstahl Heraeus (RH) Degassing Process', Metall. Mater. Trans. B, 2011, p. 477

Heat & Mass balance !!

RH Vessel Refractory

Predicted slag composition in RH vessel from RH process simulation →



Experimental and calculation conditions

Table 1: Composition of the synthetic slags (wt%).

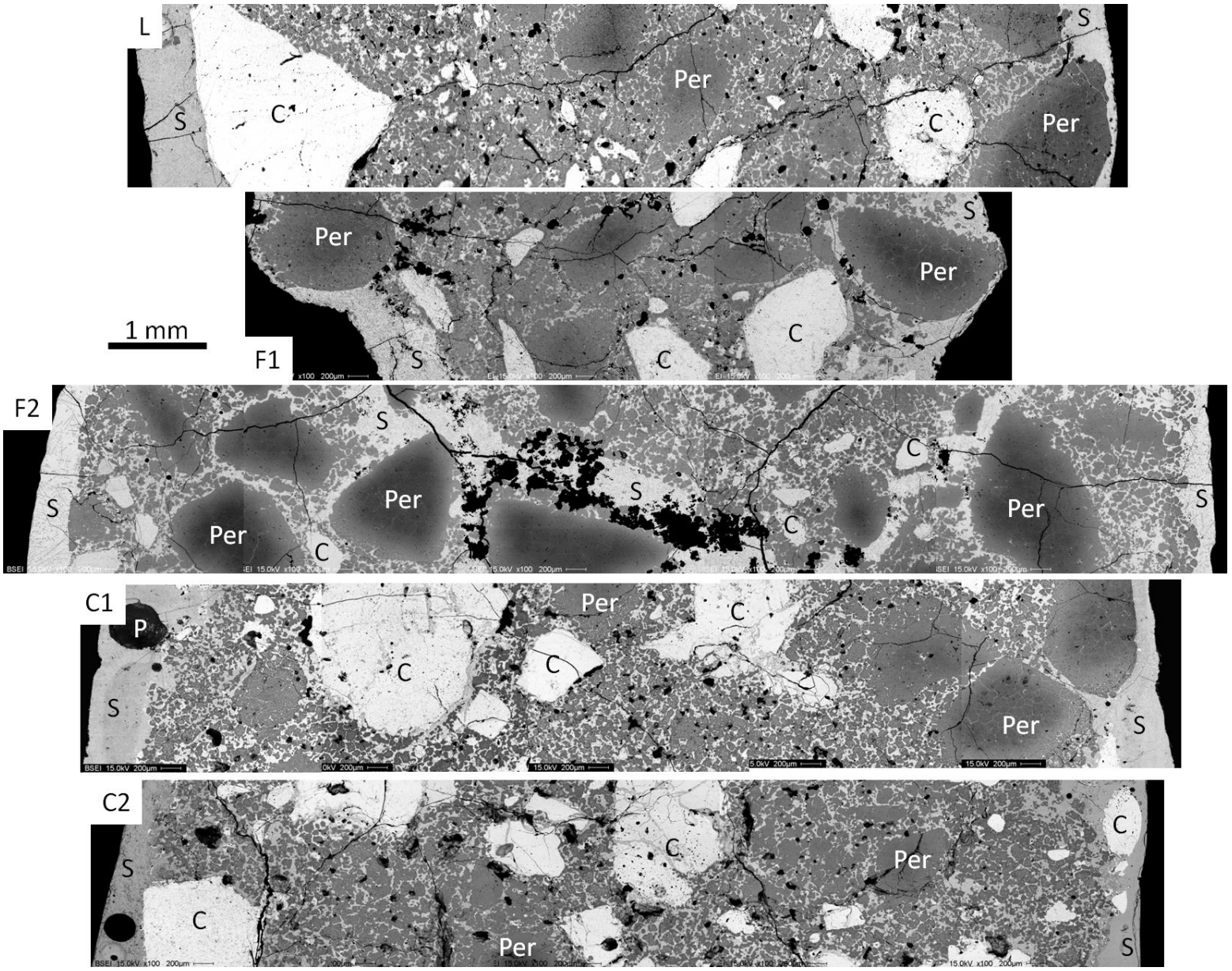
Slag	Symbol	MgO	Al_2O_3	SiO_2	CaO	FeO
Ladle slag	L	5.3	27.7	10.7	56.3	0.0
FeO-rich slag 1	F1	4.2	22.2	8.6	45.0	20.0
FeO-rich slag 2	F2	3.2	16.6	6.4	33.8	40.0
CaO-Al_2O_3 slag 1	C1	0.0	45.0	0.0	55.0	0.0
CaO-Al_2O_3 slag 2	C2	0.0	60.0	0.0	40.0	0.0

Table 2: Overall composition and apparent porosity of the investigated refractories.

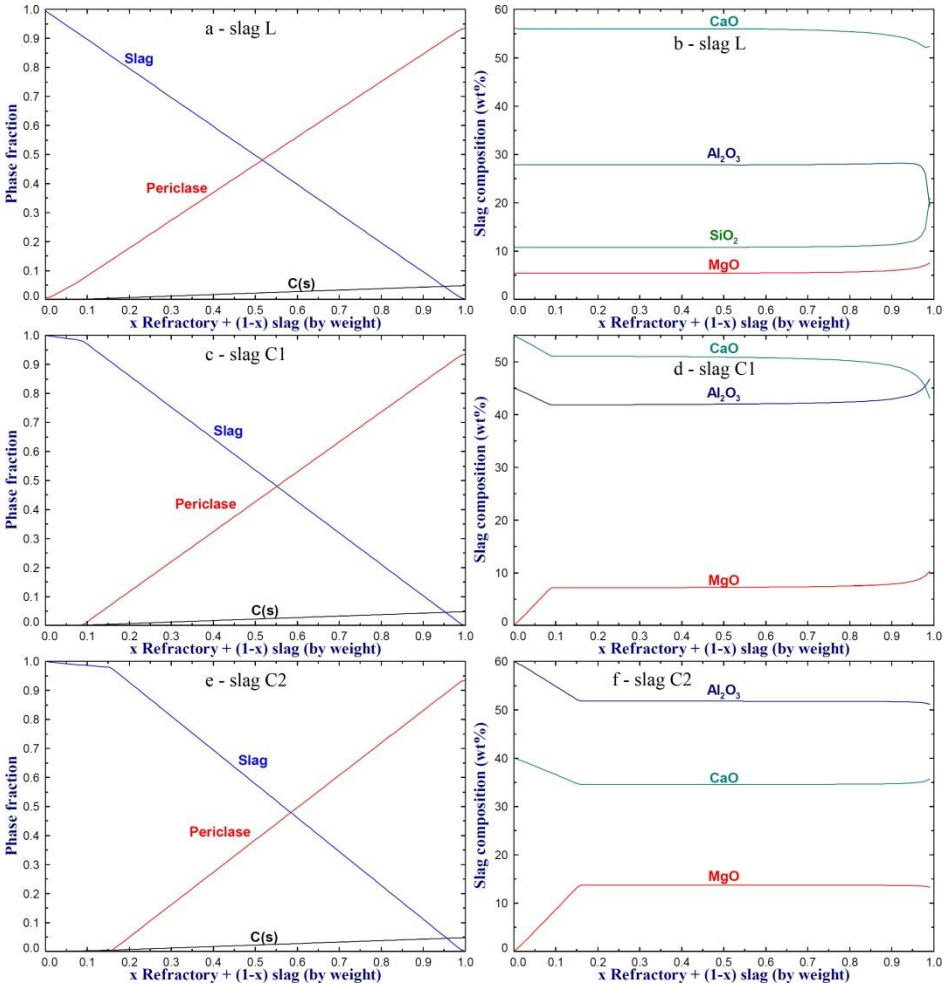
Refractory	Overall composition (wt%)							Apparent porosity (%)
	MgO	Cr_2O_3	CaO	SiO_2	Al_2O_3	FeO_t	C	
Magnesia-chromite	55.8	22.9		2.1	8.2	11.0		16~17
Magnesia-carbon	90.3		0.8	2.2	6.8		5.1	11~13

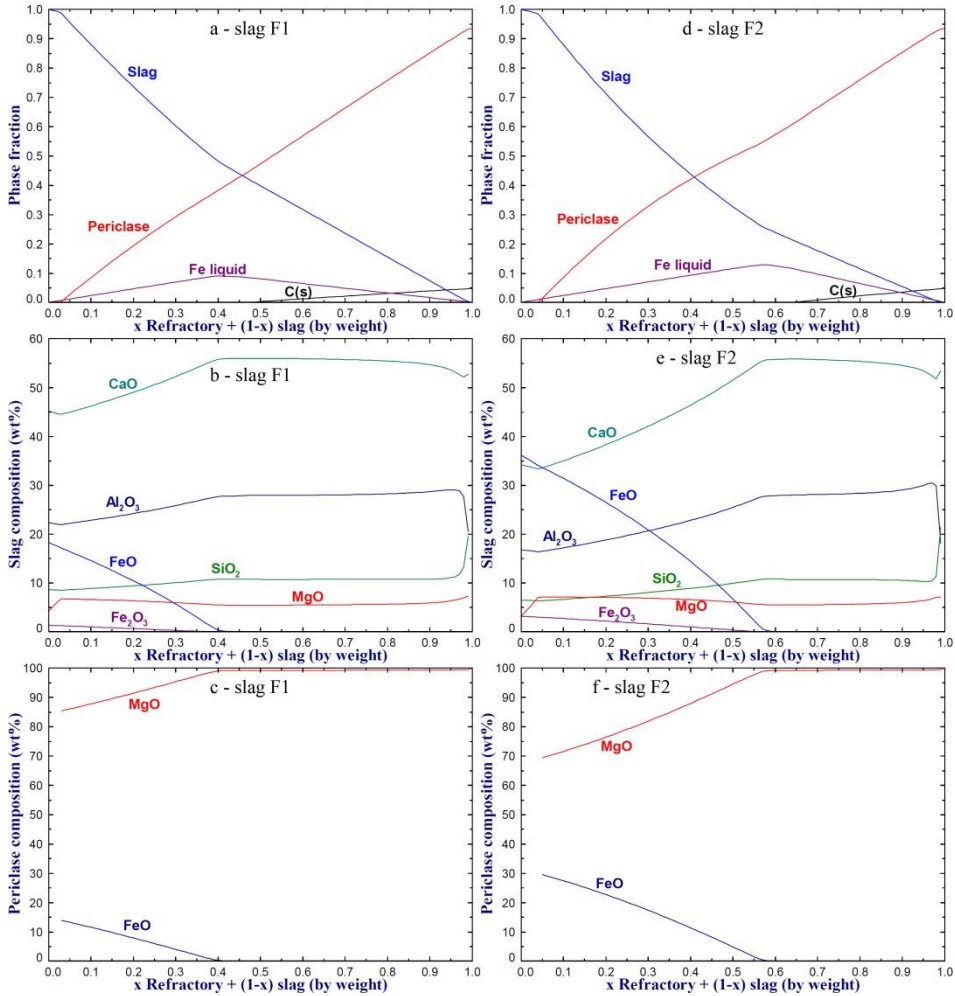
M.-K. Cho, M.-A. Van Ende, T.-H. Eun and I.-H. Jung, "Investigation of slag-refractory interactions for the Ruhrstahl Heraeus (RH) vacuum degassing process in steelmaking", J. Eur. Ceram. Soc., 2012, 32,1503-1517.

Refractory Finger tests at 1600°C

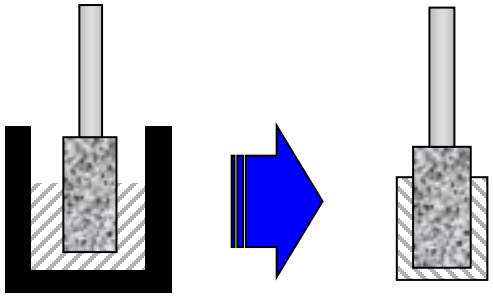


Thermodynamic Calculations: Refractories – Slag Interactions





Ladle Glaze formation



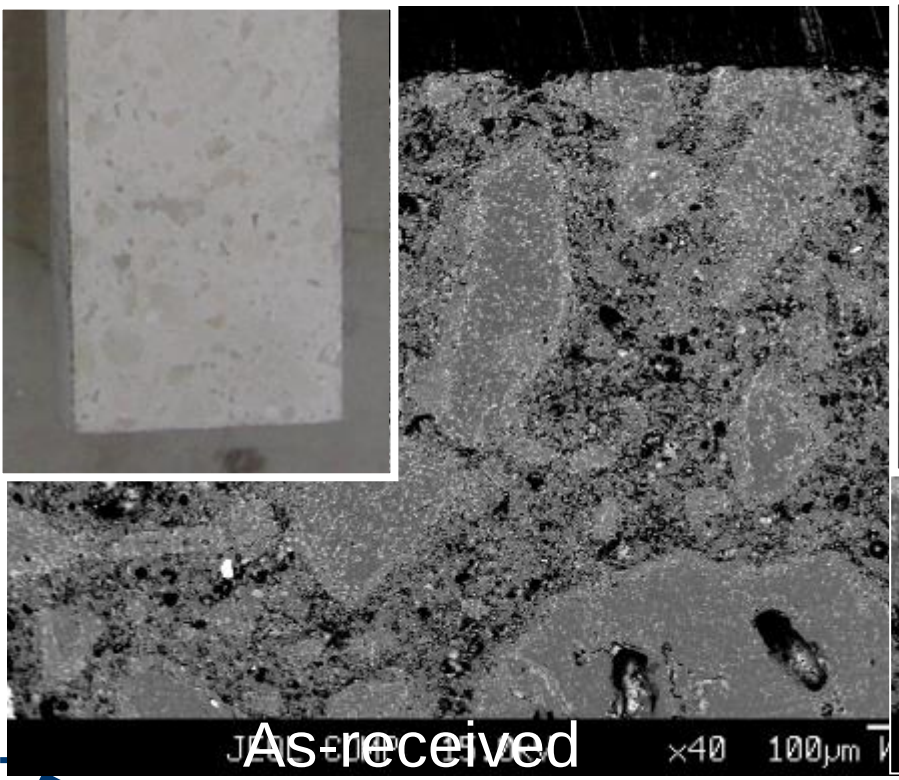
Dipping time: 120 sec

Refractory composition (wt.%)

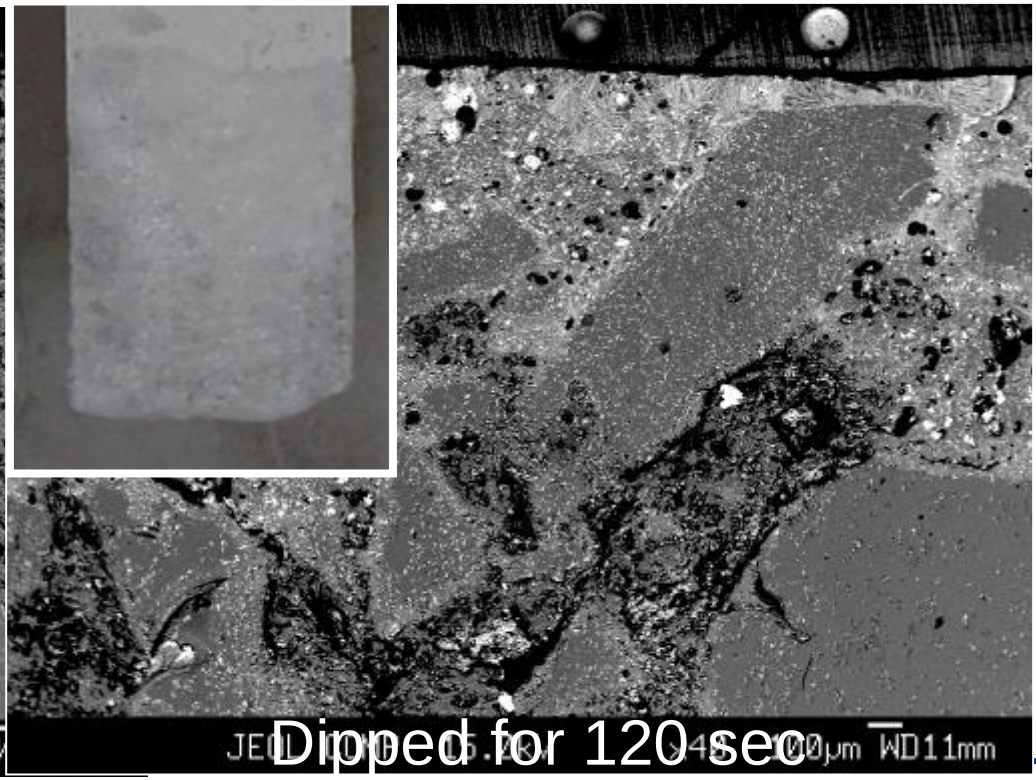
CaO	SiO2	Al2O3	MgO
2.35	0.76	88.06	8.35

Slag composition (wt.%)

CaO	SiO2	Al2O3	MgO
54.06	10.47	26.24	9.23

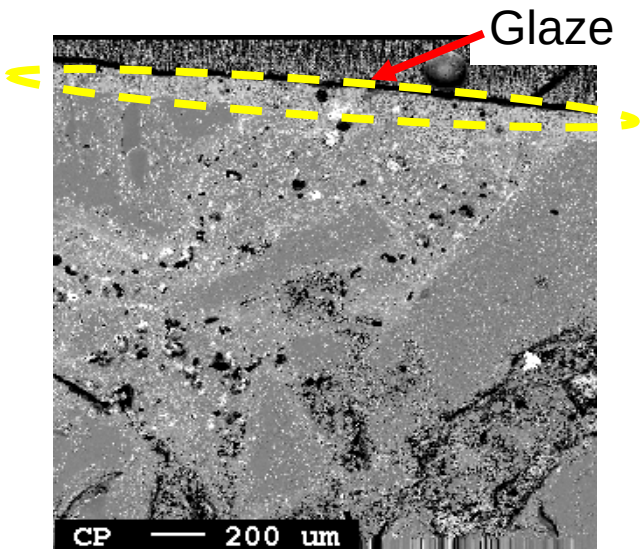


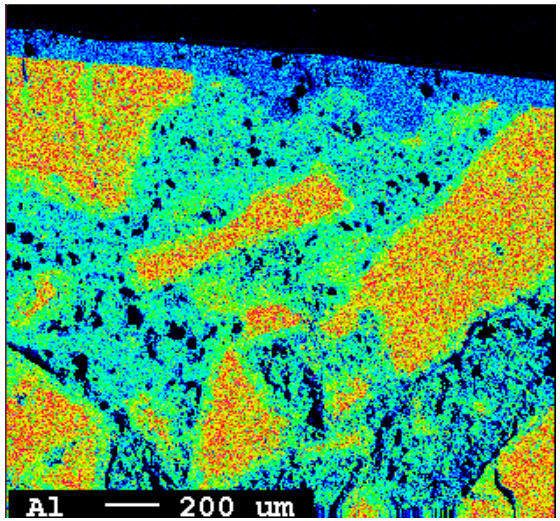
As-received

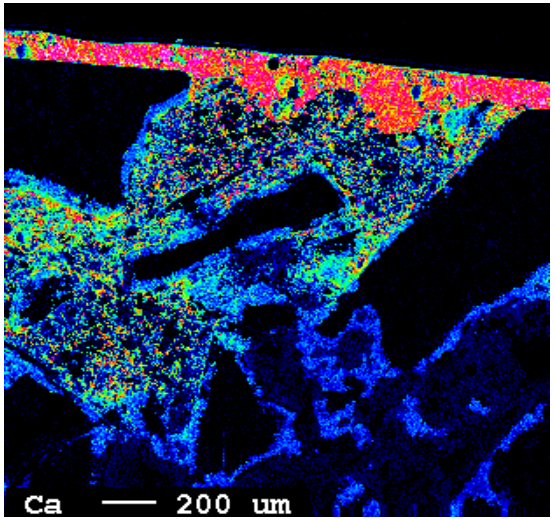


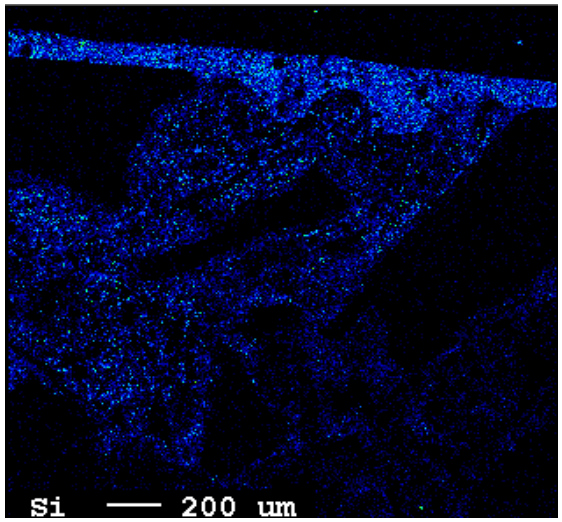
Dipped for 120 sec

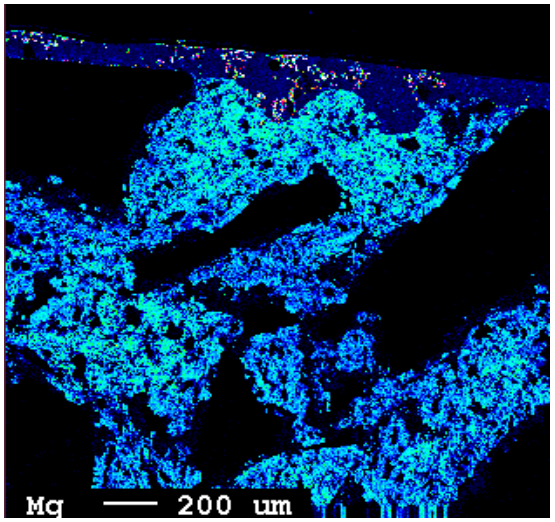
Glazed Refractory



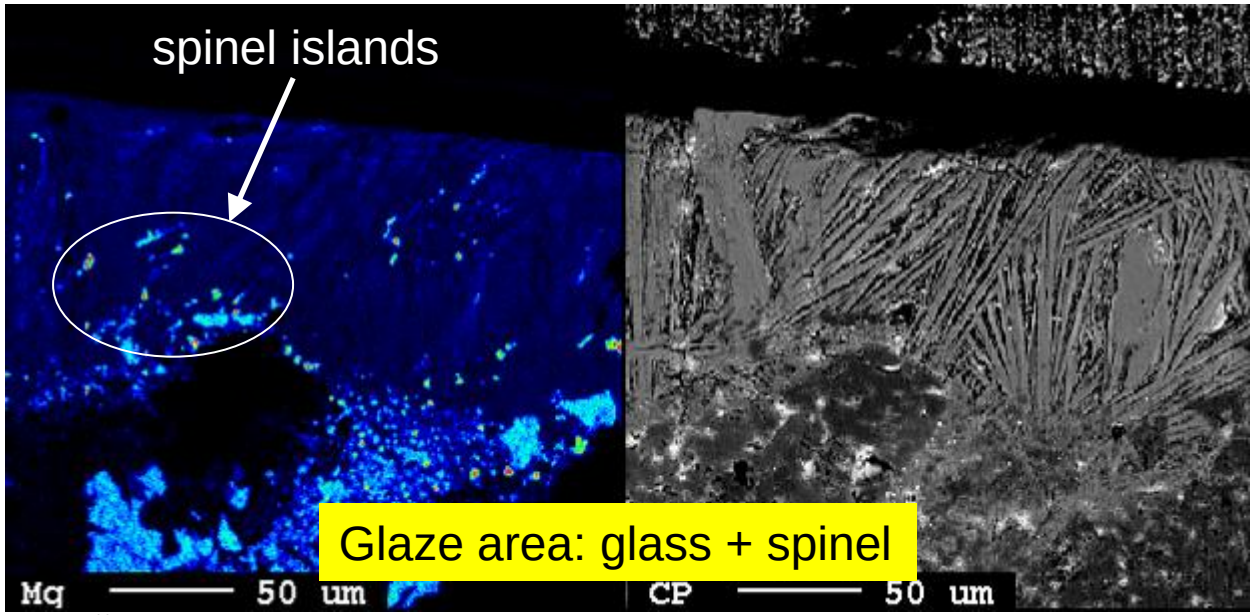






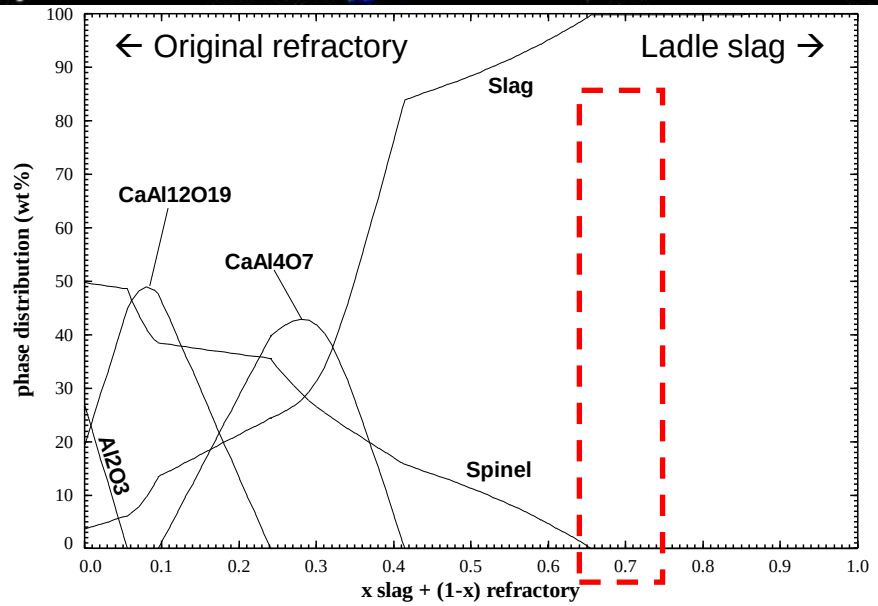


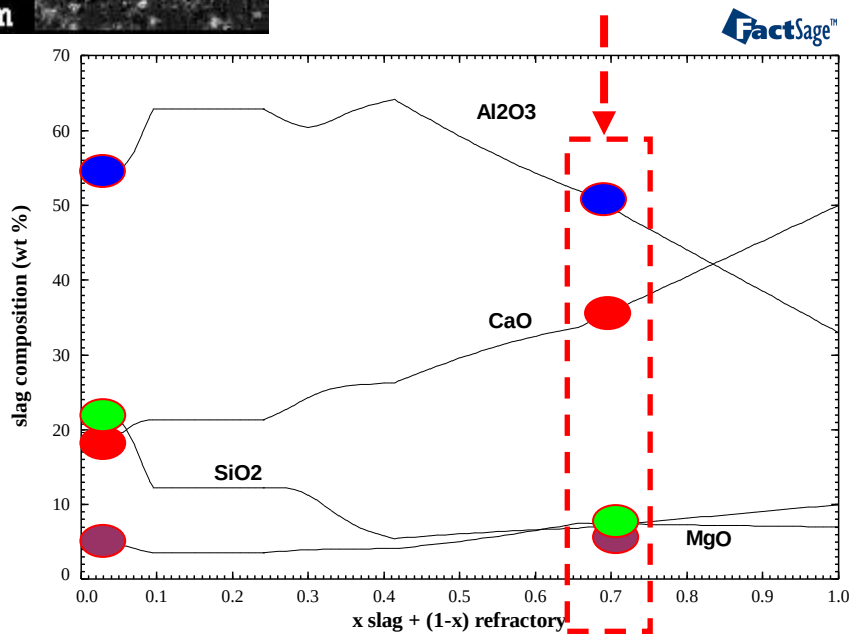
Glaze (Reaction product of slag and refractory)



Glaze composition (glass)

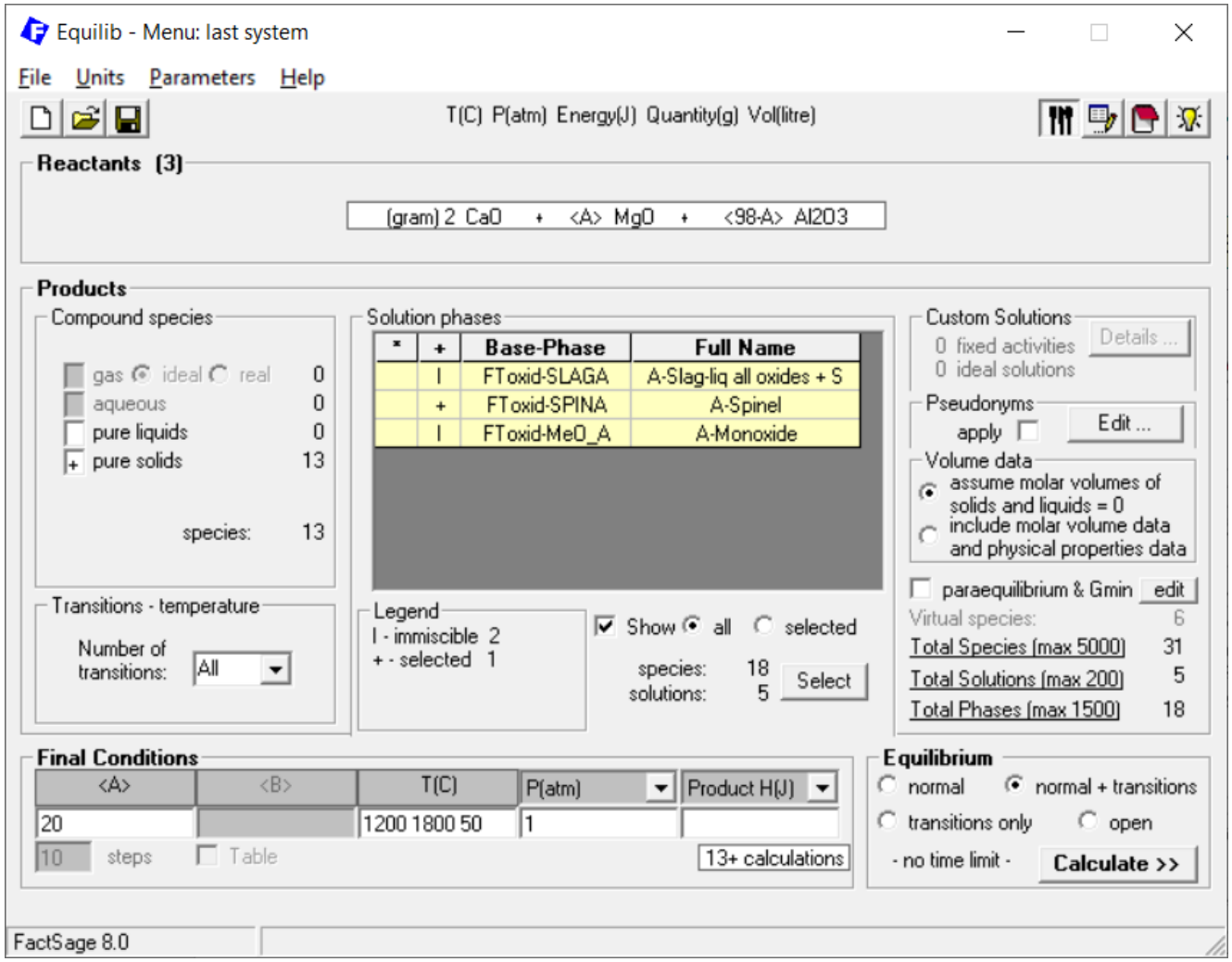
CaO	SiO2	Al2O3	MgO
35.8	6.6	51.1	6.5





Equilibrium stability calculations with temperature: refractories

Equilibrium stability of 20MgO-78Al_2O_3-2CaO refractories



Equilibrium stability calculations with temperature: refractories

Equilib - Results 1200 C (page 1/18)

Output Edit Show Pages Final Conditions

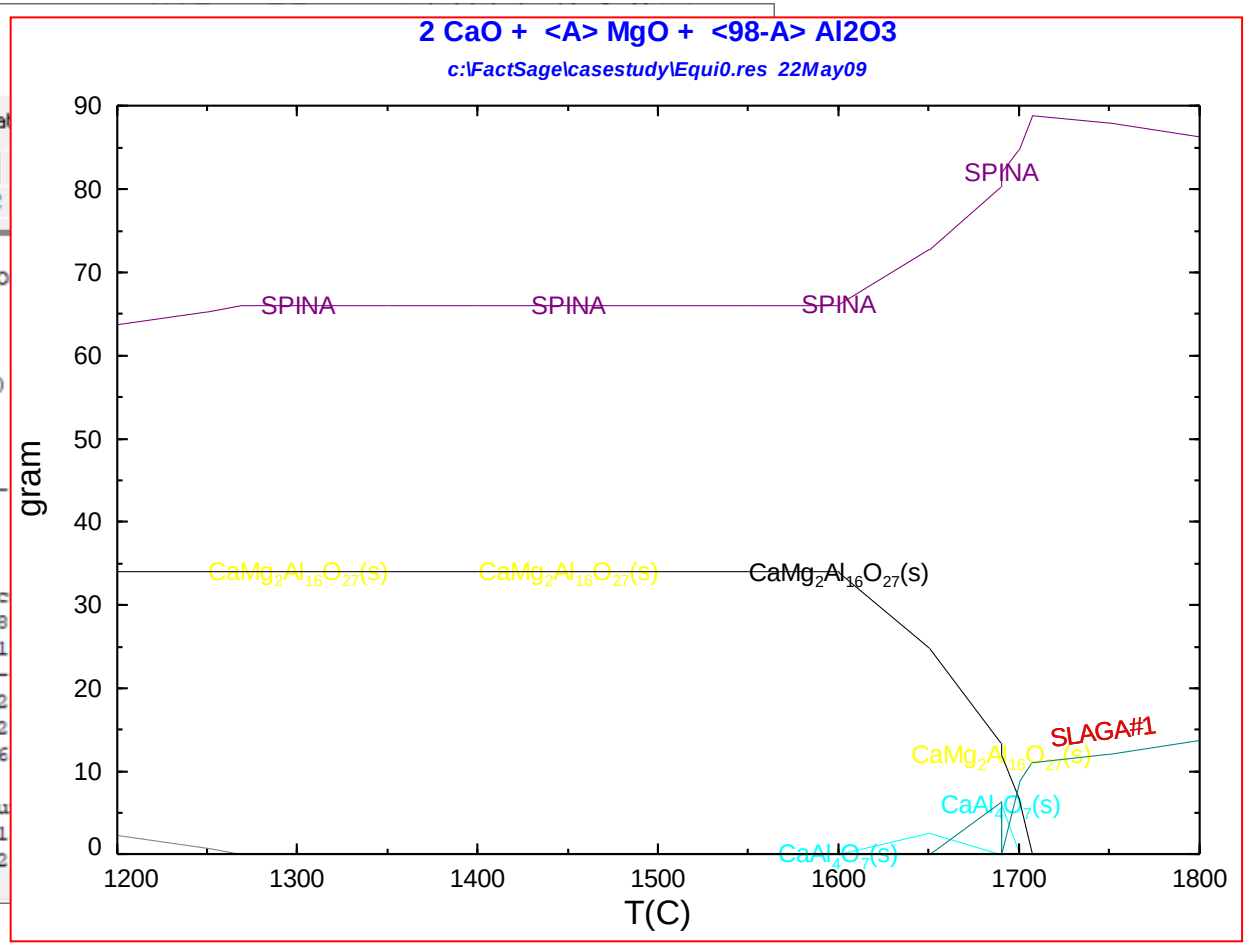
1650 C | 1690.02 C | 1690.02 C | 1700 C | 1707.18 C |
1200 C | 1250 C | 1269.16 C | 1300 C | 1350 C | 1400 C

```
(gram) 2 CaO  +  <A> MgO  +  <98-A> Al2O

   63.716     gram  Spinel
   (63.716 gram, 0.44894 mol)
           (1200 C, 1 atm,      a=1.0000)
           ( 27.539      wt.% Al3O4[1+]
           + 0.17914     wt.% Al1O4[5-]
           + 59.305      wt.% MgAl2O4
           + 3.9960      wt.% Al1Mg2O4[1-
           + 8.5991      wt.% Mg3O4[2-]
           + 0.38146     wt.% Mg1O4[6-])

           Site fraction of sublattice c
           Mg[2+]T                    0.68
           Al[3+]T                    0.31
           ---------------------------
           Va[0]O                     8.92
           Mg[2+]O                    0.12
           Al[3+]O                    0.86

           System component           Amou
           Al                         0.91
           Mg                         0.42
```

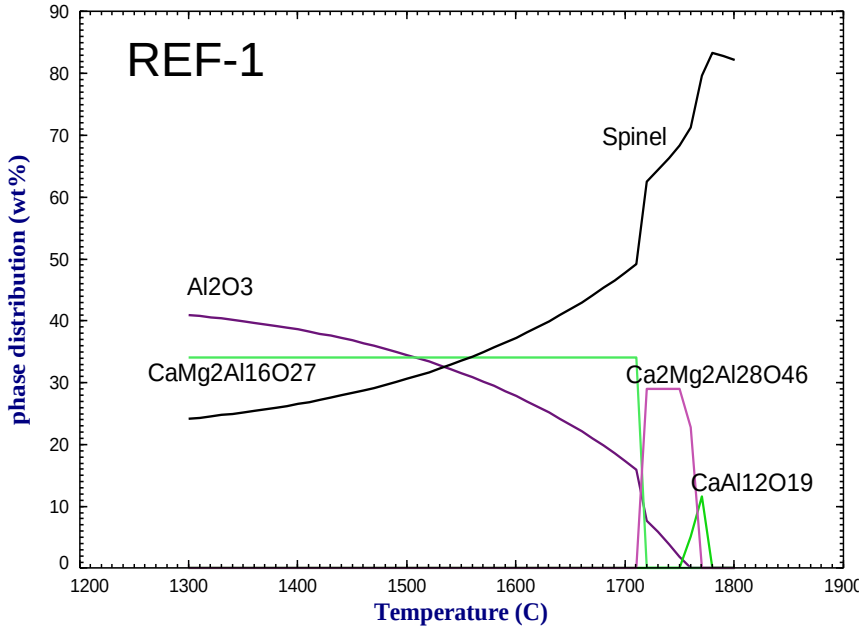


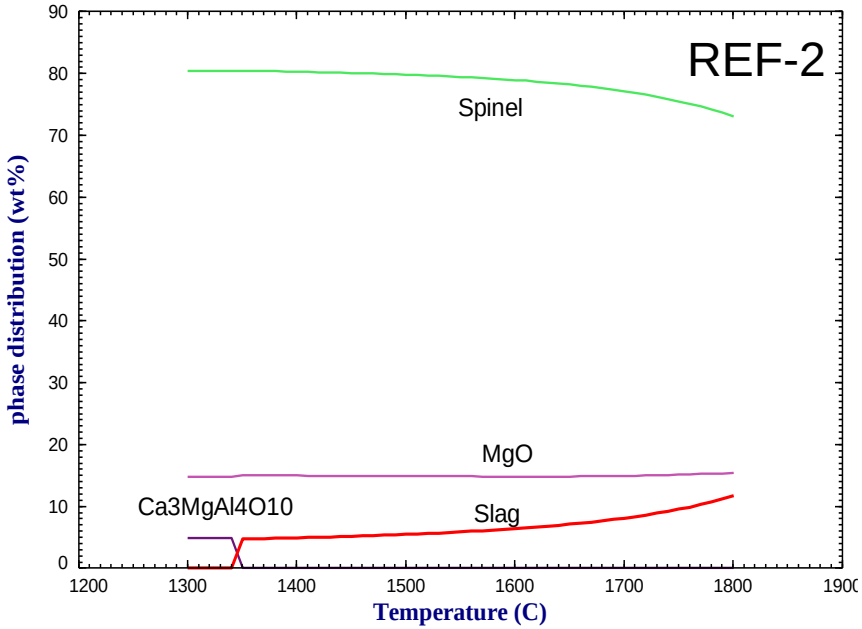
The refractory is mechanically unstable above 1600°C:
- considerable volume change due to the significant change in phase distribution

The refractory cannot be used above 1690°C:
- significant amount of liquid phase formation

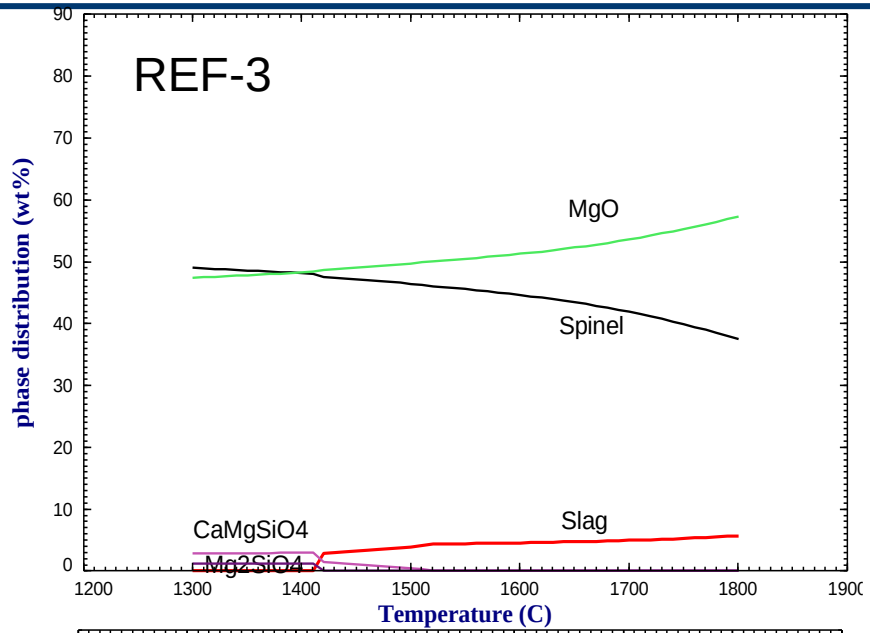
Thermal Stability test of Refractories

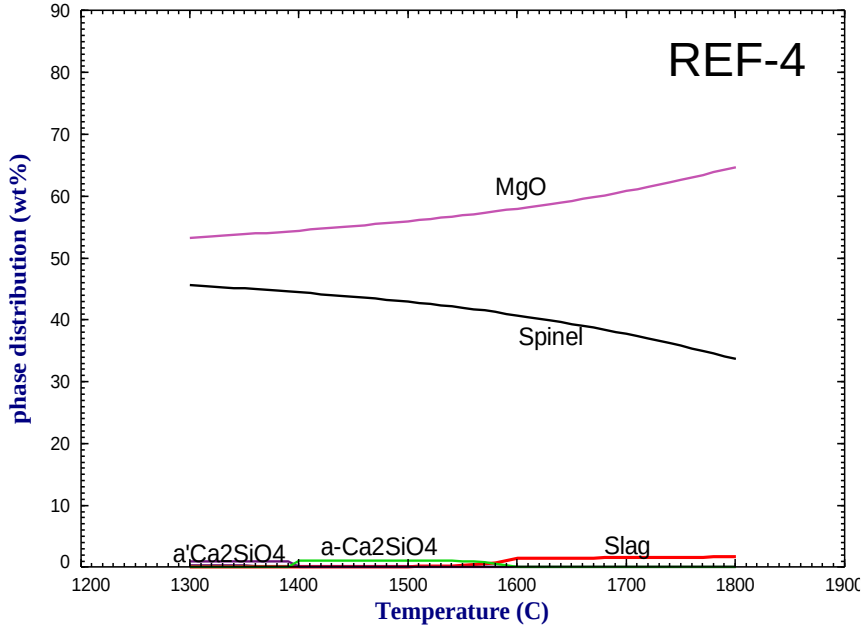
wt%	REF-1	2	3	4	5	6
Al_2O_3	88	60	11	4	0.5	0.5
MgO	9	38	58	61	89	75
CaO	2	2	0.9	0.7		
Cr_2O_3			20	29		
Fe_2O_3			8.8	4.8		
SiO_2			1.6	0.4	0.5	1.2
C					7	17
Al					2	4

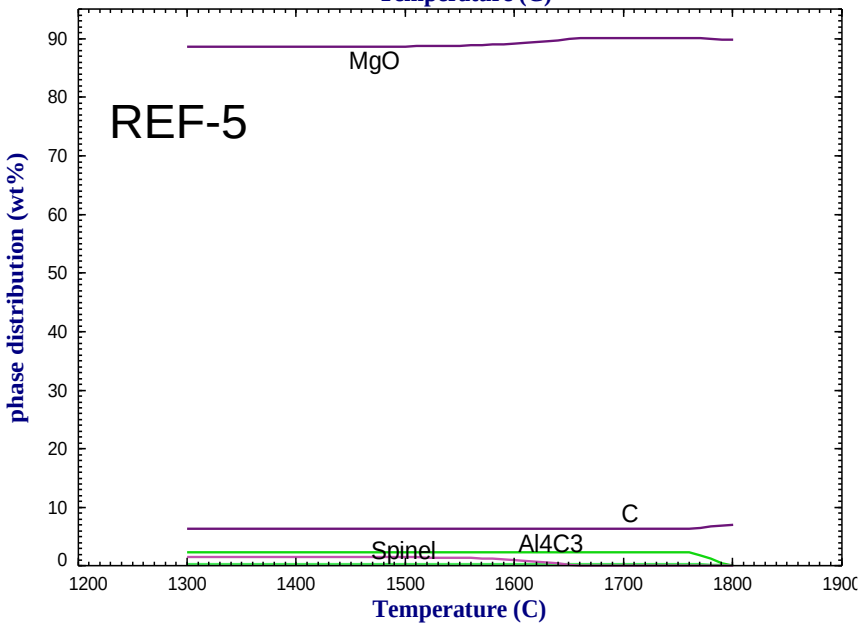




Thermal Stability test of Refractories



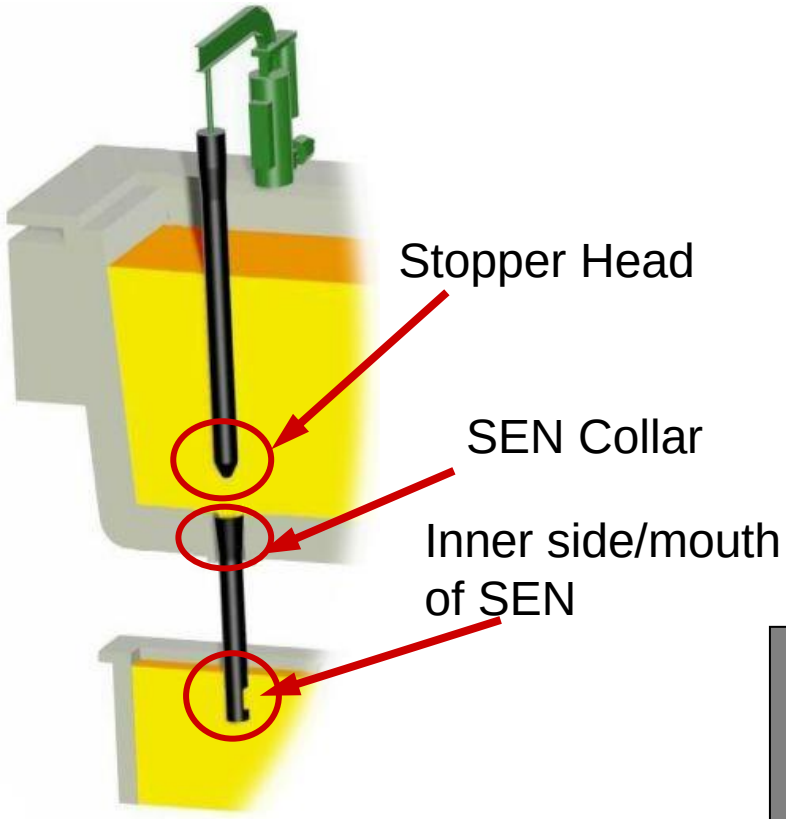




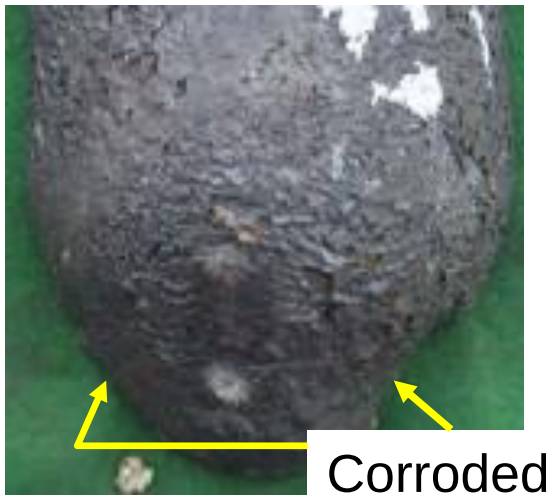
Depending on the refractory compositions, the refractory components can vary drastically.

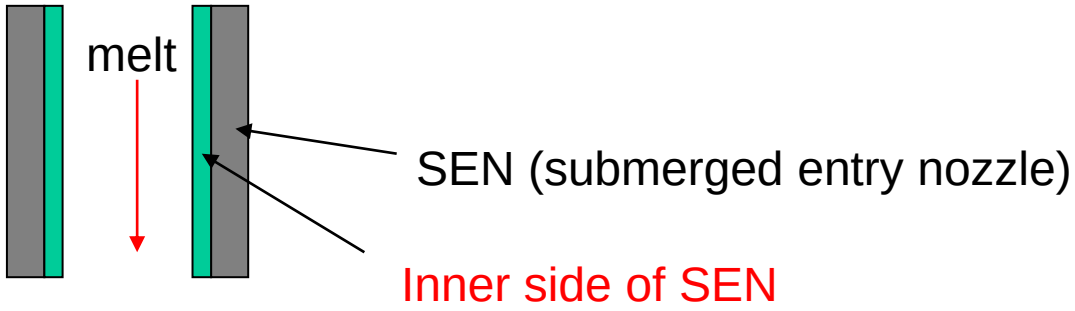
- Formation of liquid
  - Stability of refractory ↓
- Change in MgO/Spinel fraction
  - Mechanical wear resistance
  - Volume change

Refractory – Liquid Inclusion Interactions



Stopper (Al2O3-C)





M.-K. Cho and I.-H. Jung, "Corrosion of nozzle refractories by liquid inclusion in high oxygen steels", ISIJ Inter. 2012, vol. 52, pp. 1289-1296.

Refractory – Liquid Inclusion Interactions

Please see the details in the ISIJ paper

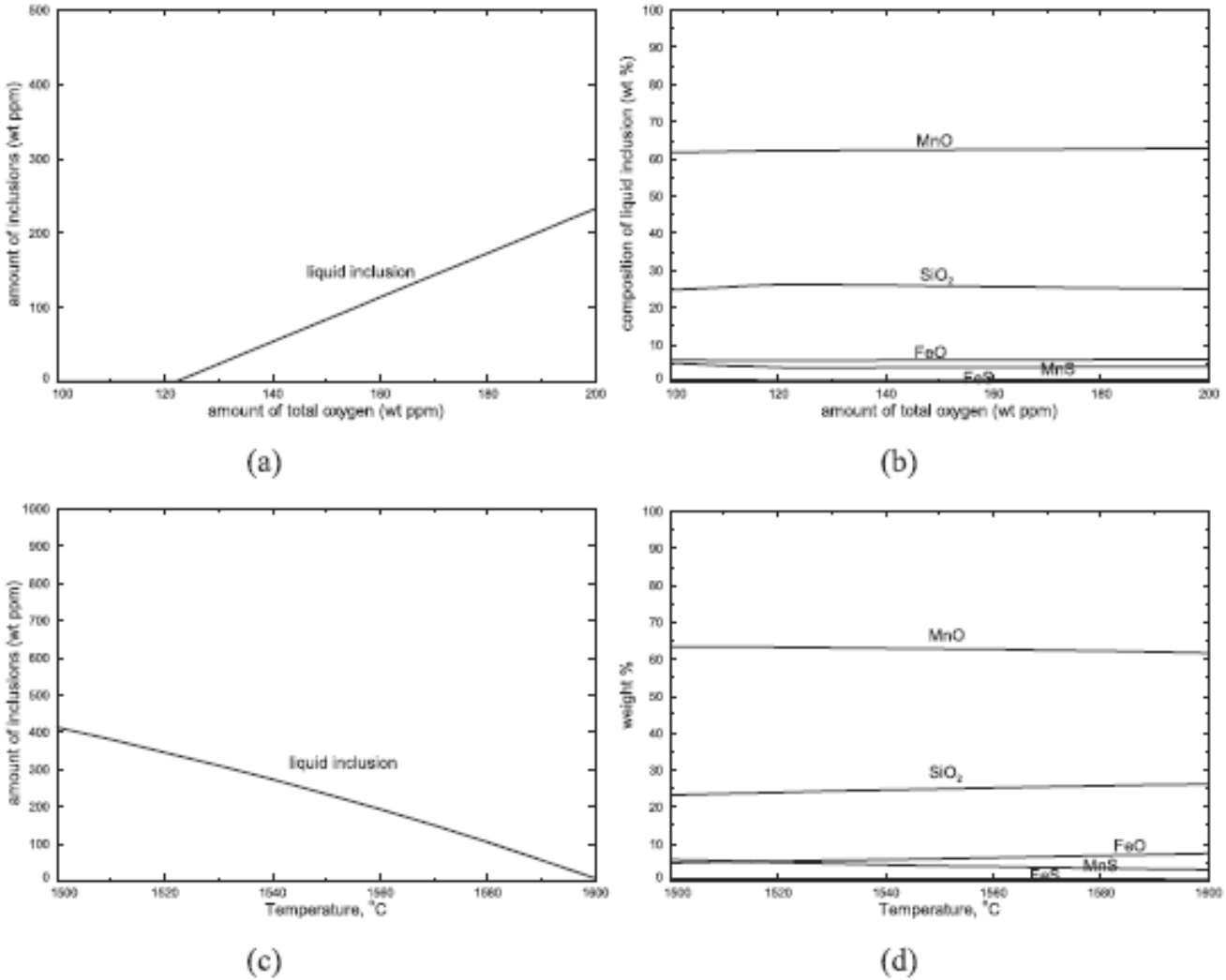


Fig. 2. Calculated inclusions formed in high oxygen steel (Fe–0.08C–1.2Mn–0.3S–0.01Si–O–minor P, Bi, *etc.* in wt%) during continuous casting process. (a) and (b): amount and composition of liquid inclusion varied with total oxygen content in steel at 1 550°C, (c) and (d) amount and composition of liquid inclusion in molten steel containing 200 wt ppm oxygen varied with temperature.

Refractory – Liquid Inclusion Interactions

Table 1. Chemical compositions of the refractories investigated in the present study.

wt%	Al_2O_3–C	Al_2O_3–AlN–C	Spinel–L–C	Spinel–H–C	ZrO_2–C
Al_2O_3	95	54	70	62	
MgO			26	25	
ZrO_2					85*
C	3	15	4	13	13
SiC	2				2
AlN		30			
etc.		1			

* CaO stabilized ZrO_2.

Please see the details in the ISIJ paper

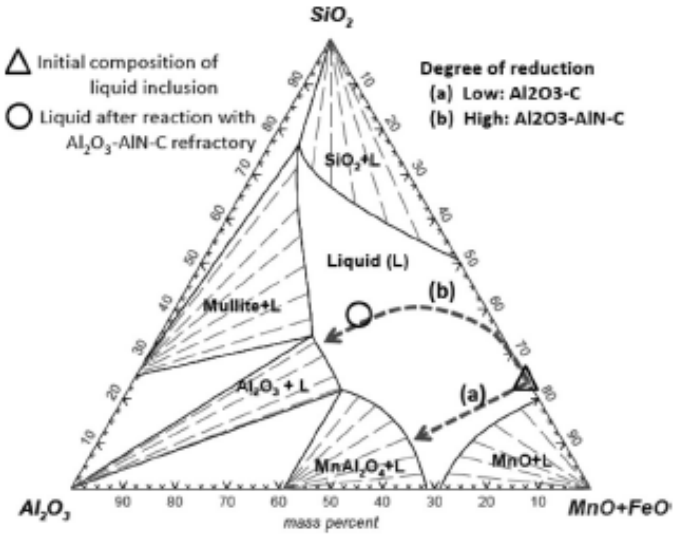


Fig. 8. Variation of liquid inclusion composition depending on the degree of reduction by carbon contained in refractory.

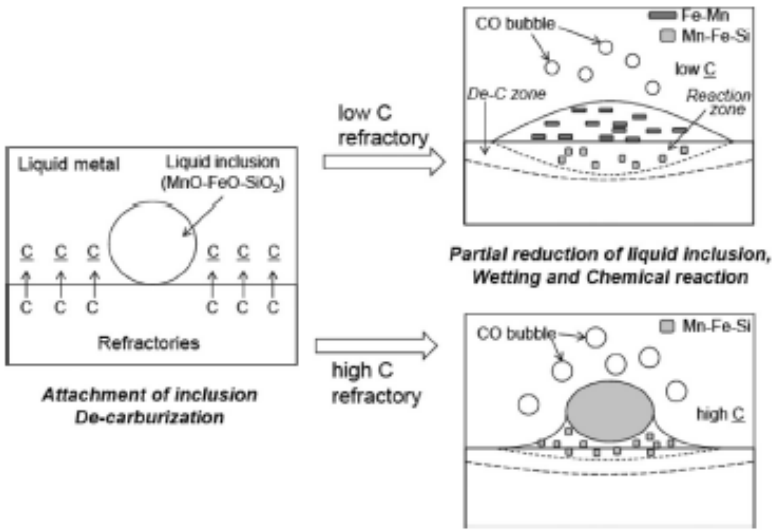


Fig. 9. Refractory corrosion mechanism by liquid inclusion in high oxygen steels.

Refractory – Liquid Inclusion Interactions

Relative Stability of the refractories against liquid MnO-SiO2 type inclusion

Please see the details in the ISIJ paper

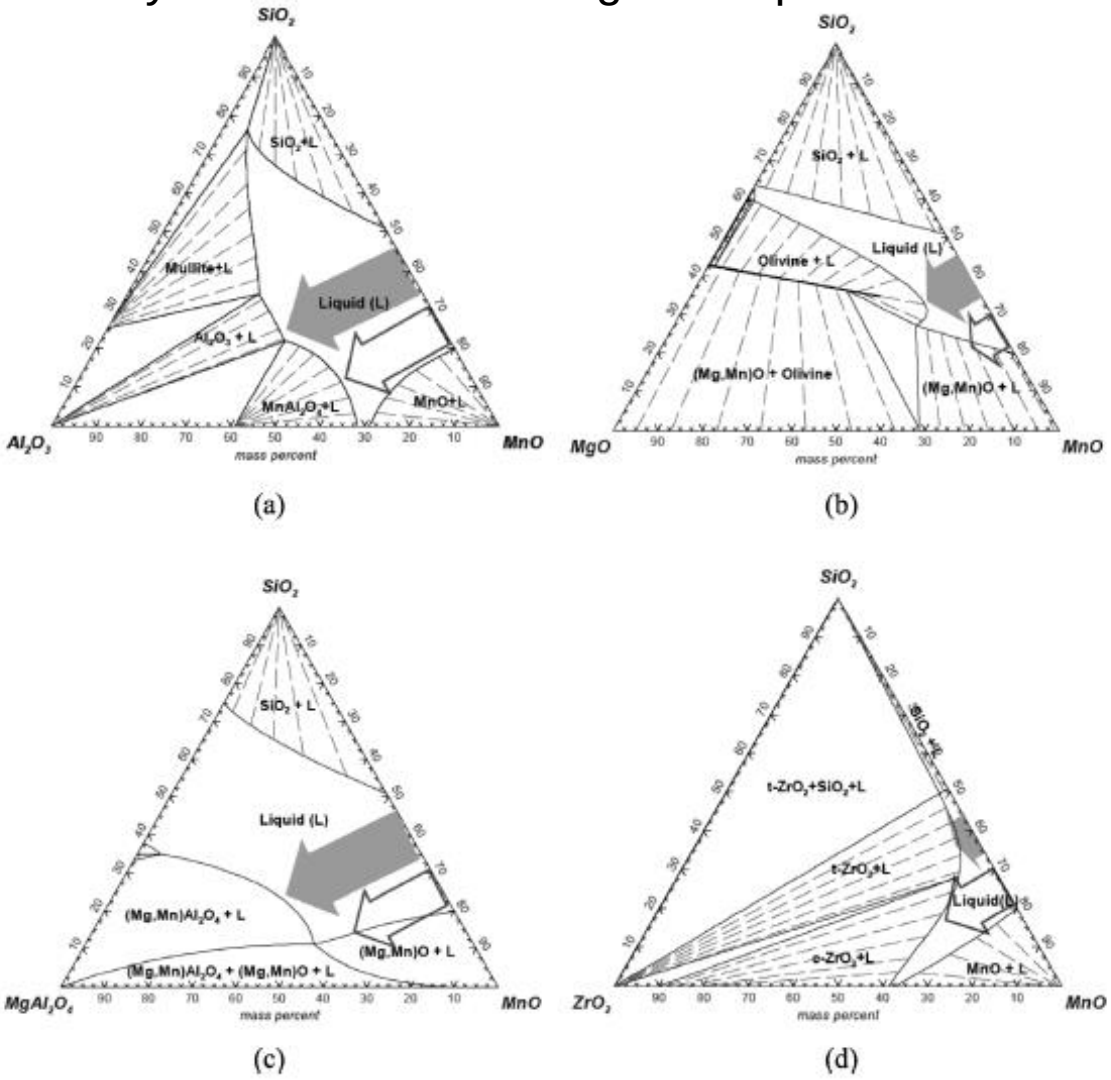
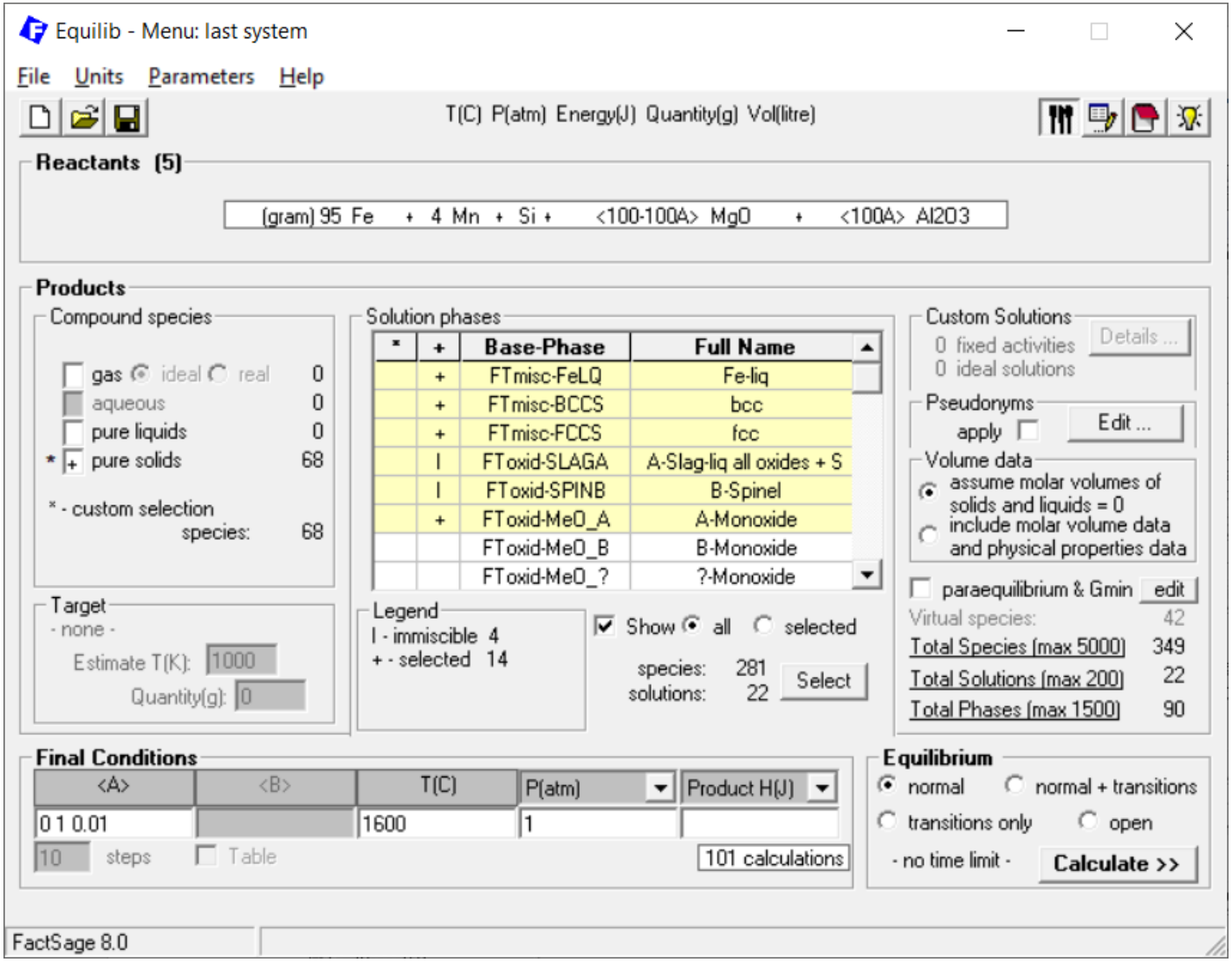
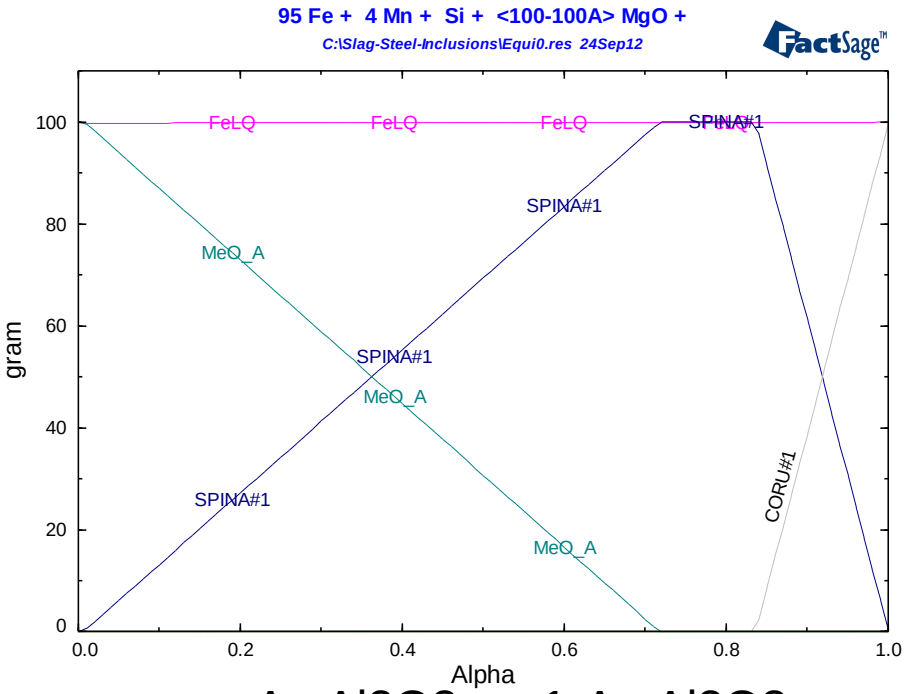


Fig. 10. Thermodynamic stability of the refractory components against liquid inclusion ($MnO–SiO_2$) at 1550°C. The arrows (gray arrow represents high degree of reduction, and empty arrow represents low degree of reduction) in phase diagrams represent the possible amount of dissolution of each refractory component.

Refractory-Steel Interaction



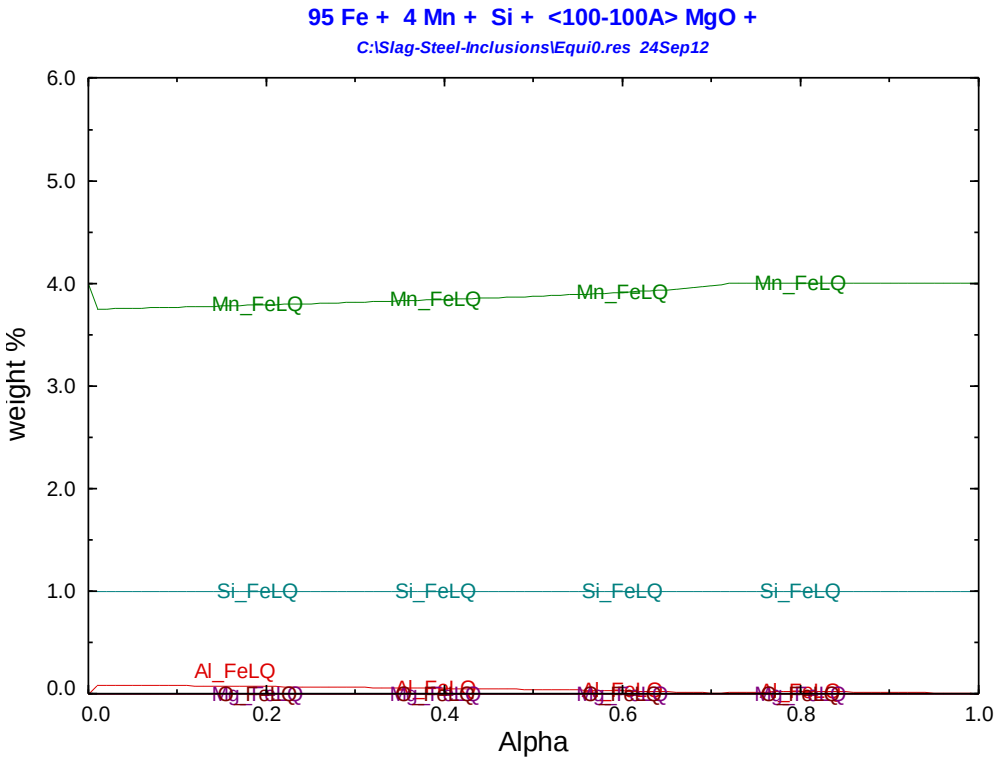
Refractory-Steel Interaction



<A> Al2O3 + <1-A> Al2O3

← Change in the amount of phases

Change in steel composition →



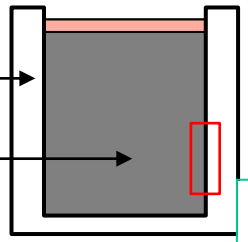
<A> Al2O3 + <1-A> Al2O3

High Mn-Fe melt storage for TWIP Steel production

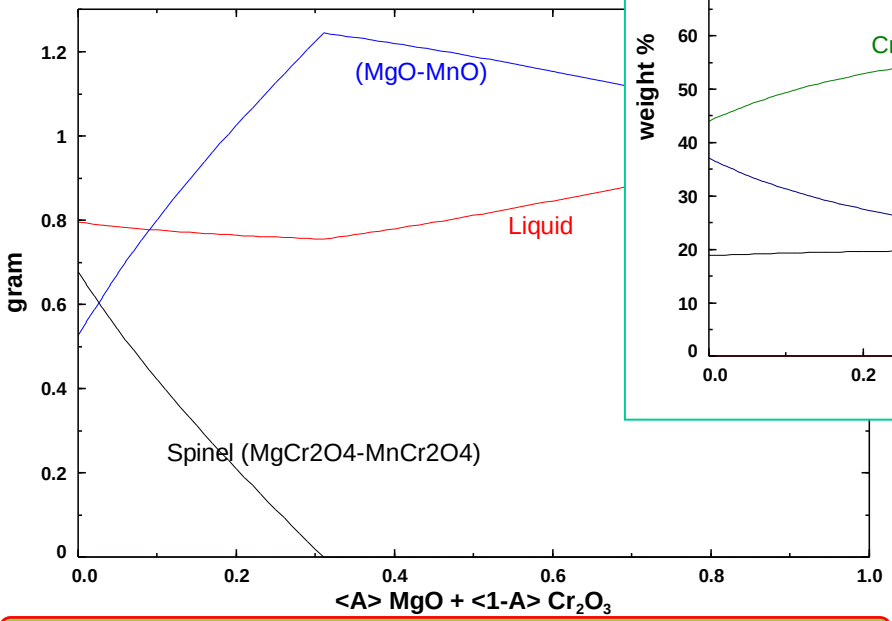
Melt / refractory reactions simulation

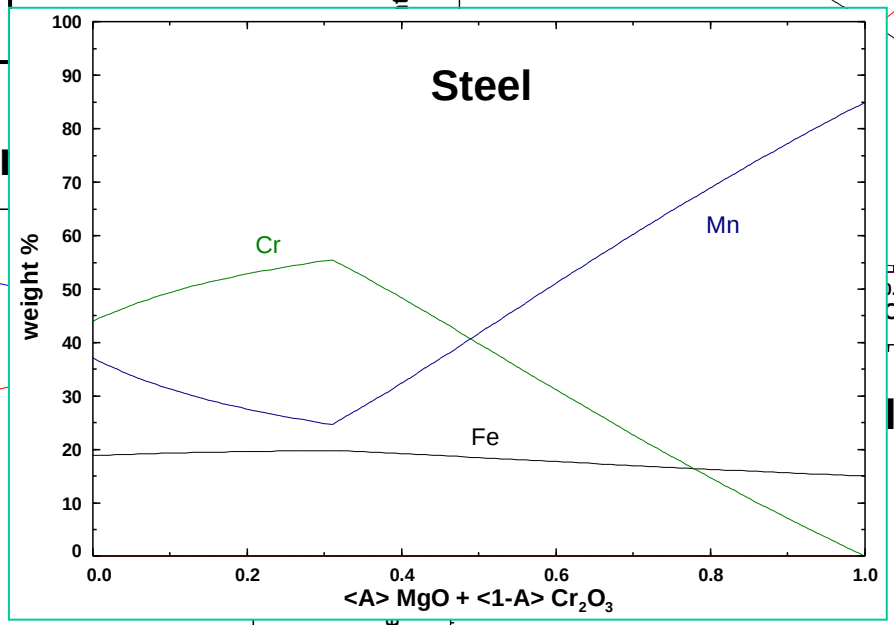
Refractories

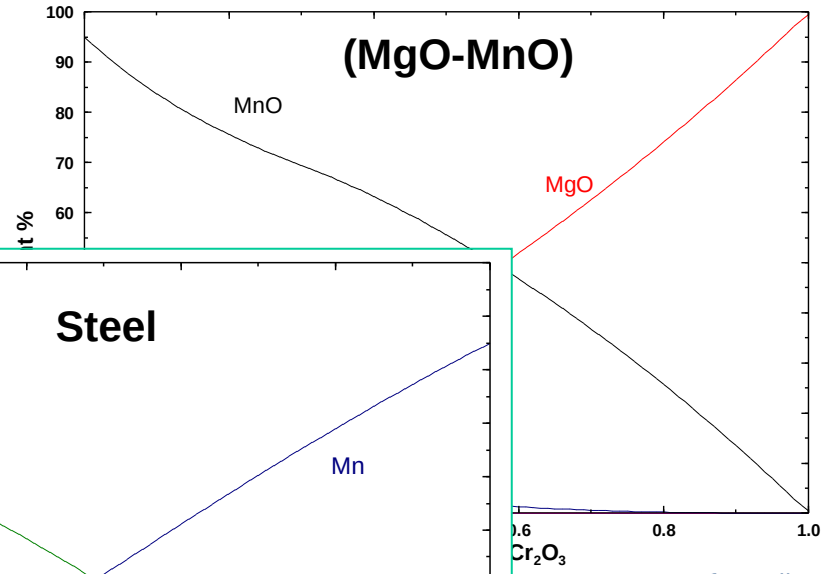
85%Mn-15%Fe melt

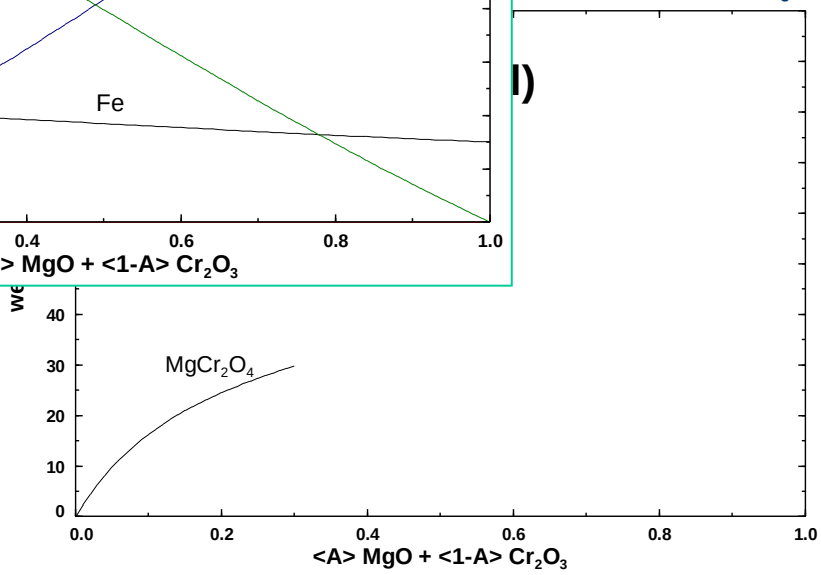


1g Mn-Fe melt + 1g refractor





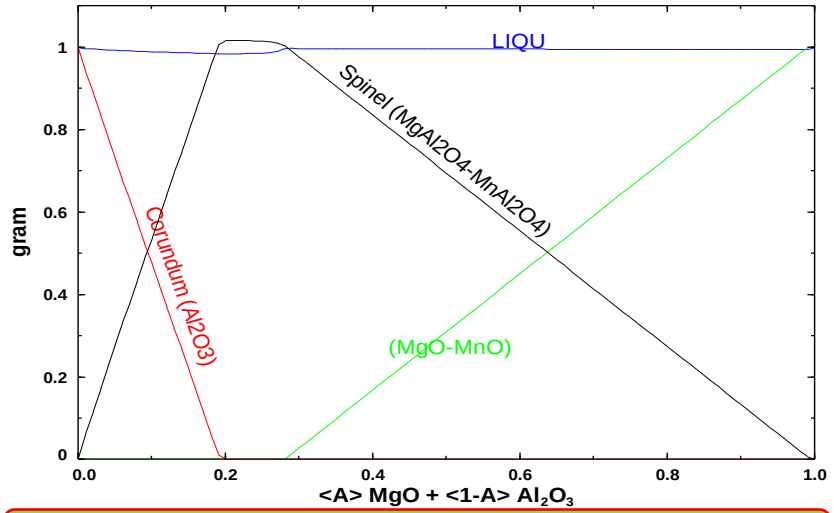




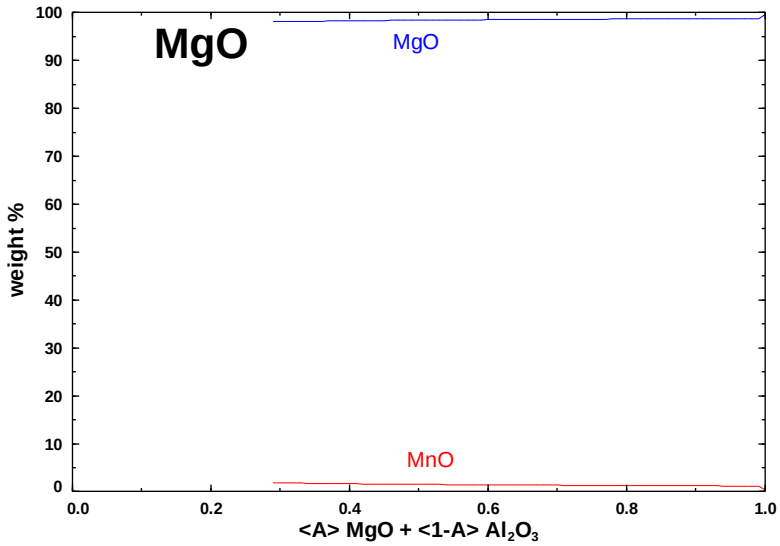
Cr_2O_3 ⇔ $MgCr_2O_4$ ⟷ MgO

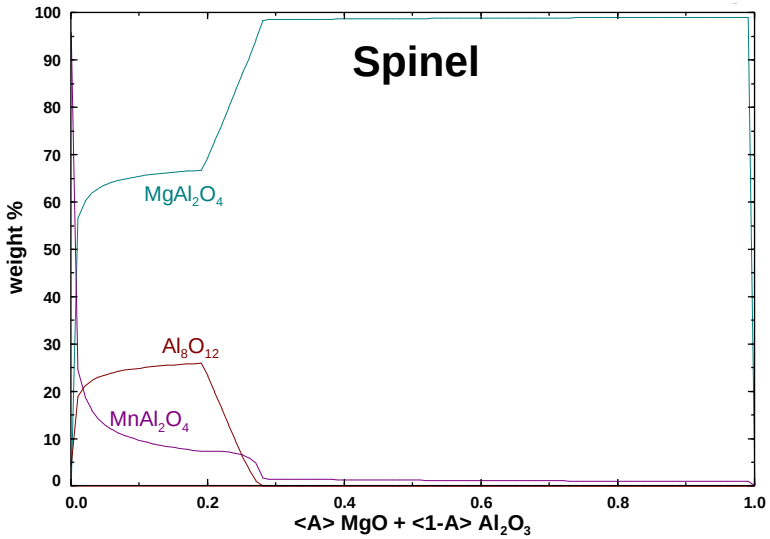
High Mn-Fe melt storage for TWIP Steel production

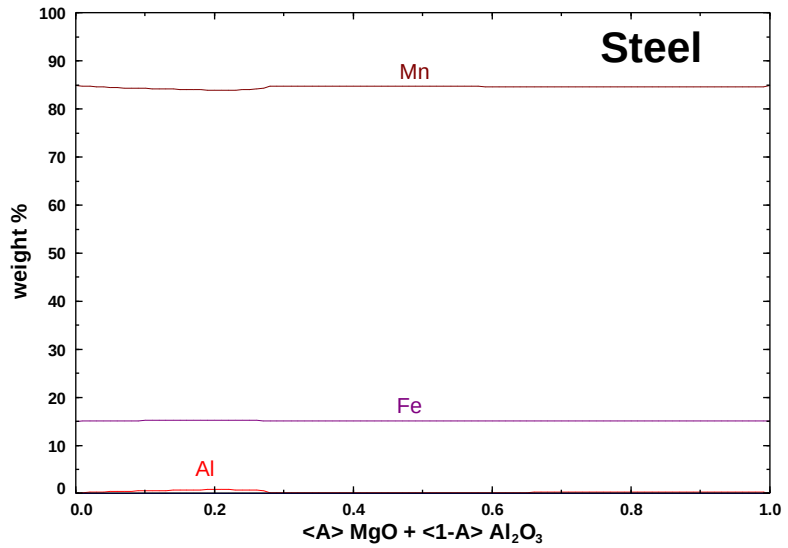
1g Mn-Fe melt + 1g refractory (MgO-Al_2O_3)



Al_2O_3 ↔ $MgAl_2O_4$ ⟷ MgO

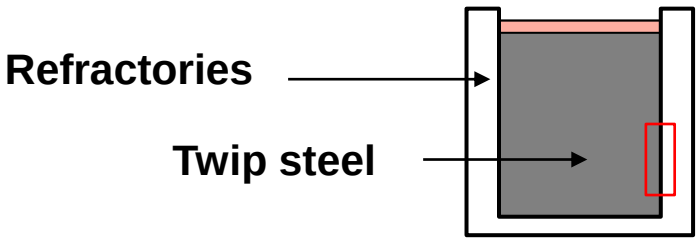


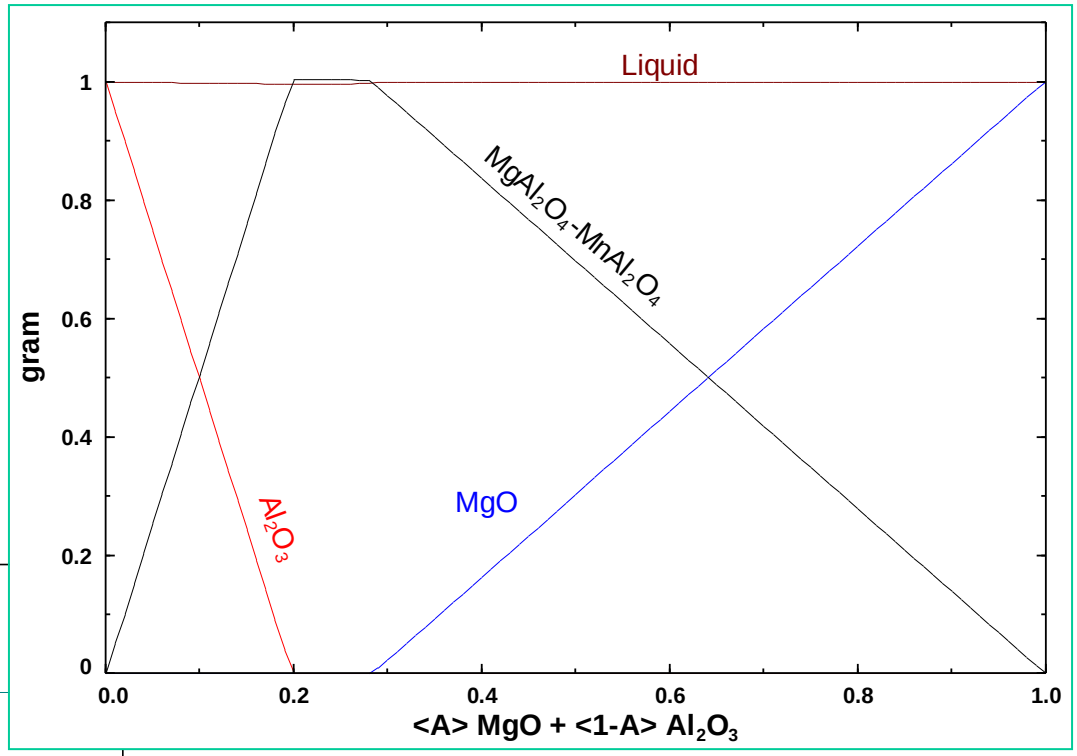


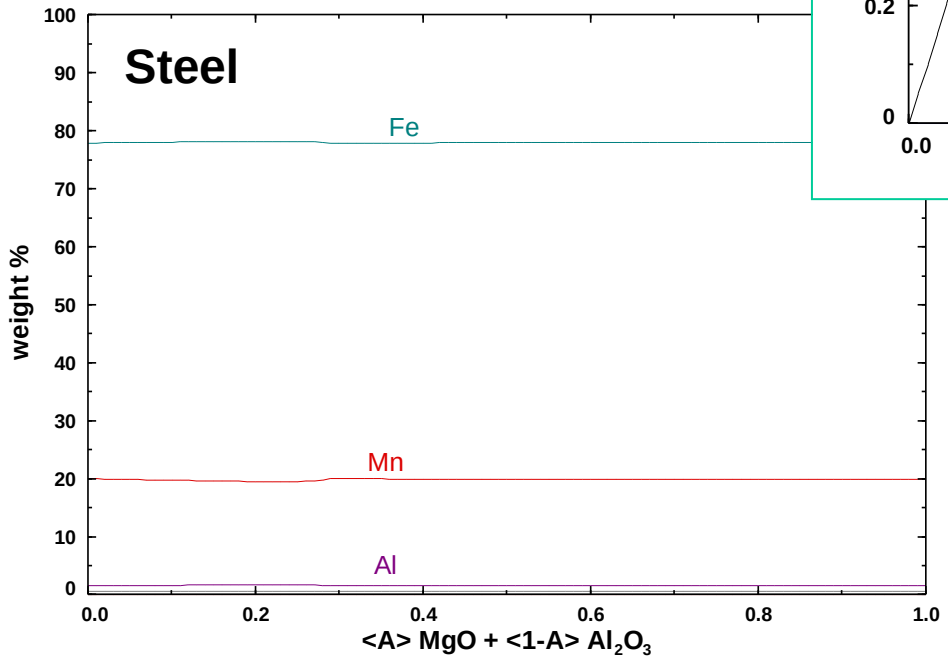


Refractory for TWIP steel: Fe-20%Mn-1.5%Al-0.6%C

T = 1500°C



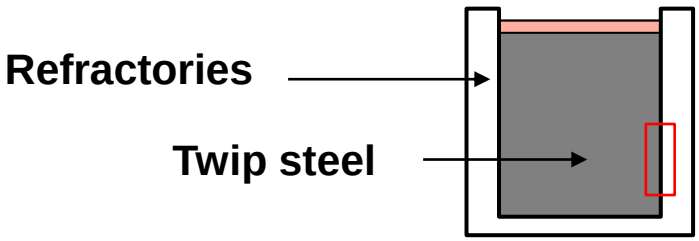


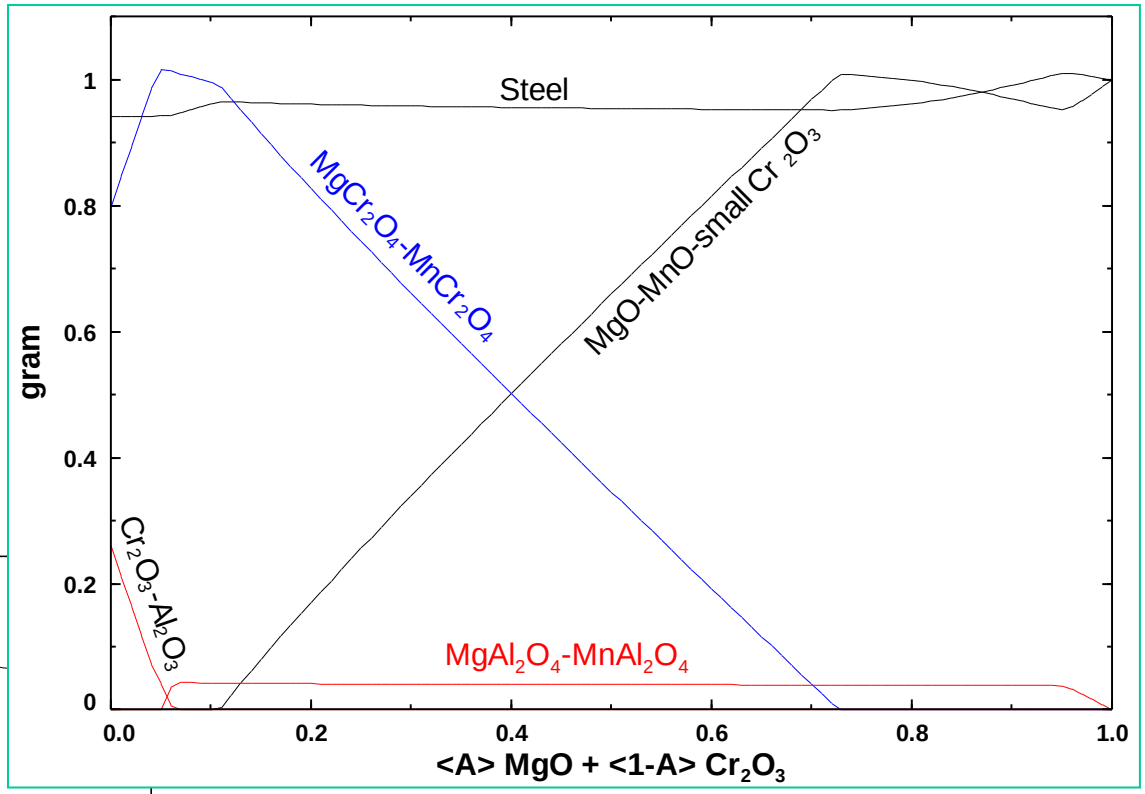


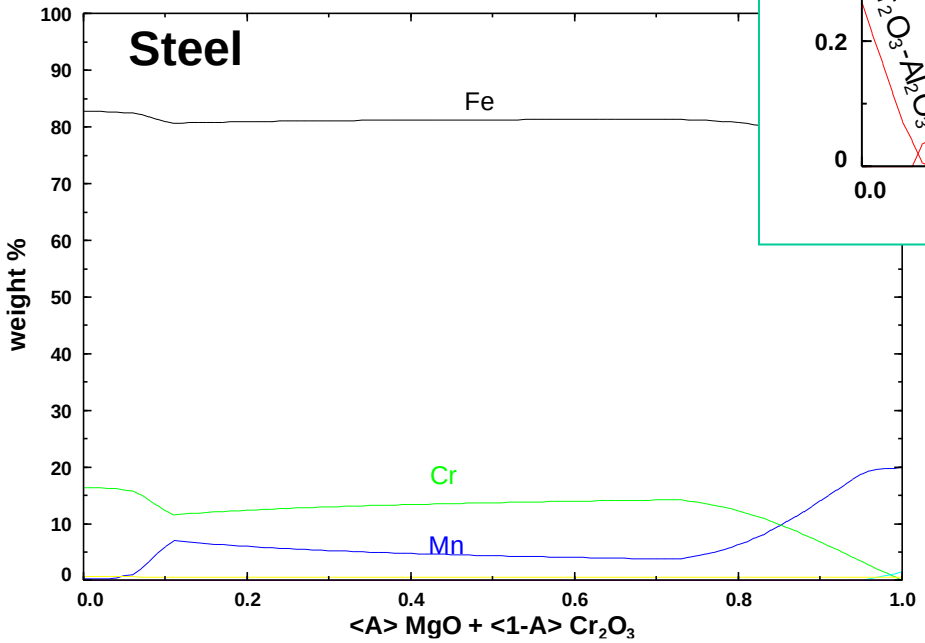
MgO-Al2O3 type: Very stable refractory

Refractory for TWIP steel: Fe-20%Mn-1.5%Al-0.6%C

T = 1500°C







MgO-Cr2O3 type: less stable
→ Cr pickup
→Al loss

Desulphurization

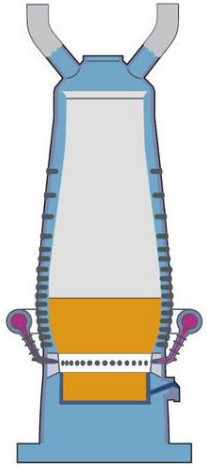
Desulphurization of Hot Metal in the De-S station,
Desulphurization of steel during Ladle treatment
and calculating Sulphide Capacity

More examples can be found in:
http://in-ho-group.snu.ac.kr/?page_id=398

Desulphurization of Hot Metal

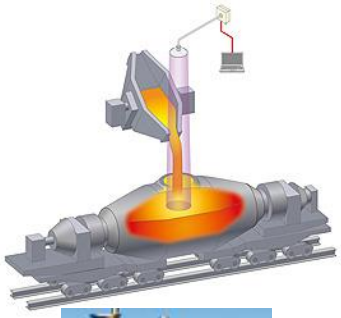
- The hot metal tapped out of the blast furnace typically contains 0.04-0.07% S.
- To reduce the amount of sulphur in the hot metal between the blast furnace and the oxygen converter, desulphurization is usually performed at a De-S station such as KR using flux (CaO, CaC2, Mg, …)
- In the secondary steelmaking (recently in LF unit), de-S can occur between slag (CaO-rich) and steel due to strong agitation.

Blast Furnace (BF)



0.04-0.07% S

Torpedo Car



KR

Basic Oxygen Furnace (BOF)

~ 0.01% S

Ladle Furnace (LF)

~ 0.001% S

Desulphurization of Hot Metal

The following reactions have been proposed to reduce the sulphur content in hot metal:

$$Mg(s) + \underline{S} \rightarrow MgS(s)$$

$$CaC_2 + \underline{S} \rightarrow CaS(s) + 2\underline{C}$$

$$CaO + \underline{S} + \underline{C} \rightarrow CaS(s) + CO(g)$$

$$Mg + CaO + \underline{S} \rightarrow CaS(s) + MgO(s)$$

$$CaO + 2\underline{Al} + \underline{S} + 3\underline{O} \rightarrow (CaO \cdot Al_2O_3)\,(S)$$

$$(CaO \cdot Al_2O_3)(s) + \underline{S} \rightarrow (CaO \cdot Al_2O_3)\,(S)$$

In the following pages, it will be shown how FactSage could be used to calculate the efficiency of each desulphurizing agent.

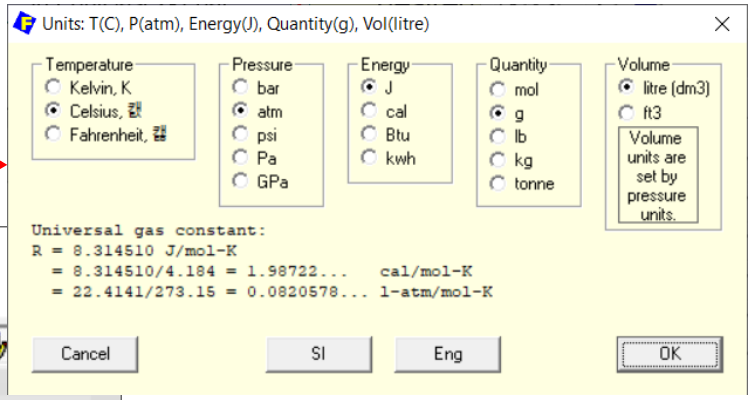
It will then be shown how the exact amount of desulphurizing agent can be selected to achieve the desired sulphur content.

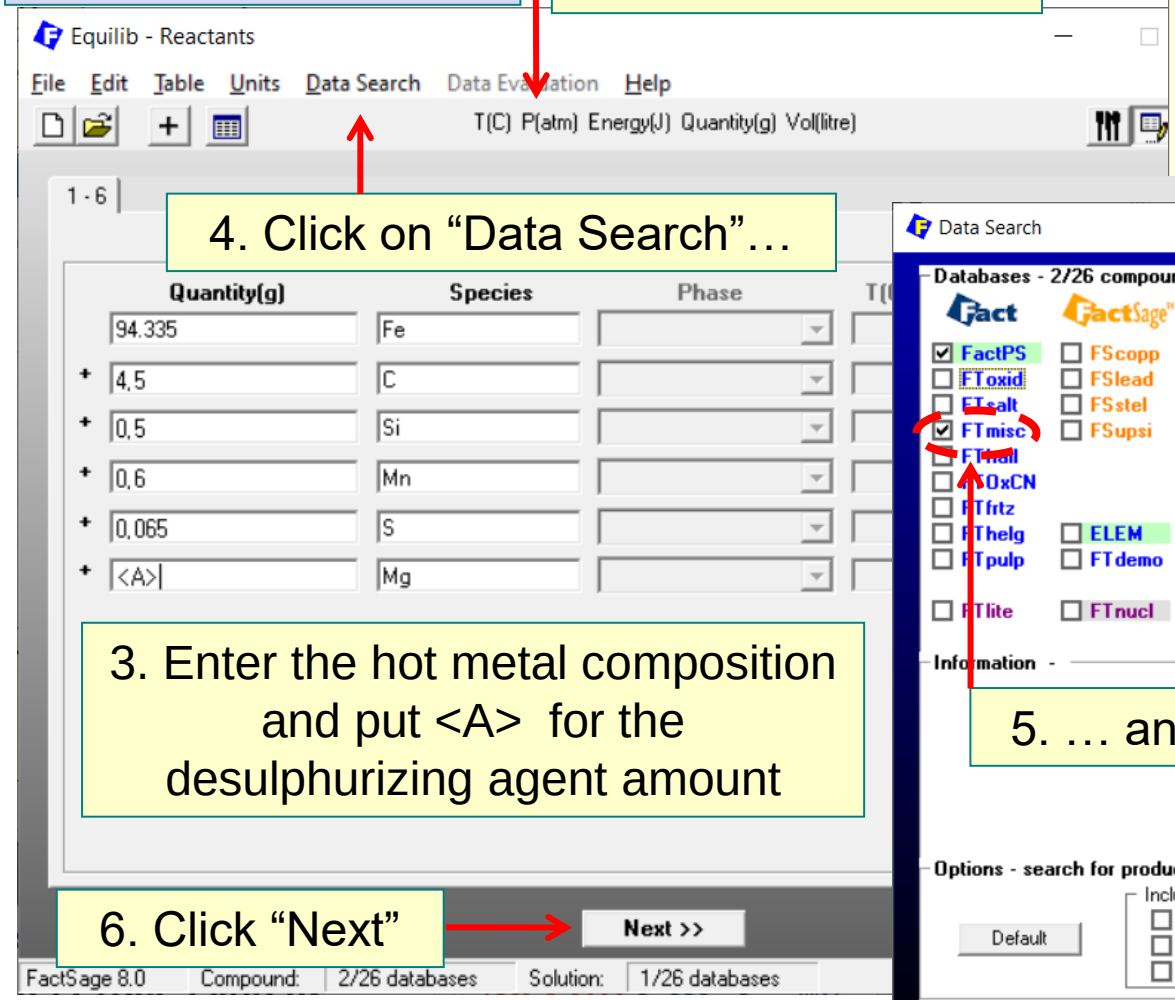
Desulphurization of Hot Metal using Mg

1. Double-click on units…

This example can be found in EquiCase2-1.dat

2. … to select the desired units

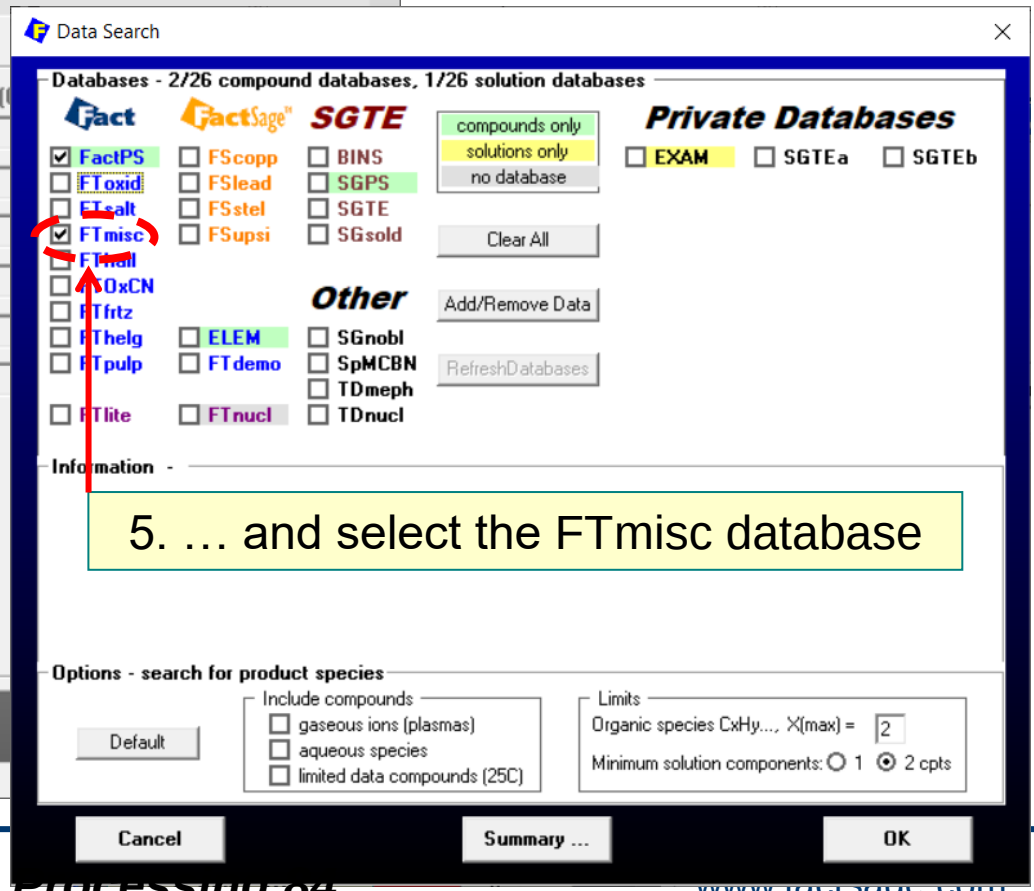




4. Click on “Data Search”…

3. Enter the hot metal composition and put <A> for the desulphurizing agent amount

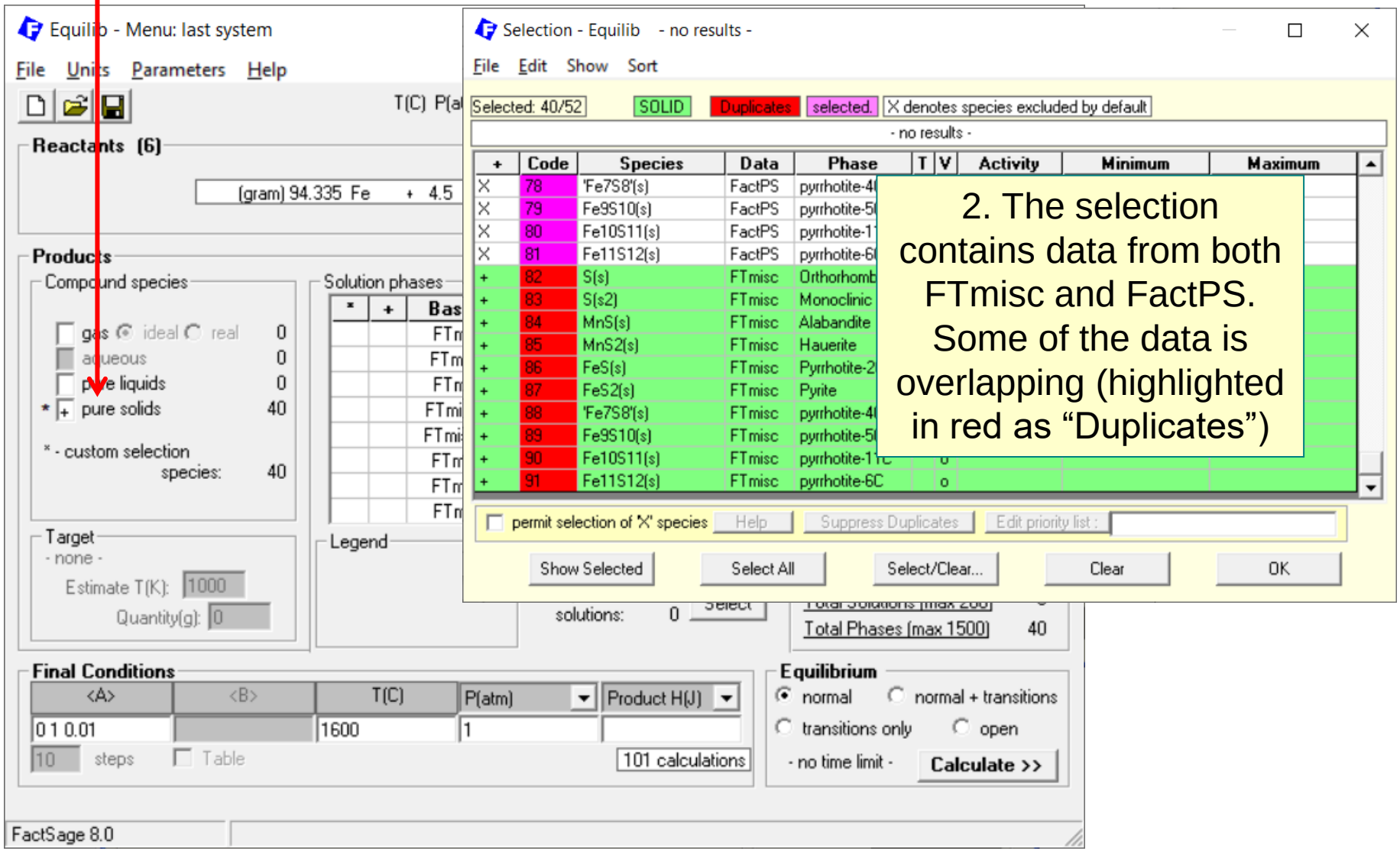
6. Click “Next”



5. … and select the FTmisc database

Desulphurization of Hot Metal using Mg

1. Right-click on “pure solids”

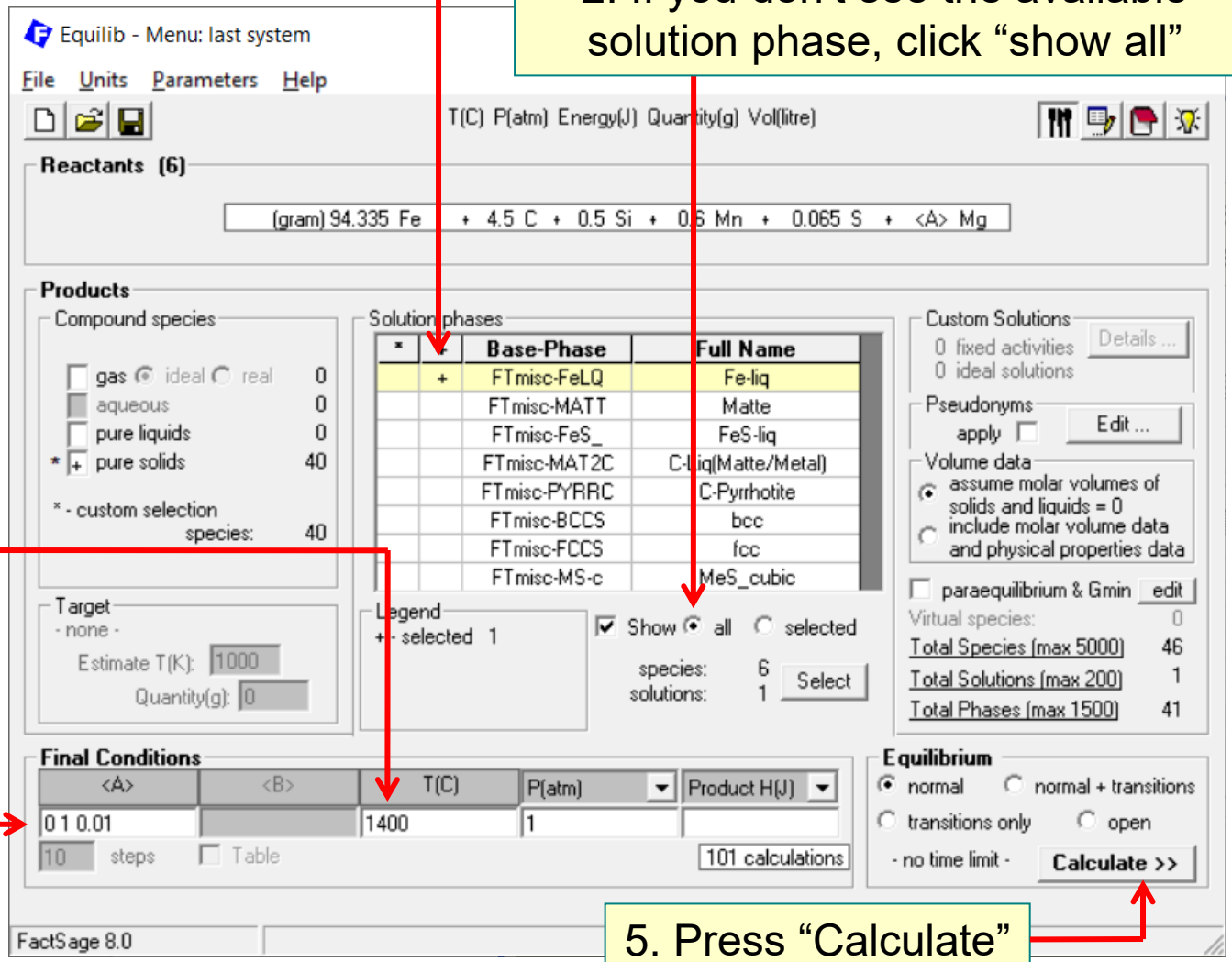


2. The selection contains data from both FTmisc and FactPS. Some of the data is overlapping (highlighted in red as “Duplicates”)

Desulphurization of Hot Metal using Mg

1. Left-click to select the liquid steel solution phase

2. If you don't see the available solution phase, click "show all"



3. Enter the desired equilibrium temperature.

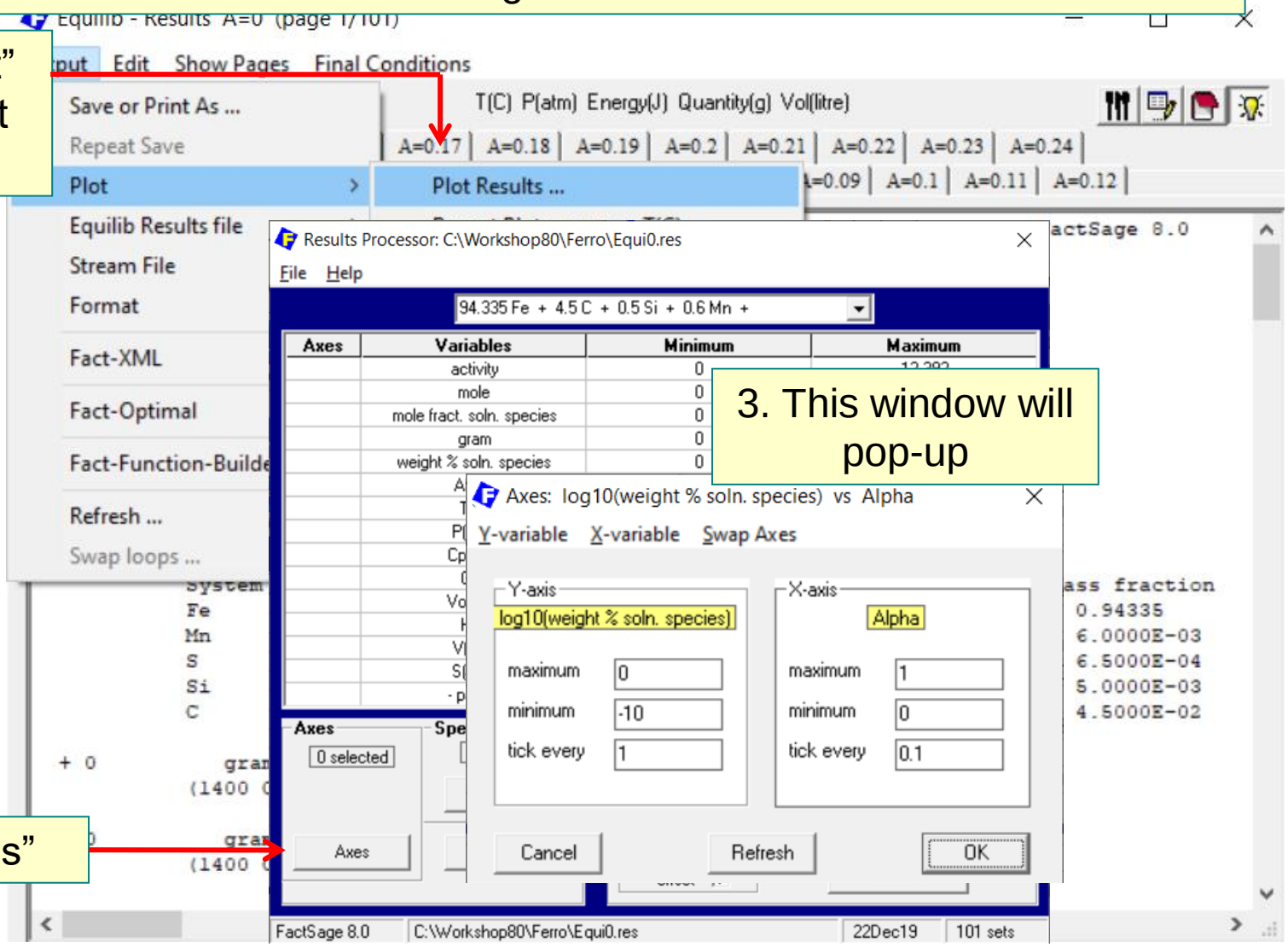
4. We will vary the amount of desulphurizing agent from 0 to 1 g in steps of 0.01g

5. Press "Calculate"

Desulphurization of Hot Metal using Mg

Now we want to see how the amount of sulphur in the hot metal decreased with the addition of magnesium.

1. Press “Output” → “Plot” → “Plot Results…”



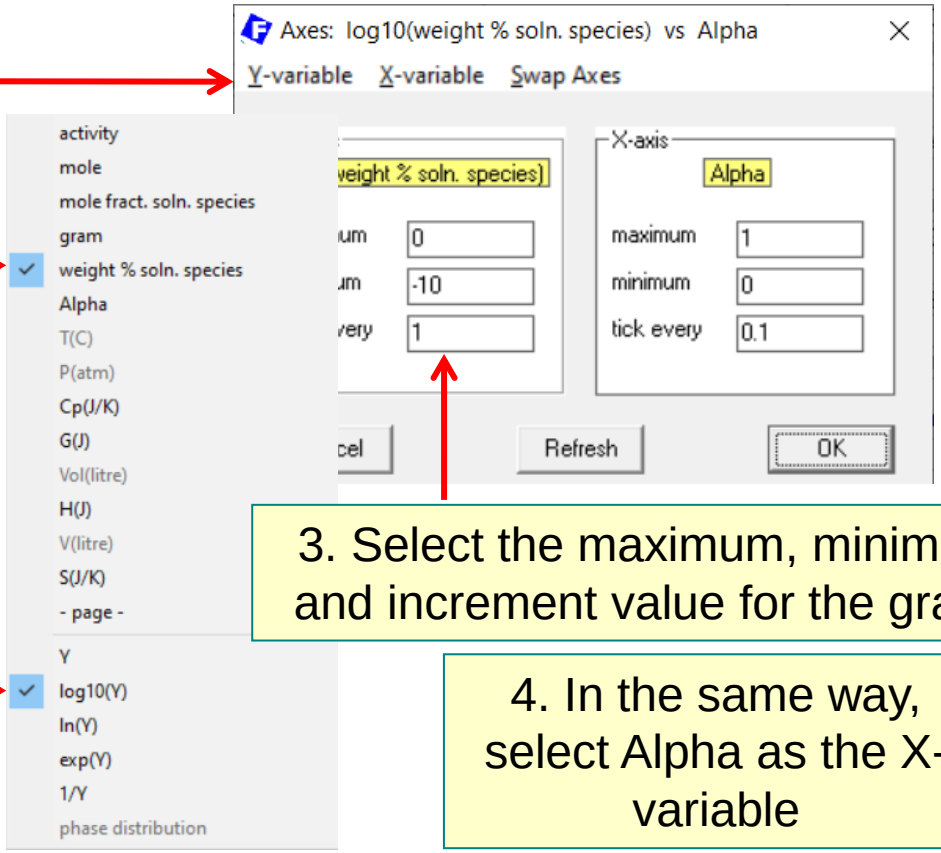
3. This window will pop-up

2. Press “Axes”

Desulphurization of Hot Metal using Mg

1. Press “Y-variable”

2. Select “weight %” in “log10(Y)” scale

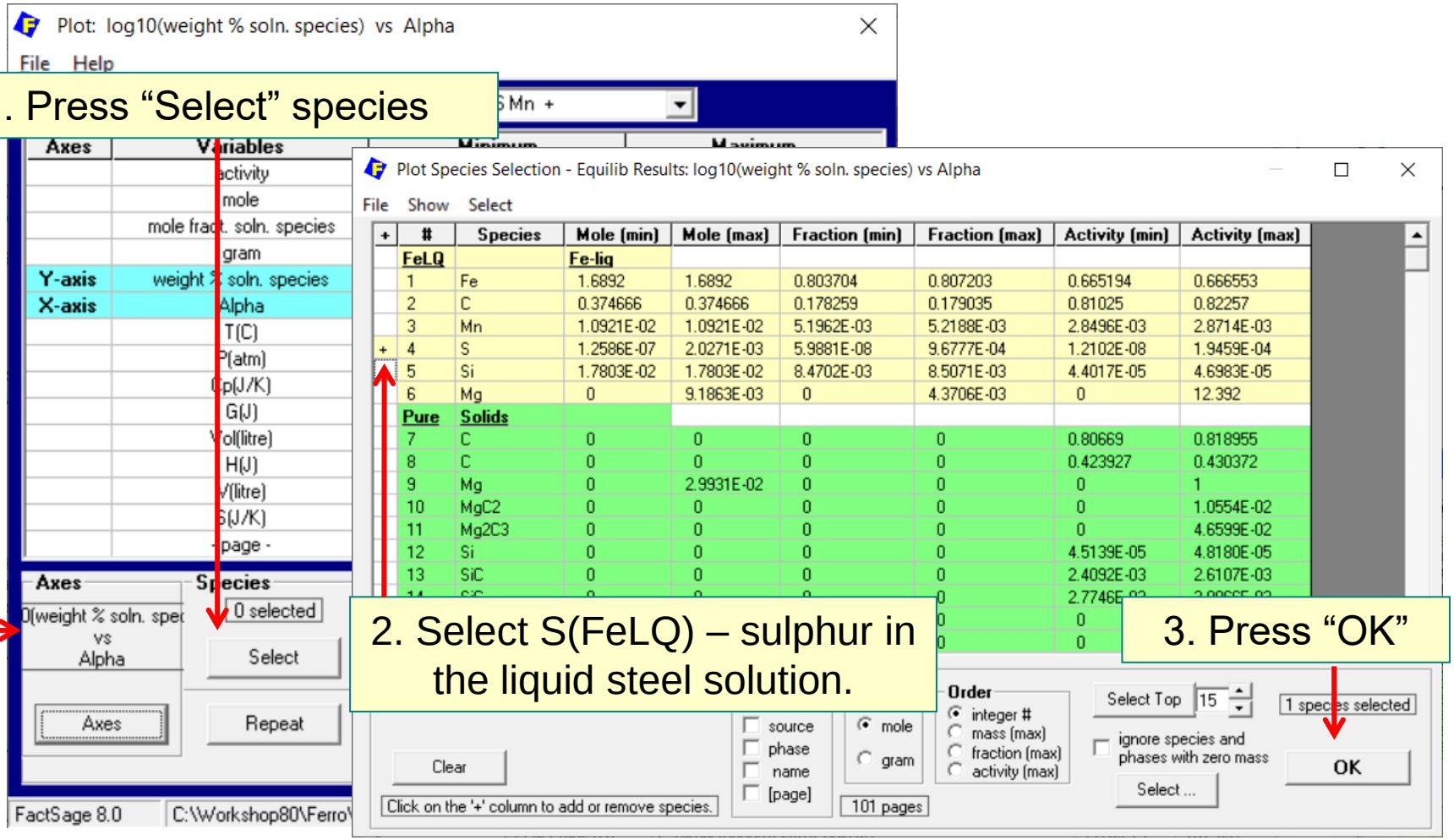


3. Select the maximum, minimum and increment value for the graph

4. In the same way, select Alpha as the X-variable

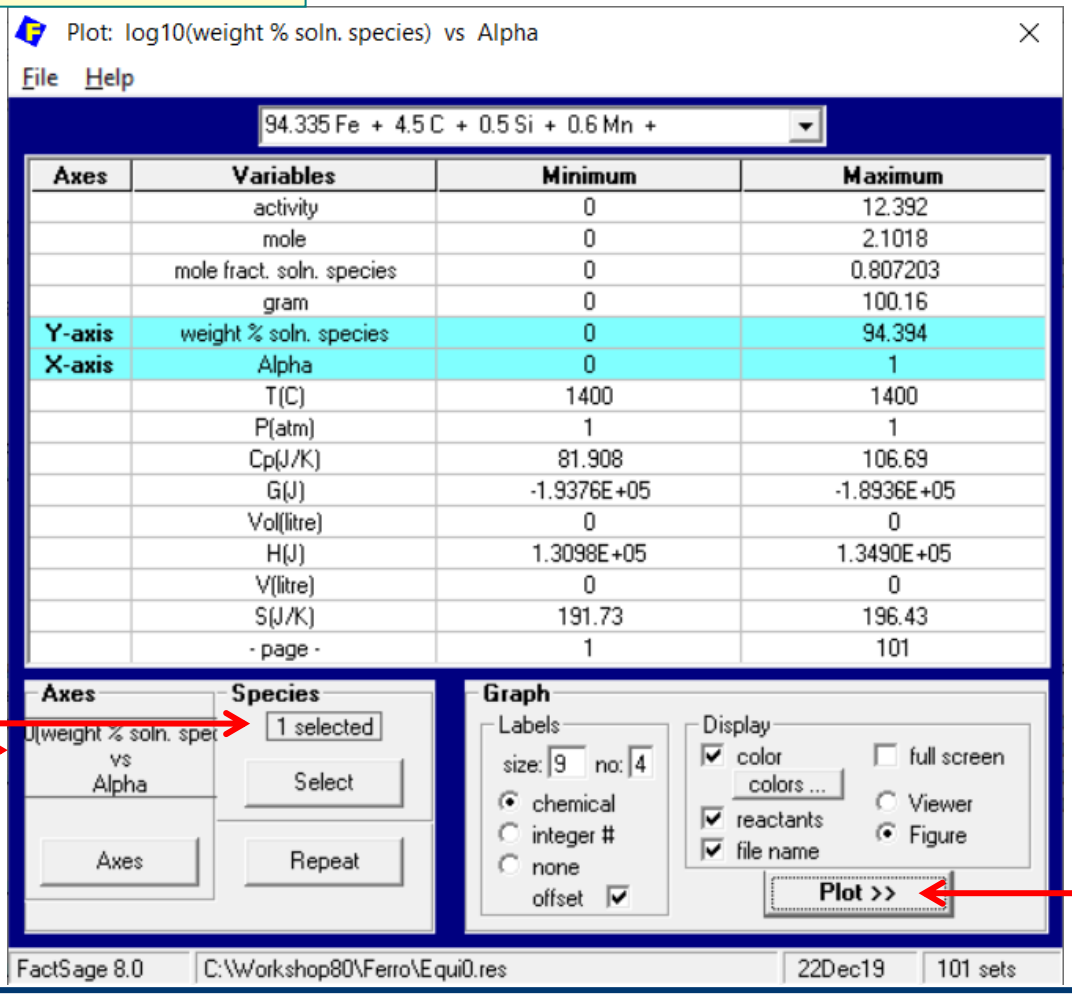
Desulphurization of Hot Metal using Mg

Now we can see that the axes have been selected. We just need to choose sulphur as the species.



Desulphurization of Hot Metal using Mg

1. Now we can see that both the axes and the species have been selected.



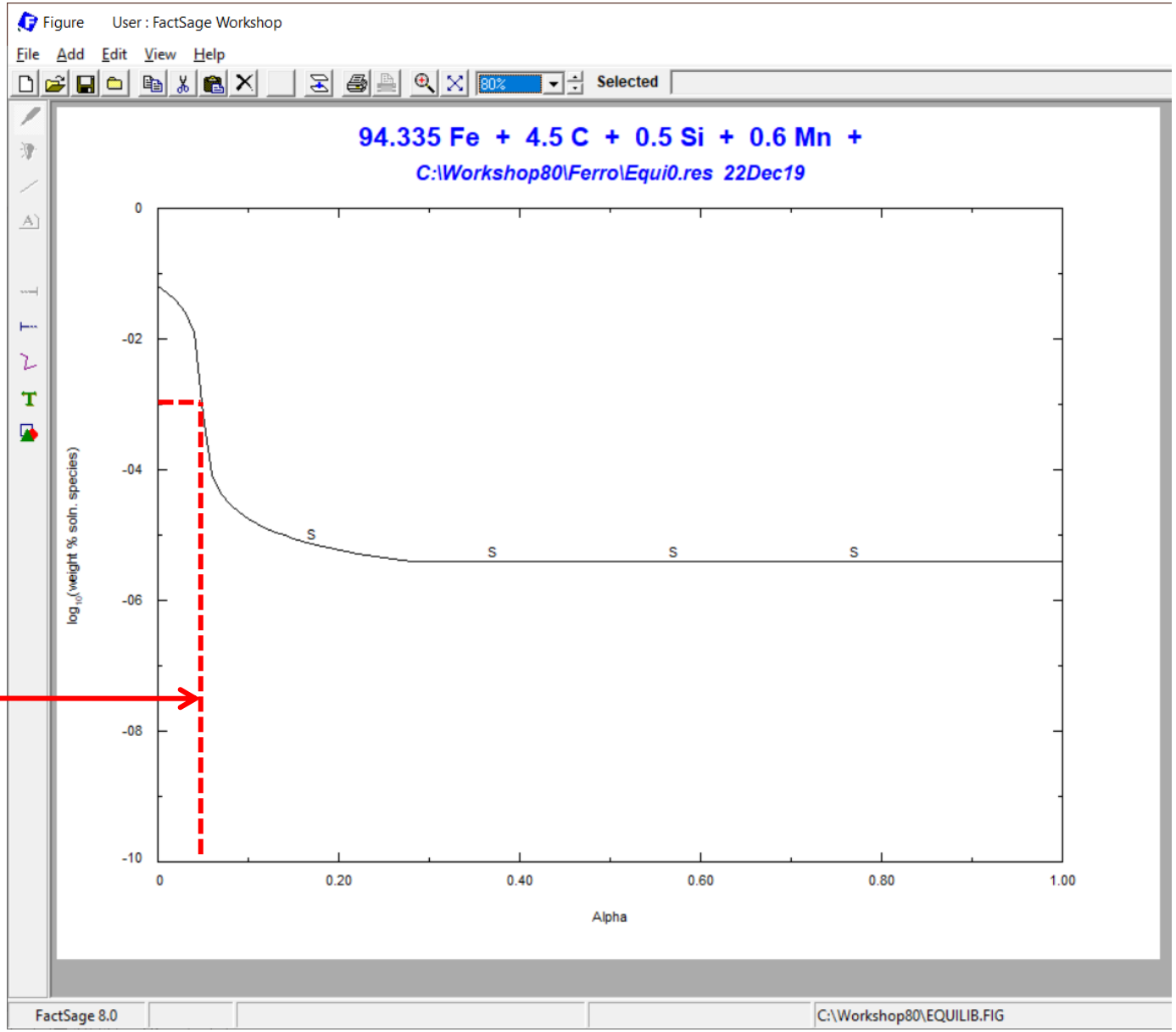
2. The “Plot” button is now activated. Click it!

Desulphurization of Hot Metal using Mg

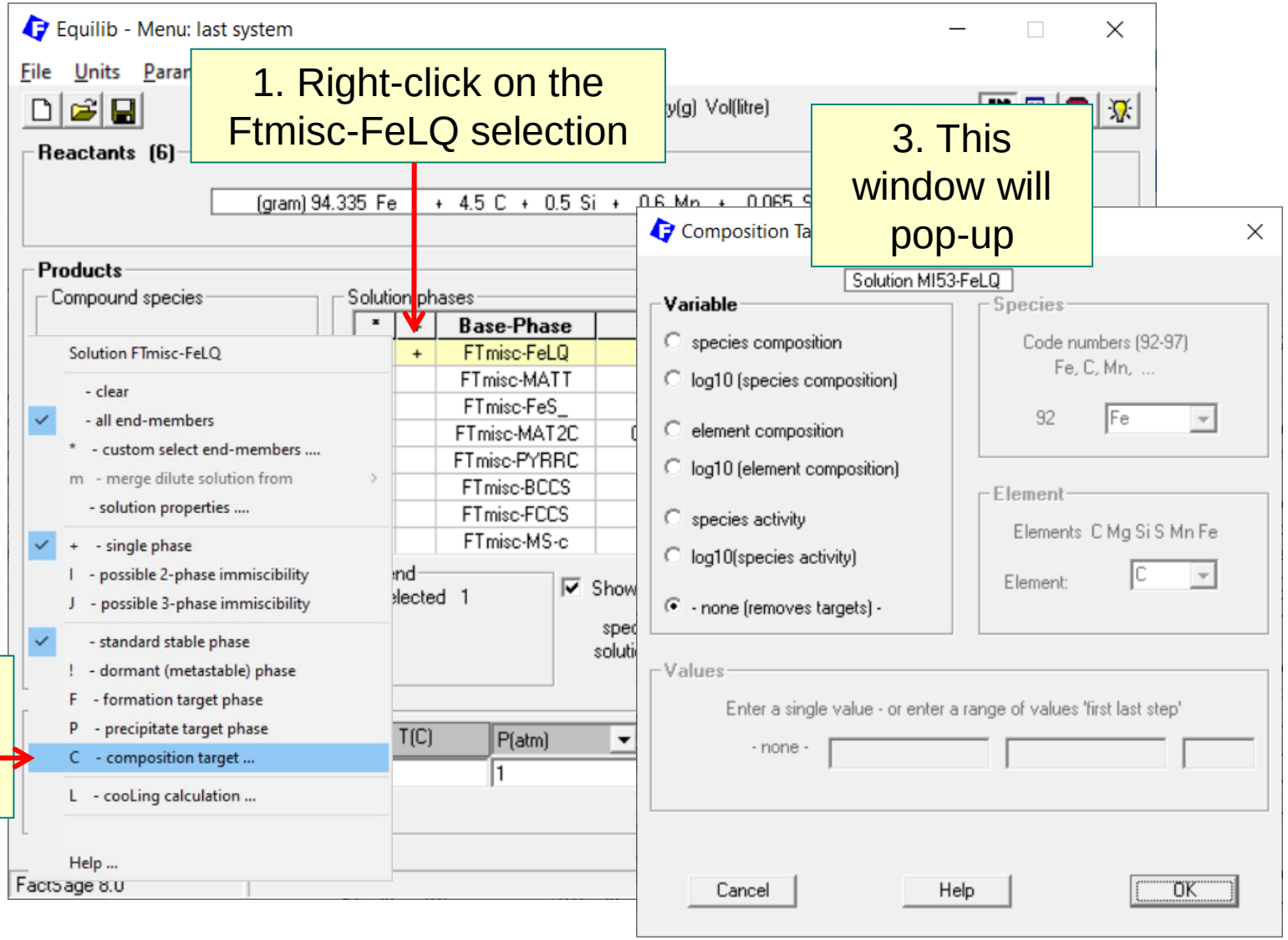
1. It can be seen that after the addition of 0.1g Mg, the desulphurization is not so effective.

2. If our target was 0.001% S, we can read off the graph that this sulphur level will be achieved after adding approximately 0.05g Mg.

3. However, there is a better way.

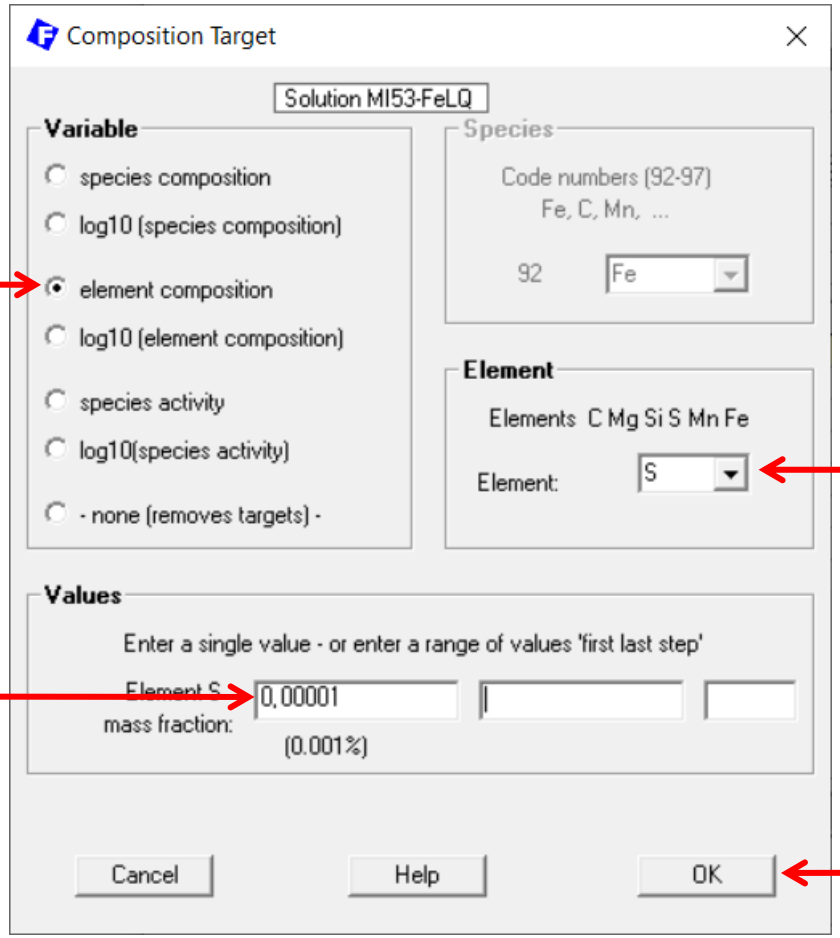


Desulphurization of Hot Metal using Mg: Composition target



Desulphurization of Hot Metal using Mg: Composition target

1. Select “element composition”



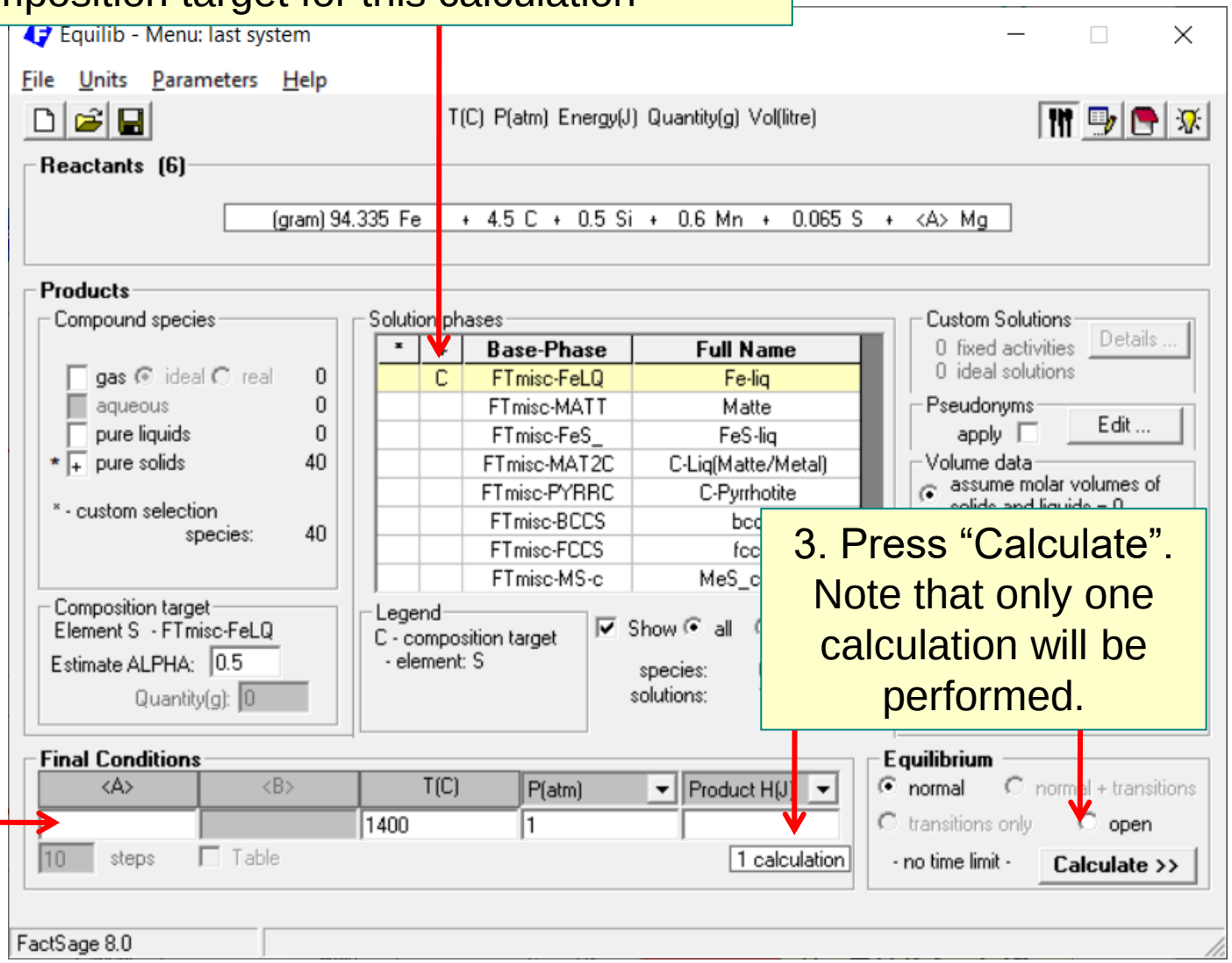
2. Choose element S

3. Enter the desired value (here – 0.001%)

4. Press “OK”

Desulphurization of Hot Metal using Mg: Composition target

1. Now “C” indicates that we have selected a composition target for this calculation

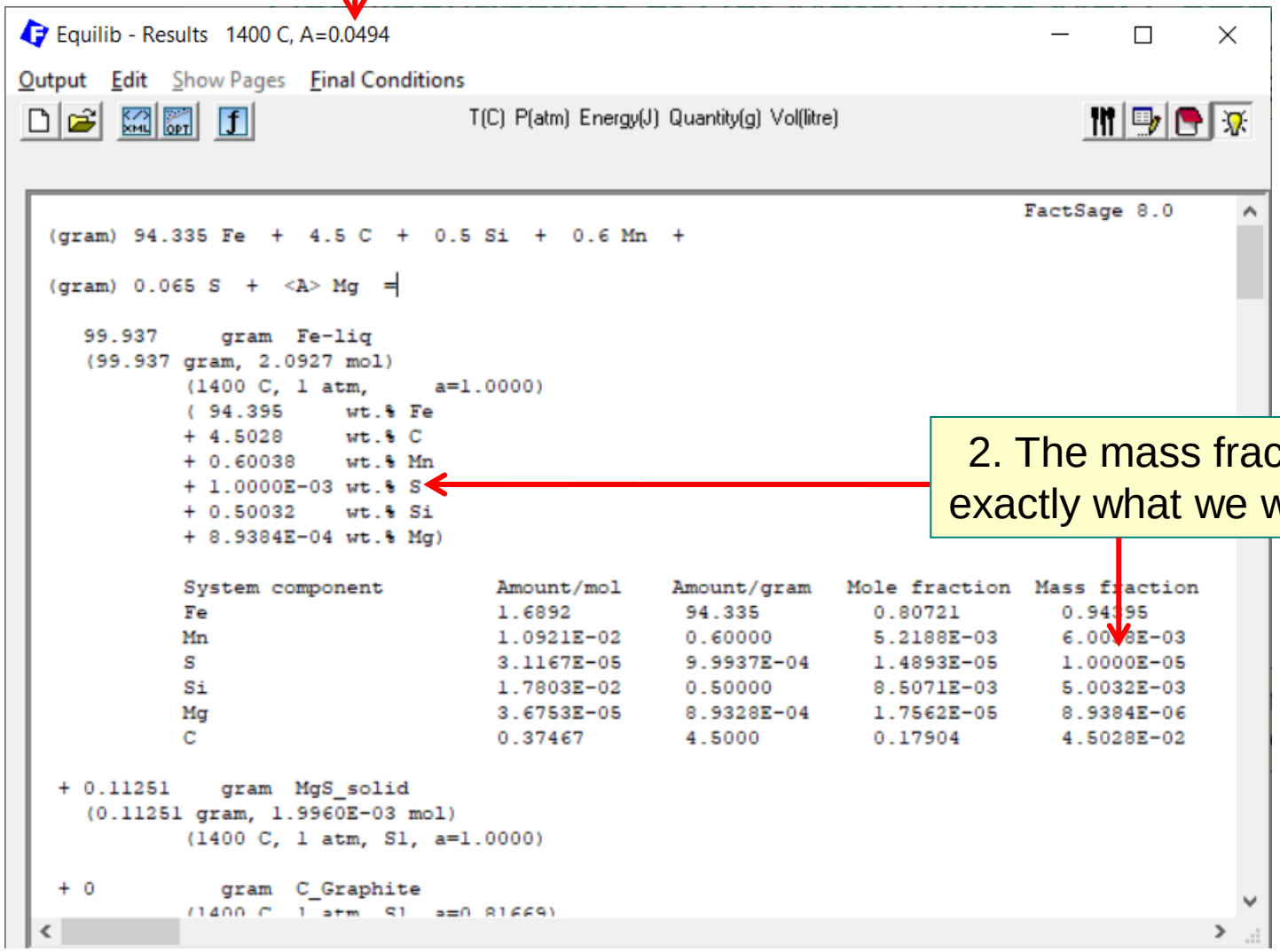


2. We must leave the <A> field blank, because <A> is what we want to calculate.

3. Press “Calculate”. Note that only one calculation will be performed.

Desulphurization of Hot Metal using Mg: Composition target

1. The <A> value for reducing sulphur content to 0.001% is 0.0494g.

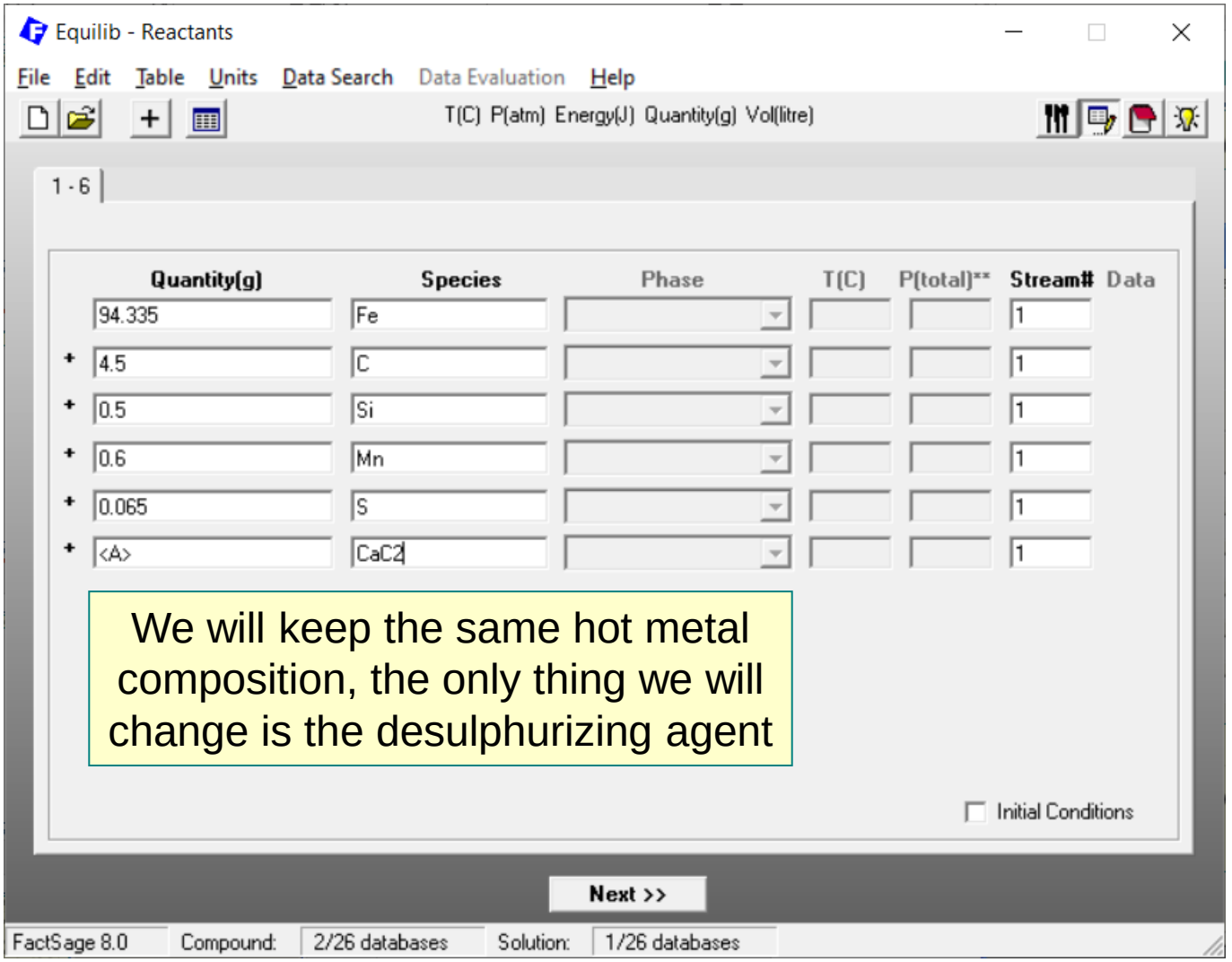


2. The mass fraction of S is exactly what we want it to be.

Desulphurization of Hot Metal using CaC_2

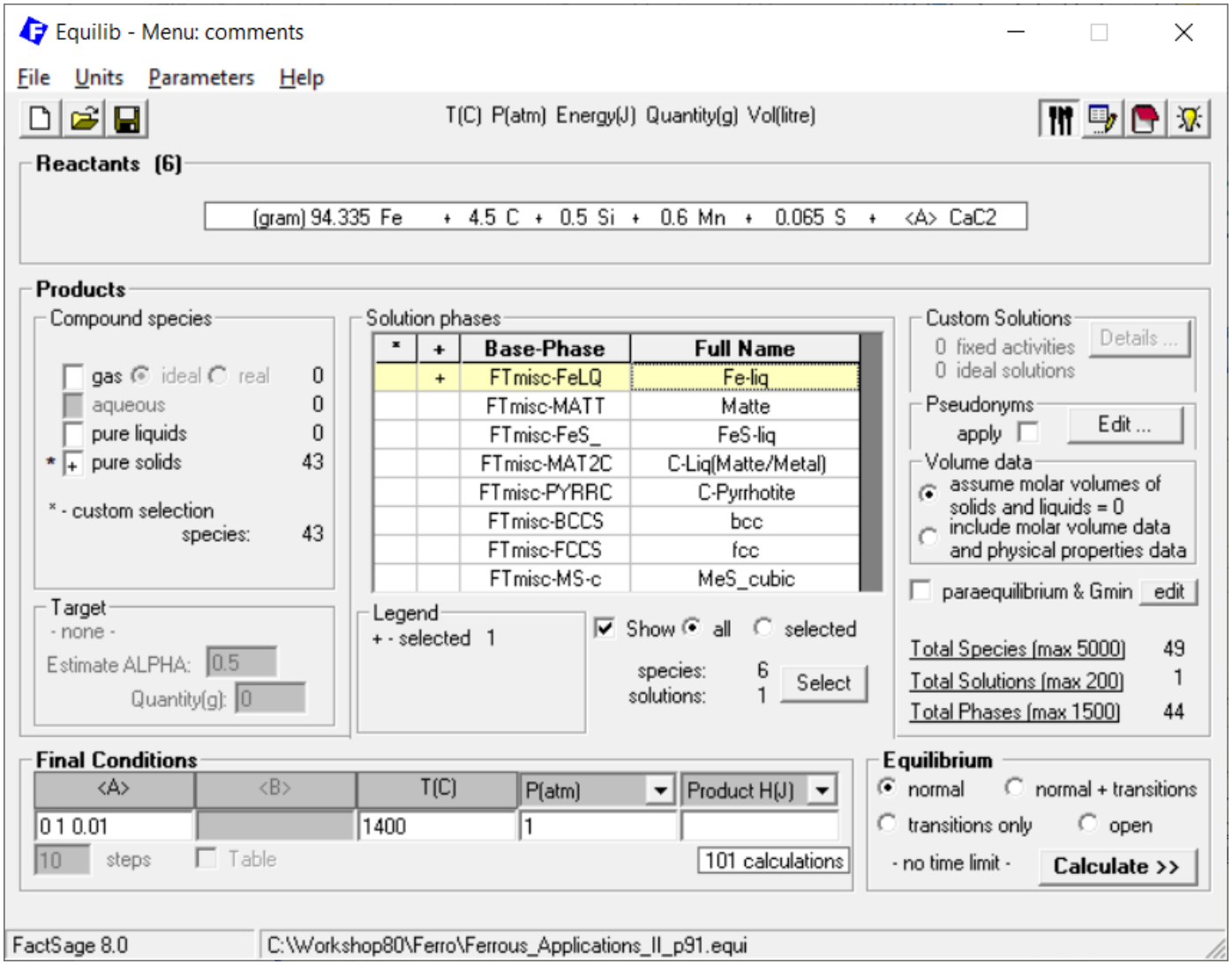
In the same manner, we can calculate the desulphurization ability of CaC_2

$$CaC_2 + \underline{S} \rightarrow CaS(s) + 2\underline{C}$$



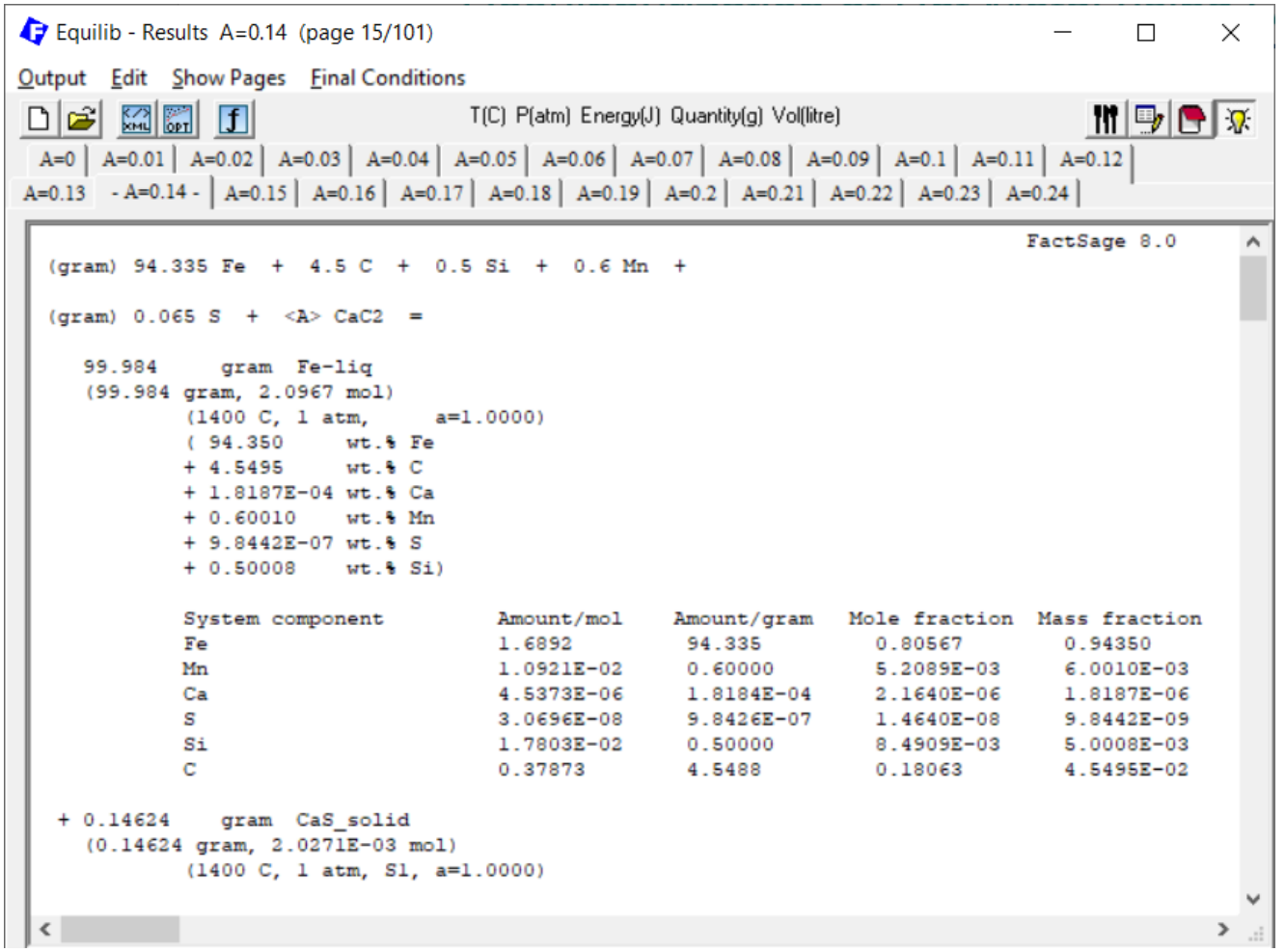
Desulphurization of Hot Metal using CaC_2

The same conditions are selected



Desulphurization of Hot Metal using CaC_2

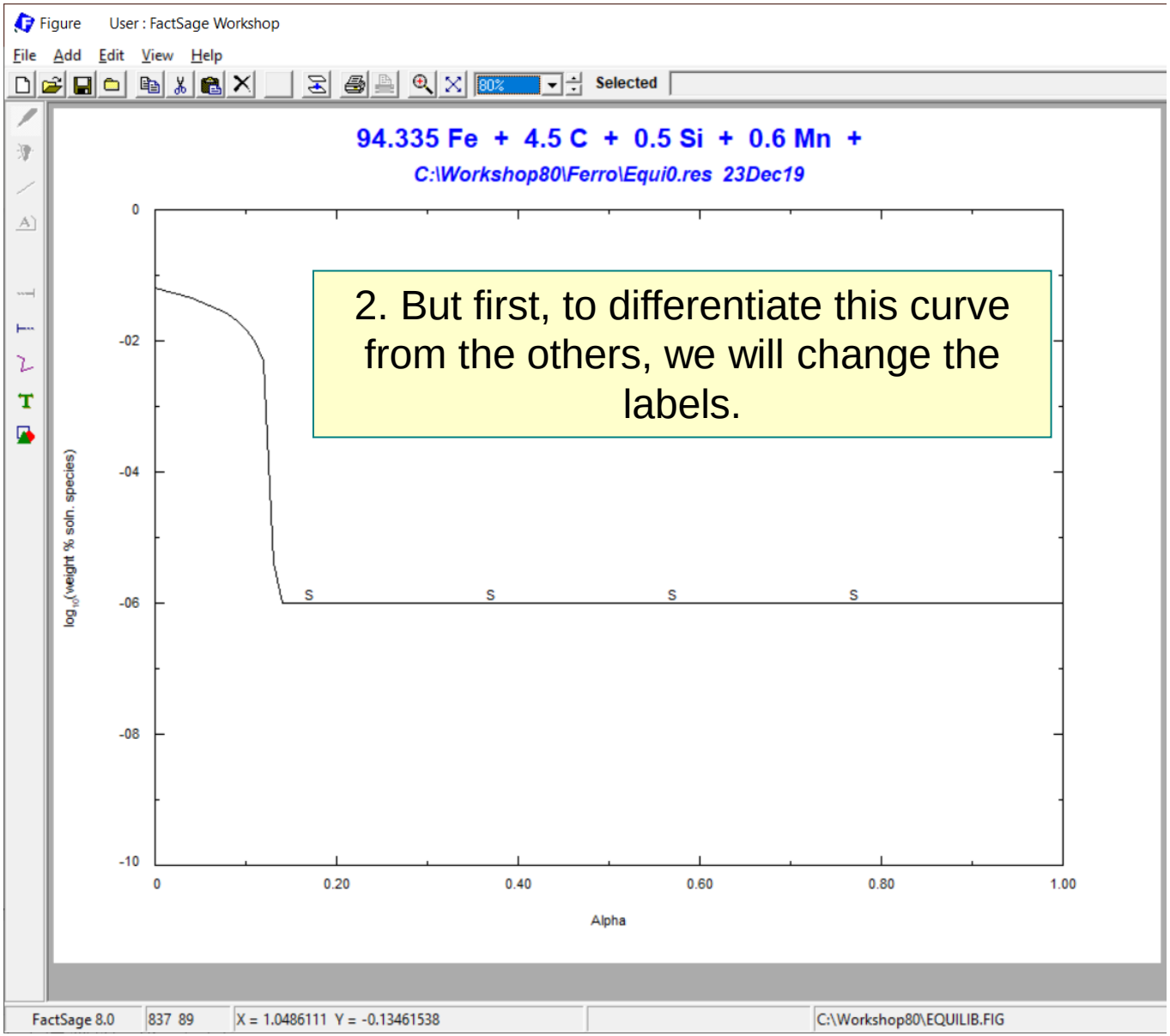
After addition of 0.14g of CaC_2, the amount of S in the hot metal becomes so small, that the reaction does not proceed and CaC_2 is precipitated as a solid phase.



Desulphurization of Hot Metal using CaC_2

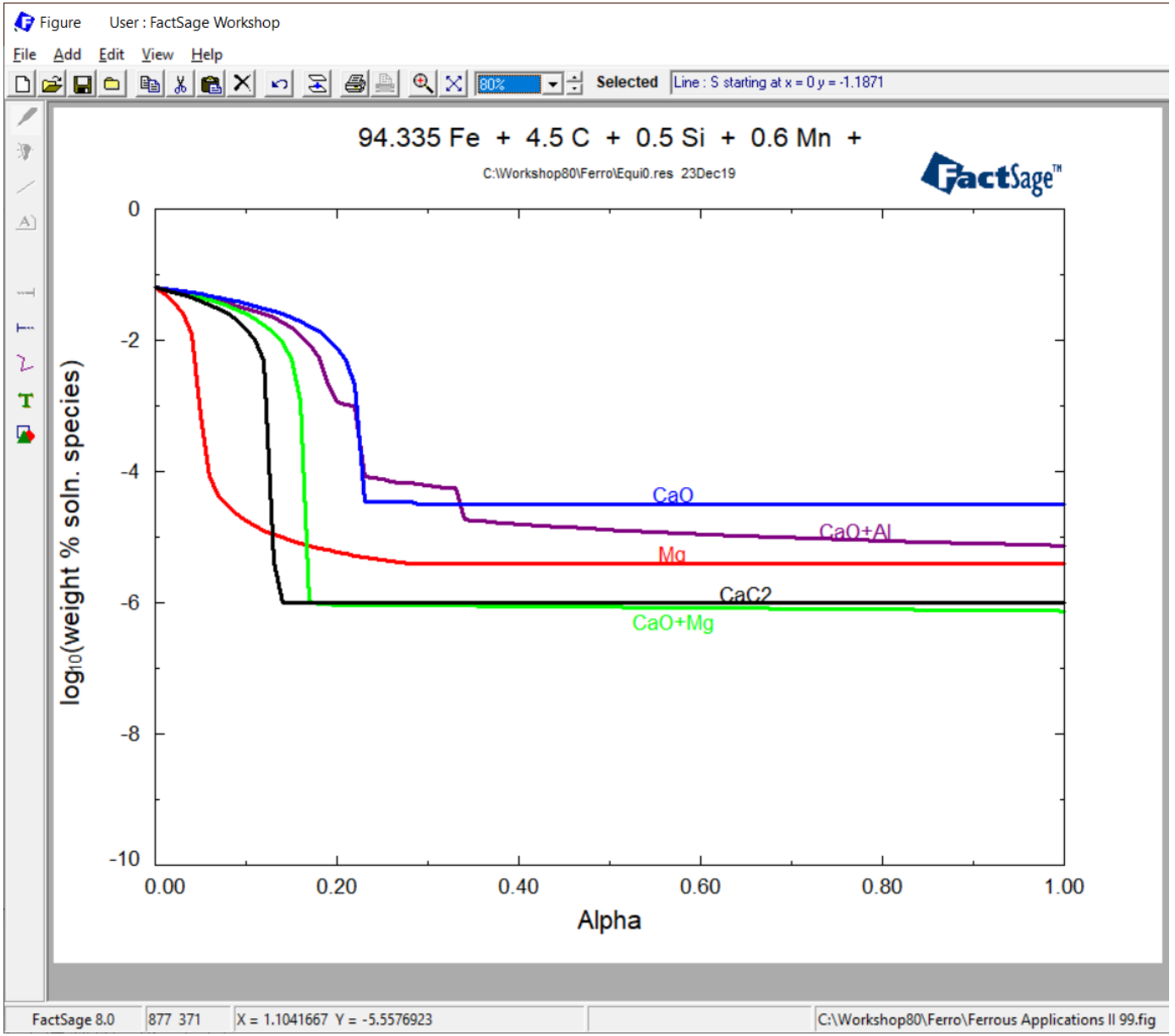
This can also be seen on the graph – after <A>=0.14, the sulphur level remains constant.

1. In order to compare this graph with the graph for Mg desulphurization, we should save this figure.



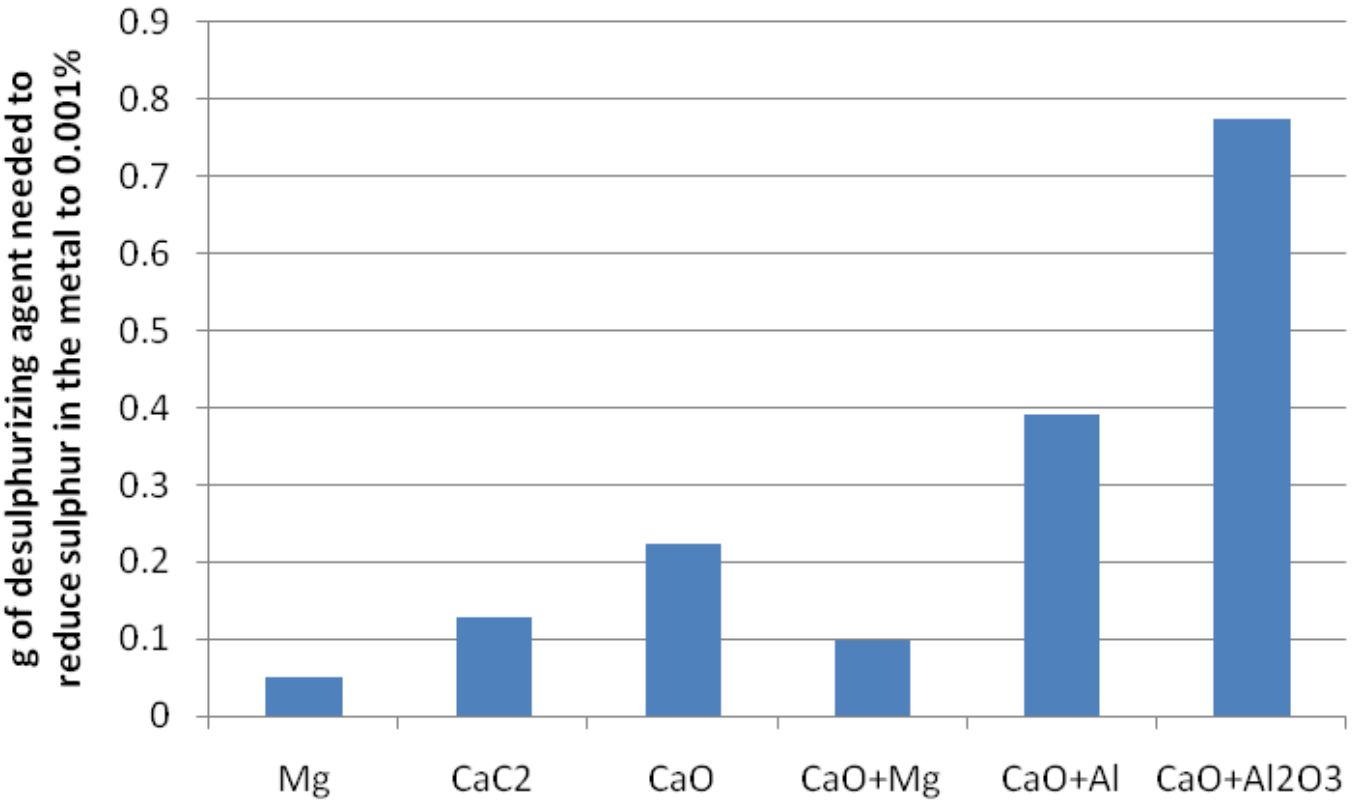
Desulphurization of Hot Metal

It can now readily be seen that Mg and CaO+Mg are the most effective hot metal desulphurizing agents.



Desulphurization of Hot Metal

It is also convenient to compare the amounts obtained using “Composition Target”



Desulphurization of Steel using Slag

We will now apply the same calculations for the desulphurization of steel in the ladle.

The starting steel contains 0.01% S and it needs to be reduced down to 0.001% S

We will also assume that a slag is present in the ladle. It consists of 40% CaO, 40% Al_2O_3, 10% MgO and 10% SiO_2. The ratio of slag to metal is 1/10

Desulphurization of Steel using Slag

We will now apply the same calculations for the desulphurization of steel in the ladle.

The starting steel contains 0.01% S and it needs to be reduced down to 0.001% S

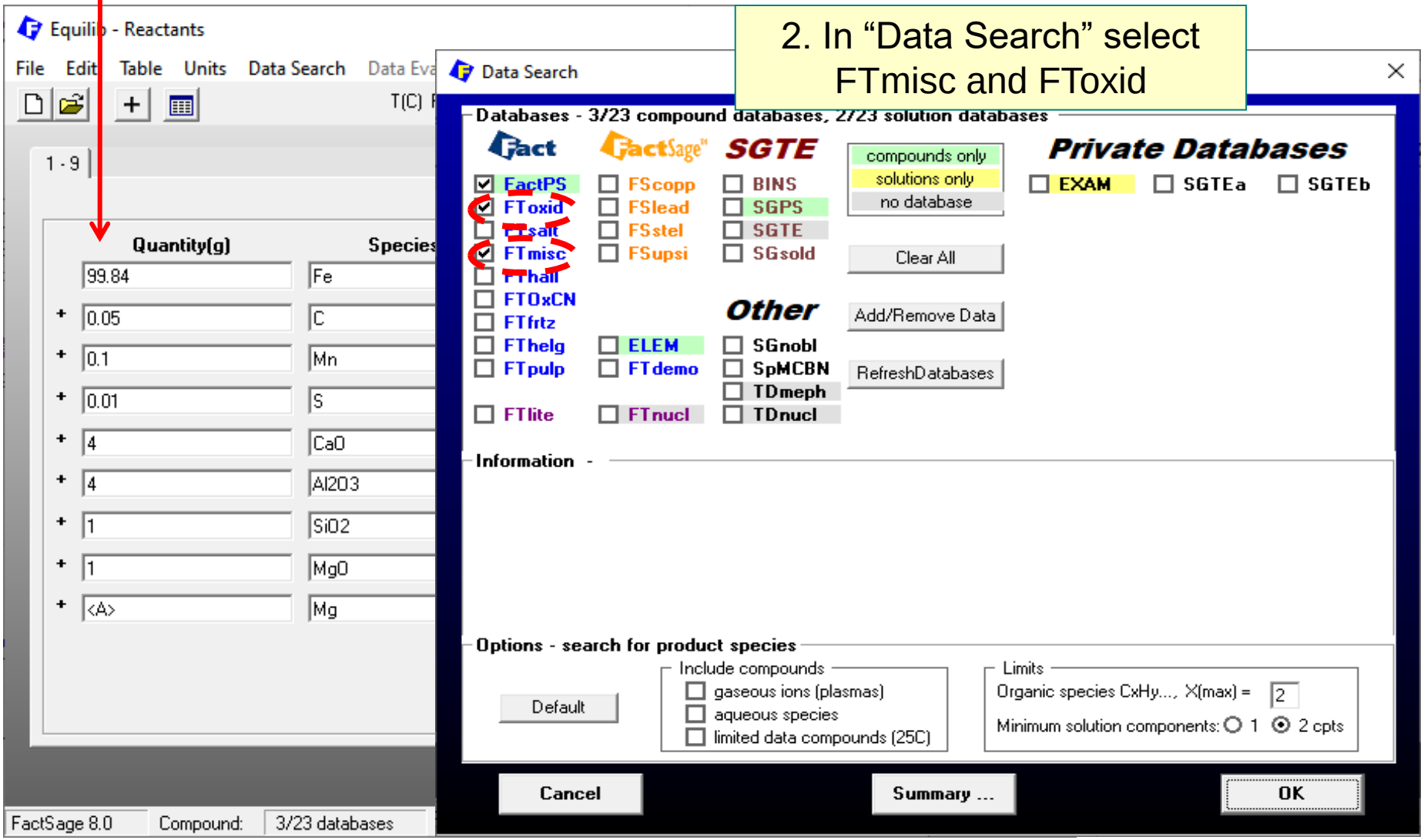
We will also assume that a slag is present in the ladle. It consists of 40% CaO, 40% Al_2O_3, 10% MgO and 10% SiO_2. The ratio of slag to metal is 1/10

Desulphurization of Steel using Slag

1. Enter the metal and slag composition

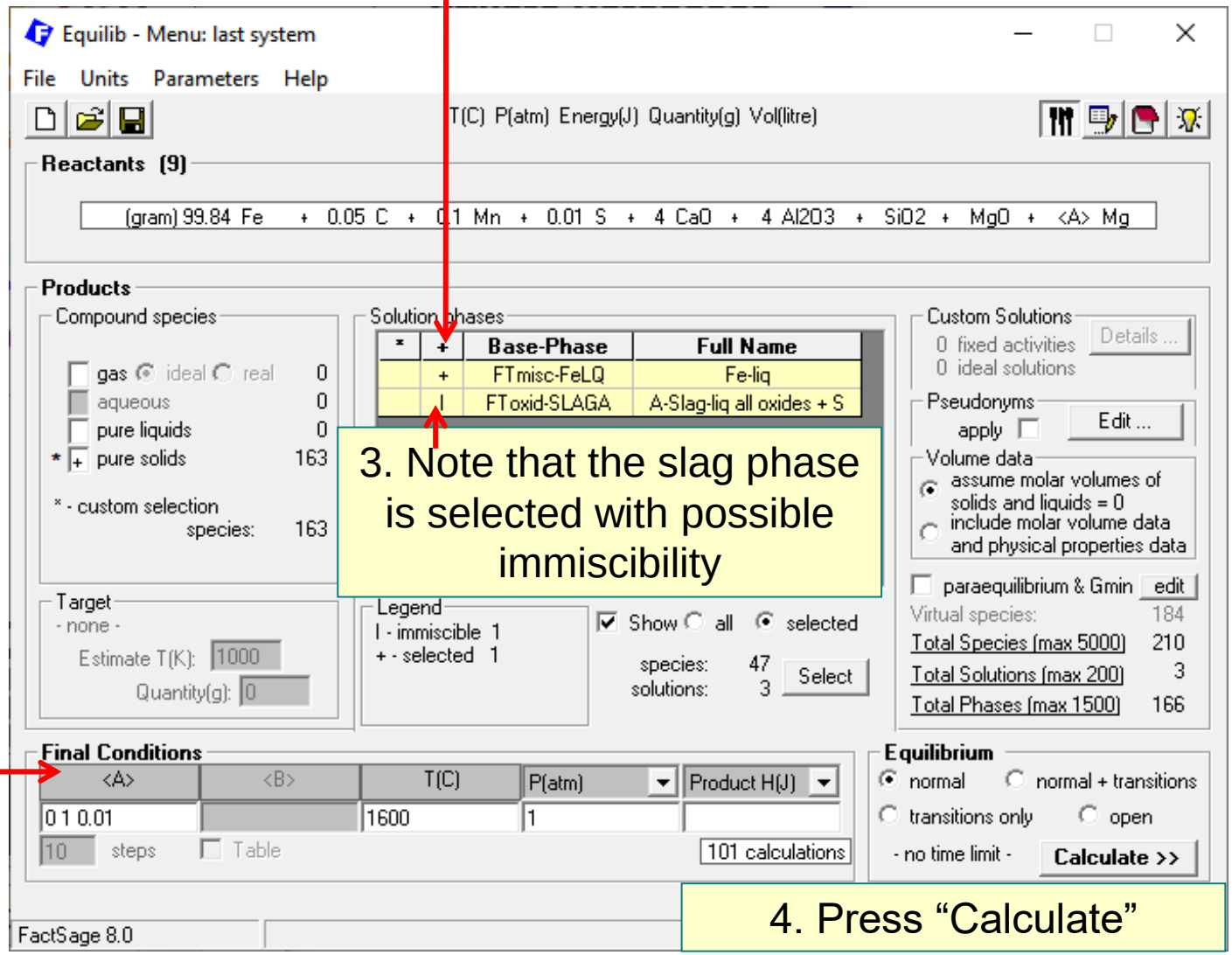
This example can be found in EquiCase2-7.dat

2. In “Data Search” select FTmisc and FToxid



Desulphurization of Steel using Slag

2. Select liquid steel and SlagA as the solutions



3. Note that the slag phase is selected with possible immiscibility

1. Enter the <A> and Temperature

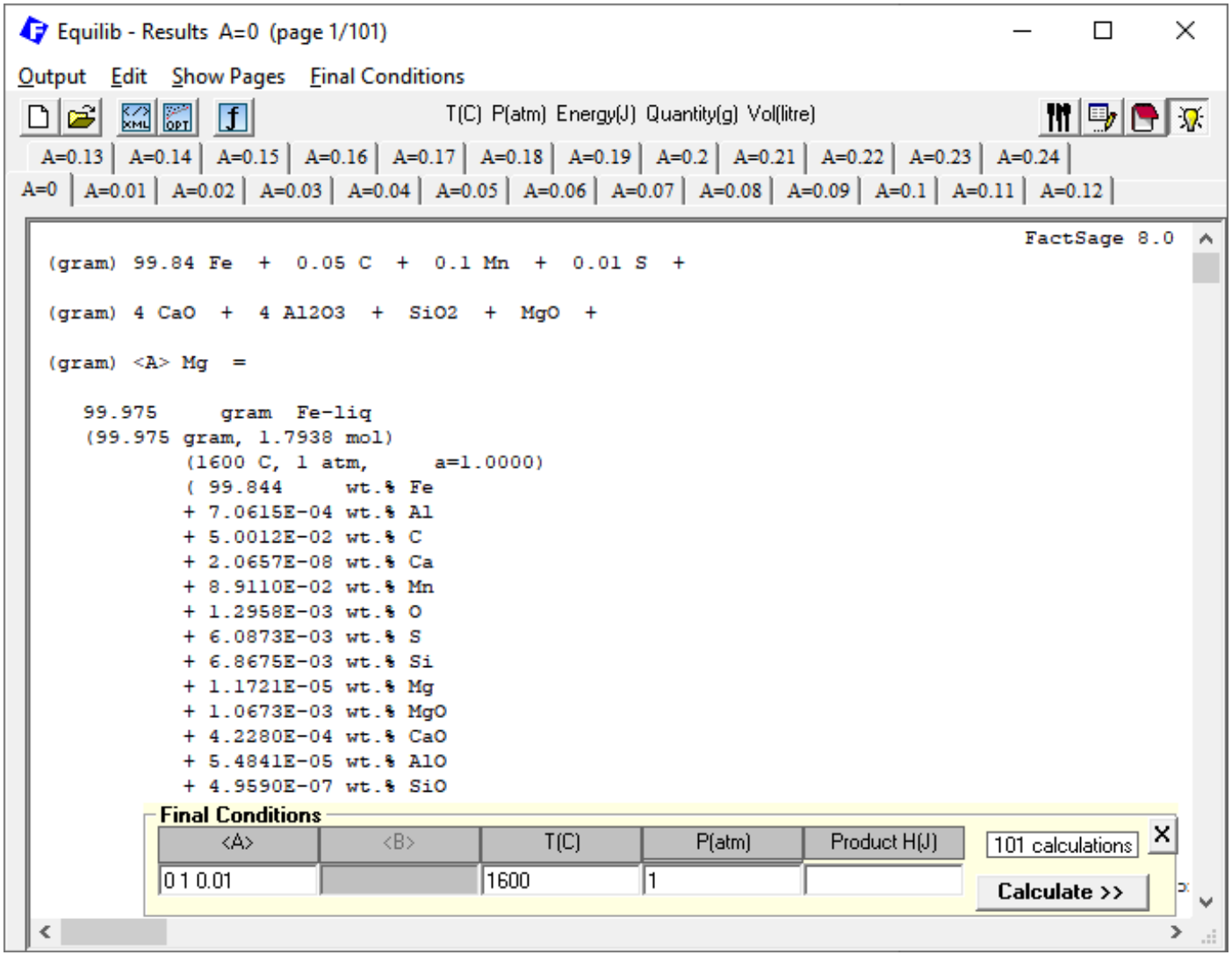
4. Press “Calculate”

Desulphurization of Steel using Slag

Results show a slag phase and a metal phase

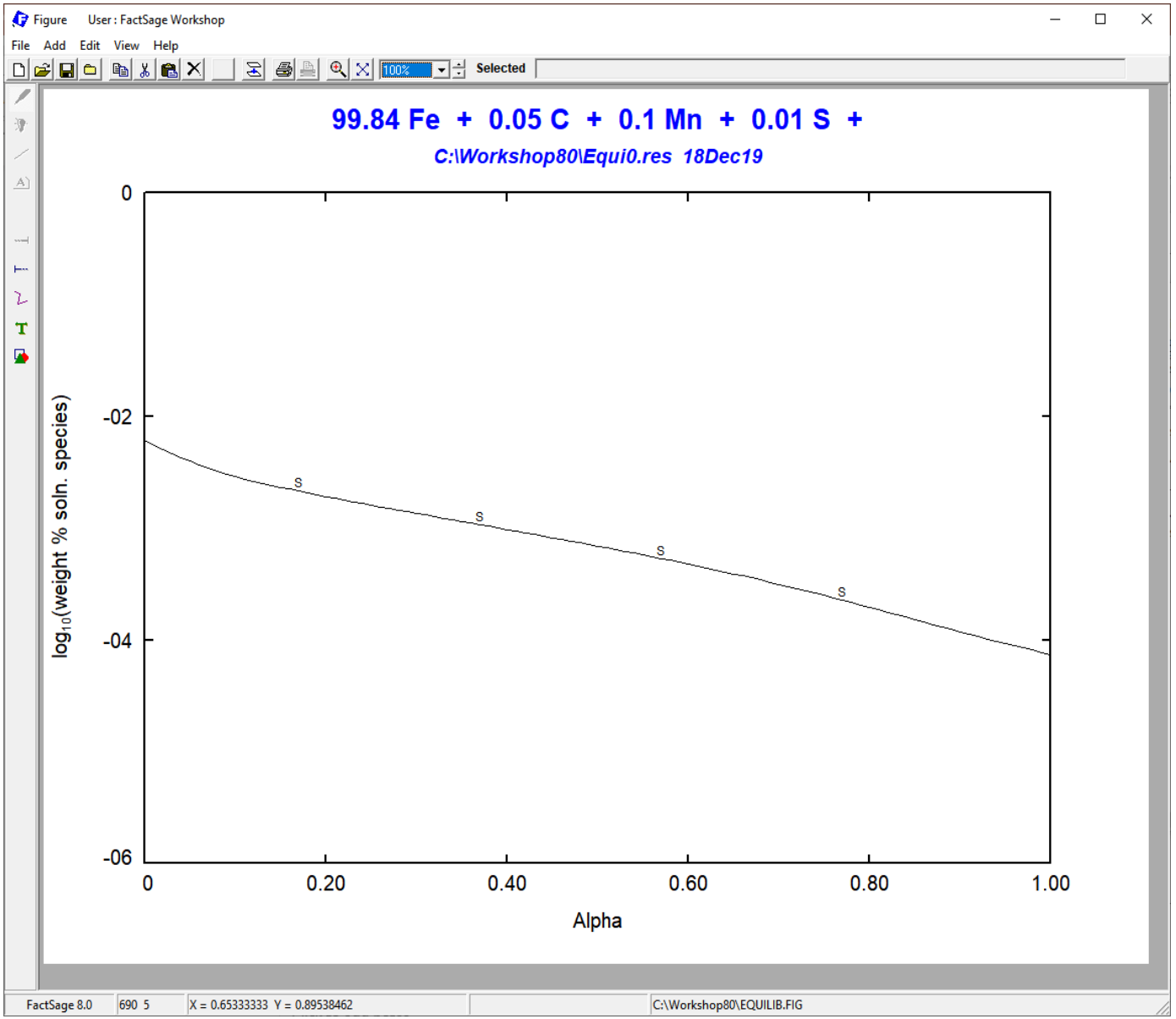
Solid periclase (MgO) appears as <A> is increased

We can plot the results in the same way as was done for the hot metal desulphurization in the previous slides



Desulphurization of Steel using Mg

A constant decrease in metal sulphur content is observed



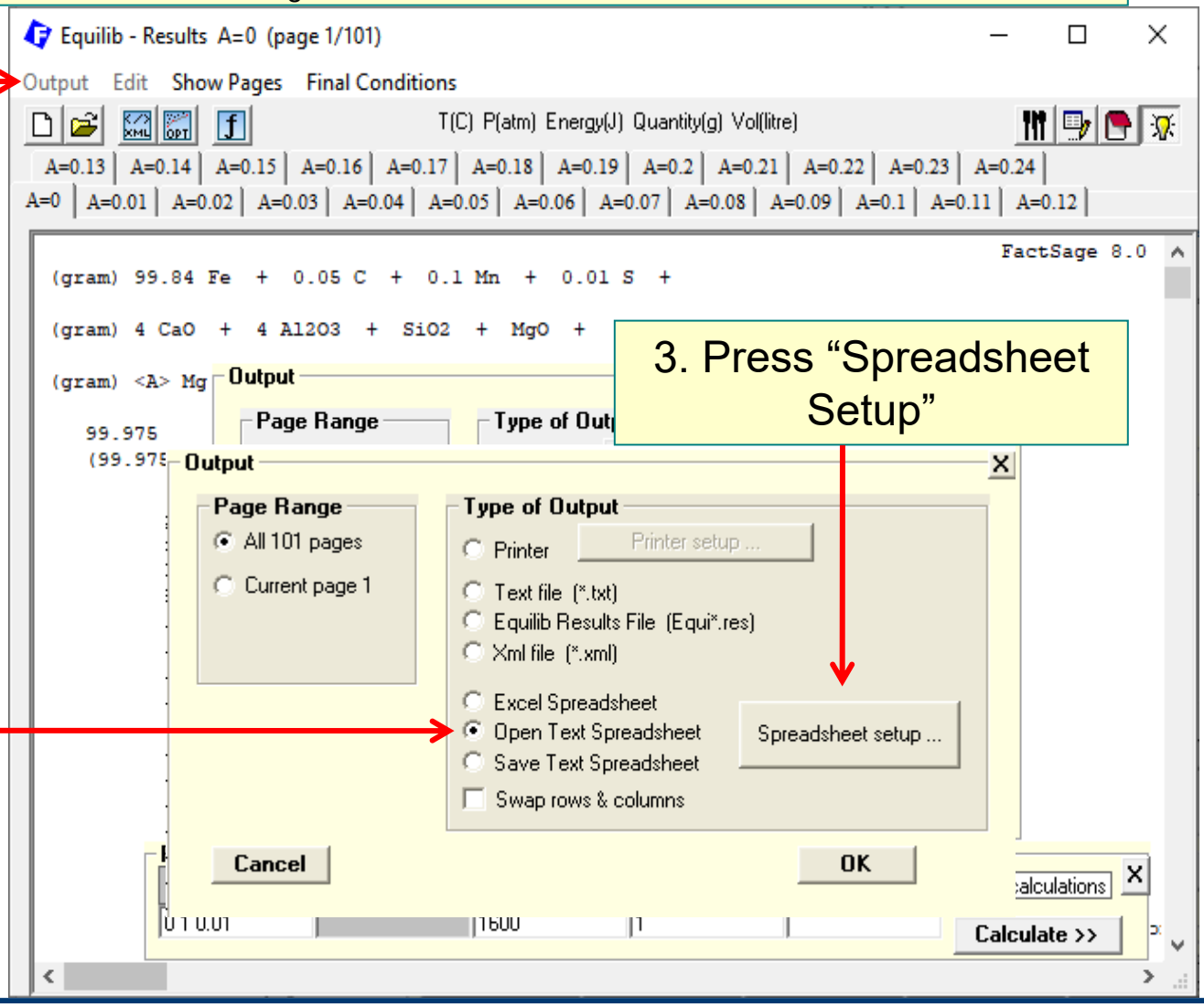
Desulphurization of Steel using Mg

Another useful way to visualize these results, is the sulphur partition coefficient:
$Ls=(S_{in\ slag})/[S_{in\ metal}]$

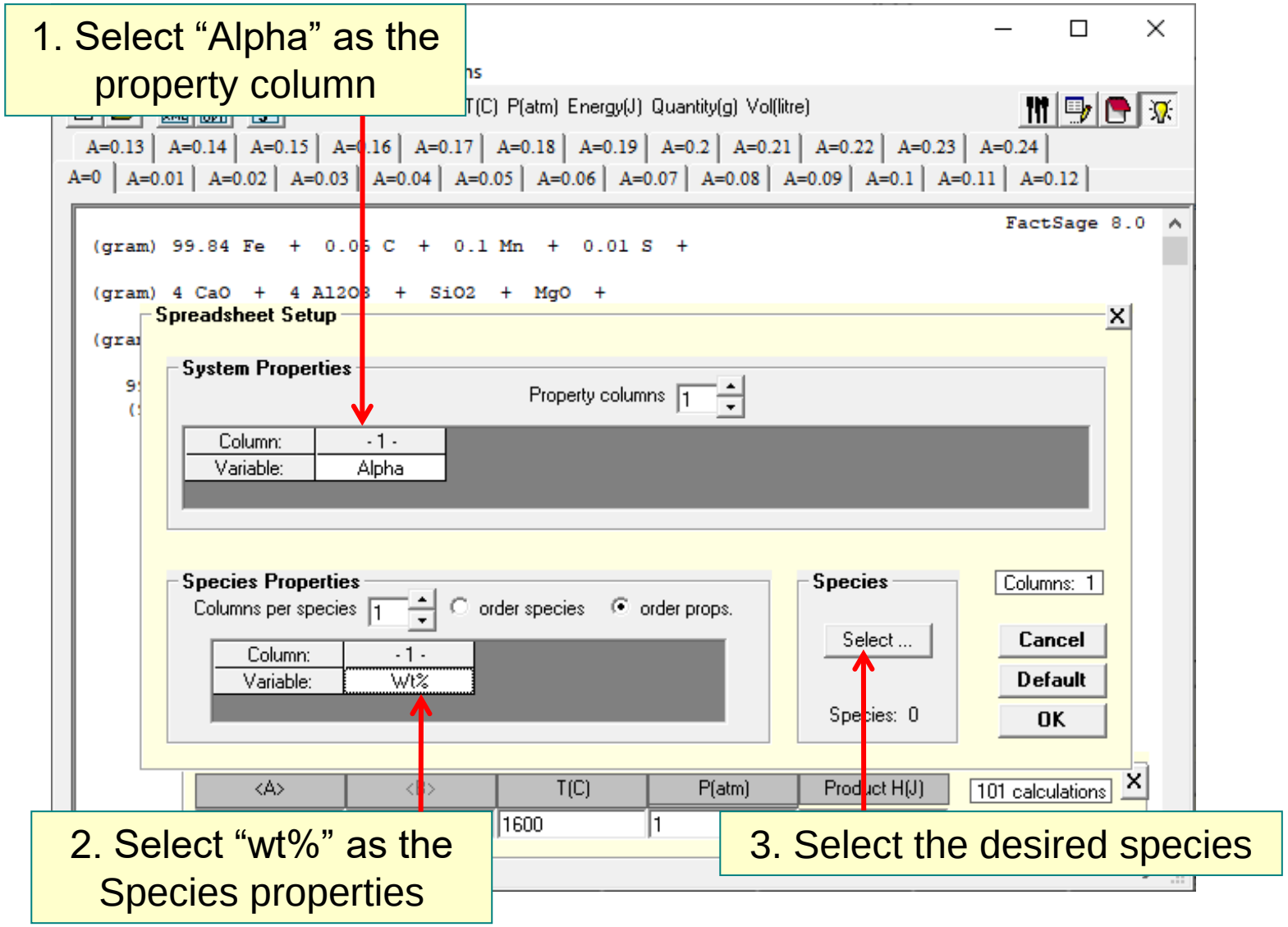
1. Press “Output” → “Save or Print As”

2. Select “Open Text Spreadsheet”

3. Press “Spreadsheet Setup”

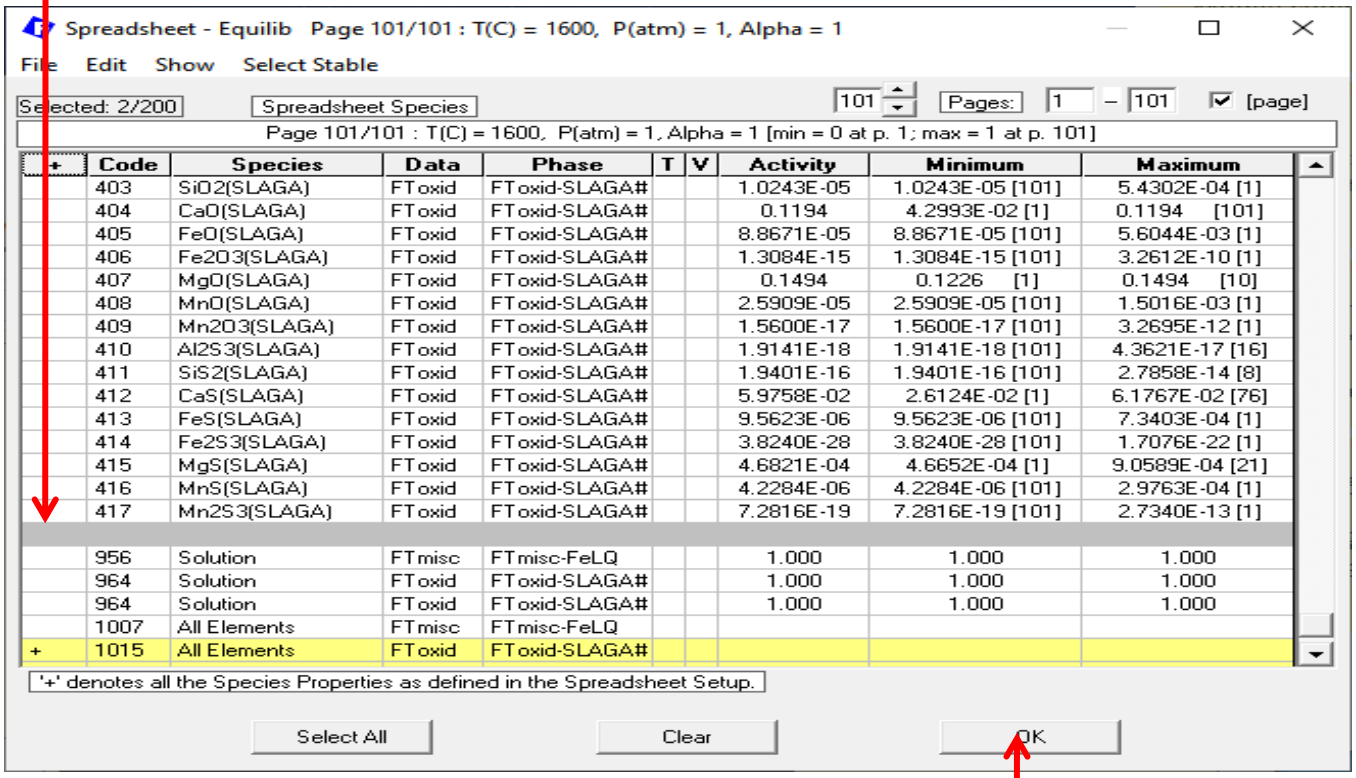


Desulphurization of Steel using Mg



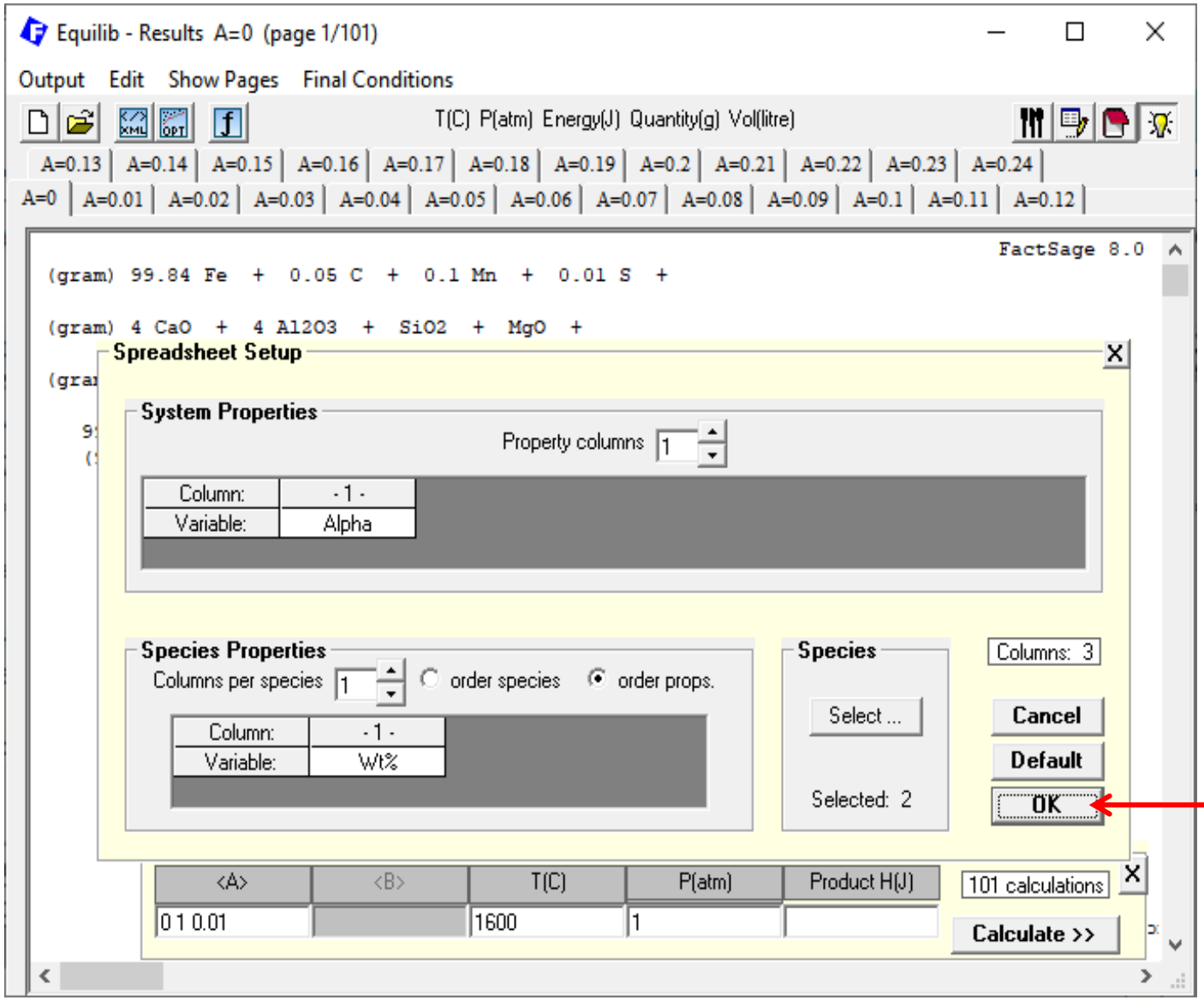
Desulphurization of Steel using Mg

1. Select sulphur from liquid steel and all elements from the slag



2. Press “OK”

Desulphurization of Steel using Mg



1. Press “OK” on this window and the next one

Desulphurization of Steel using Mg

1. A spreadsheet with the composition of slag and metal at each <Alpha> value will appear.

2. It is convenient to copy the whole table and paste it in Excel.

Equilib Results

File Edit Swap rows and columns

Alpha	Wt%-S(FeLQ)	Wt%-Fe_FToxid-SLAGA#1	Wt%-Mn_FToxid-SLAGA#1	Wt%-Ca_FToxid-SLAGA#1	Wt%-S_FToxid-SLAGA#1	Wt%-Si_FToxid-SLAGA#1	Wt%-Al_FToxid-SLAGA#1	Wt%-Mg_FTox
0.0000000E+00	6.0872865E-03	2.0547678E-01	1.0870141E-01	2.8513378E+01	3.9044801E-02	4.5942107E+00	2.1109887E+01	6.008795
1.0000000E-02	5.5225548E-03	1.6564708E-01	8.8667249E-02	2.8510641E+01	4.4667417E-02	4.5581833E+00	2.1105213E+01	6.107786
2.0000000E-02	5.0337812E-03	1.3913174E-01	7.4715083E-02	2.8504557E+01	4.9527274E-02	4.5157601E+00	2.1097873E+01	6.206024
3.0000000E-02	4.6167677E-03	1.2065334E-01	6.4657395E-02	2.8496514E+01	5.3667022E-02	4.4693002E+00	2.1089018E+01	6.303784
4.0000000E-02	4.2585811E-03	1.0711369E-01	5.7090835E-02	2.8487309E+01	5.7216547E-02	4.4202732E+00	2.1079294E+01	6.401224
5.0000000E-02	3.9470613E-03	9.6751746E-02	5.1175530E-02	2.8477384E+01	6.0297849E-02	4.3695512E+00	2.1069051E+01	6.498433
6.0000000E-02	3.6726691E-03	8.8536064E-02	4.6402166E-02	2.8466994E+01	6.3006610E-02	4.3176633E+00	2.1058484E+01	6.595464
7.0000000E-02	3.4282375E-03	8.1834264E-02	4.2450319E-02	2.8456290E+01	6.5414709E-02	4.2649440E+00	2.1047707E+01	6.692345
8.0000000E-02	3.2083949E-03	7.6240456E-02	3.9110084E-02	2.8445368E+01	6.7576026E-02	4.2116136E+00	2.1036788E+01	6.789098
9.0000000E-02	3.0141722E-03	7.1490402E-02	3.6277282E-02	2.8441841E+01	6.9499072E-02	4.1589003E+00	2.1031348E+01	6.871593
1.0000000E-01	2.8712463E-03	6.7434155E-02	3.4058621E-02	2.8490517E+01	7.1041455E-02	4.1131828E+00	2.1064473E+01	6.856172
1.1000000E-01	2.7408098E-03	6.3883364E-02	3.2101881E-02	2.8539279E+01	7.2464348E-02	4.0670142E+00	2.1097652E+01	6.840637
1.2000000E-01	2.6209568E-03	6.0739609E-02	3.0357977E-02	2.8588138E+01	7.3786197E-02	4.0204494E+00	2.1130891E+01	6.825014
1.3000000E-01	2.5101776E-03	5.7929062E-02	2.8789783E-02	2.8637101E+01	7.5021608E-02	3.9735304E+00	2.1164190E+01	6.809320
1.4000000E-01	2.4072591E-03	5.5395195E-02	2.7368663E-02	2.8686175E+01	7.6182305E-02	3.9262900E+00	2.1197550E+01	6.793570
1.5000000E-01	2.3112135E-03	5.3093943E-02	2.6072142E-02	2.8735364E+01	7.7277833E-02	3.8787543E+00	2.1230973E+01	6.777776
1.6000000E-01	2.2212269E-03	5.0990405E-02	2.4882312E-02	2.8784673E+01	7.8316045E-02	3.8309447E+00	2.1264456E+01	6.761945
1.7000000E-01	2.1366218E-03	4.9056552E-02	2.3784707E-02	2.8834103E+01	7.9303478E-02	3.7828785E+00	2.1297998E+01	6.746087
1.8000000E-01	2.0568285E-03	4.7269589E-02	2.2767501E-02	2.8883659E+01	8.0245624E-02	3.7345702E+00	2.1331599E+01	6.730205
1.9000000E-01	1.9813636E-03	4.5610765E-02	2.1820916E-02	2.8933341E+01	8.1147135E-02	3.6860323E+00	2.1365257E+01	6.714306
2.0000000E-01	1.9098140E-03	4.4064505E-02	2.0936793E-02	2.8983153E+01	8.2011988E-02	3.6372753E+00	2.1398970E+01	6.698393
2.1000000E-01	1.8418238E-03	4.2617746E-02	2.0108258E-02	2.9033096E+01	8.2843605E-02	3.5883085E+00	2.1432736E+01	6.682468
2.2000000E-01	1.7770845E-03	4.1259446E-02	1.9329477E-02	2.9083171E+01	8.3644951E-02	3.5391399E+00	2.1466554E+01	6.666535
2.3000000E-01	1.7153267E-03	3.9980196E-02	1.8595457E-02	2.9133381E+01	8.4418610E-02	3.4897770E+00	2.1500421E+01	6.650596

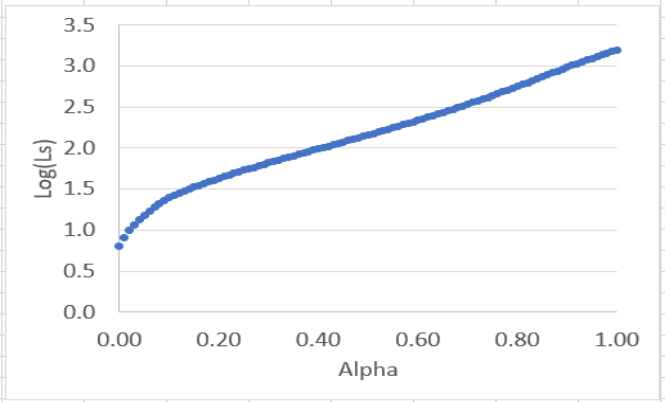
Desulphurization of Steel using Mg

1. All unnecessary columns were deleted keeping only the sulphur content in the steel and the slag.

2. The last column was used to calculate the sulphur partition coefficient Ls.

3. Plotting Alpha against log(Ls)

	A	B	C	D
1	Alpha	Wt%-S(FeLQ)	Wt%-S_FToxid-SLAGA#1	log(Ls)
2	0.00E+00	0.01	0.04	B2)
3	1.00E-02	0.01	0.04	0.91
4	2.00E-02	0.01	0.05	0.99
5	3.00E-02	0.00	0.05	1.07
6	4.00E-02	0.00	0.06	1.13
7	5.00E-02	0.00	0.06	1.18
8	6.00E-02	0.00	0.06	1.23
9	7.00E-02	0.00	0.07	1.28
10	8.00E-02	0.00	0.07	1.32
11	9.00E-02	0.00	0.07	1.36
12	1.00E-01	0.00	0.07	1.39
13	1.10E-01	0.00	0.07	1.42
14	1.20E-01	0.00	0.07	1.45
15	1.30E-01	0.00	0.08	1.48
16	1.40E-01	0.00	0.08	1.50
17	1.50E-01	0.00	0.08	1.52
18	1.60E-01	0.00	0.08	1.55
19	1.70E-01	0.00	0.08	1.57
20	1.80E-01	0.00	0.08	1.59
21	1.90E-01	0.00	0.08	1.61
22	2.00E-01	0.00	0.08	1.63
23	2.10E-01	0.00	0.08	1.65
24	2.20E-01	0.00	0.08	1.67



Calculating Slag Sulphide Capacity

A good way of comparing the ability of a slag to absorb sulphur is the sulphide capacity calculated in the following manner:

$$C_S=(S_{in\ slag})*(P_{O2}/P_{S2})^{1/2}$$

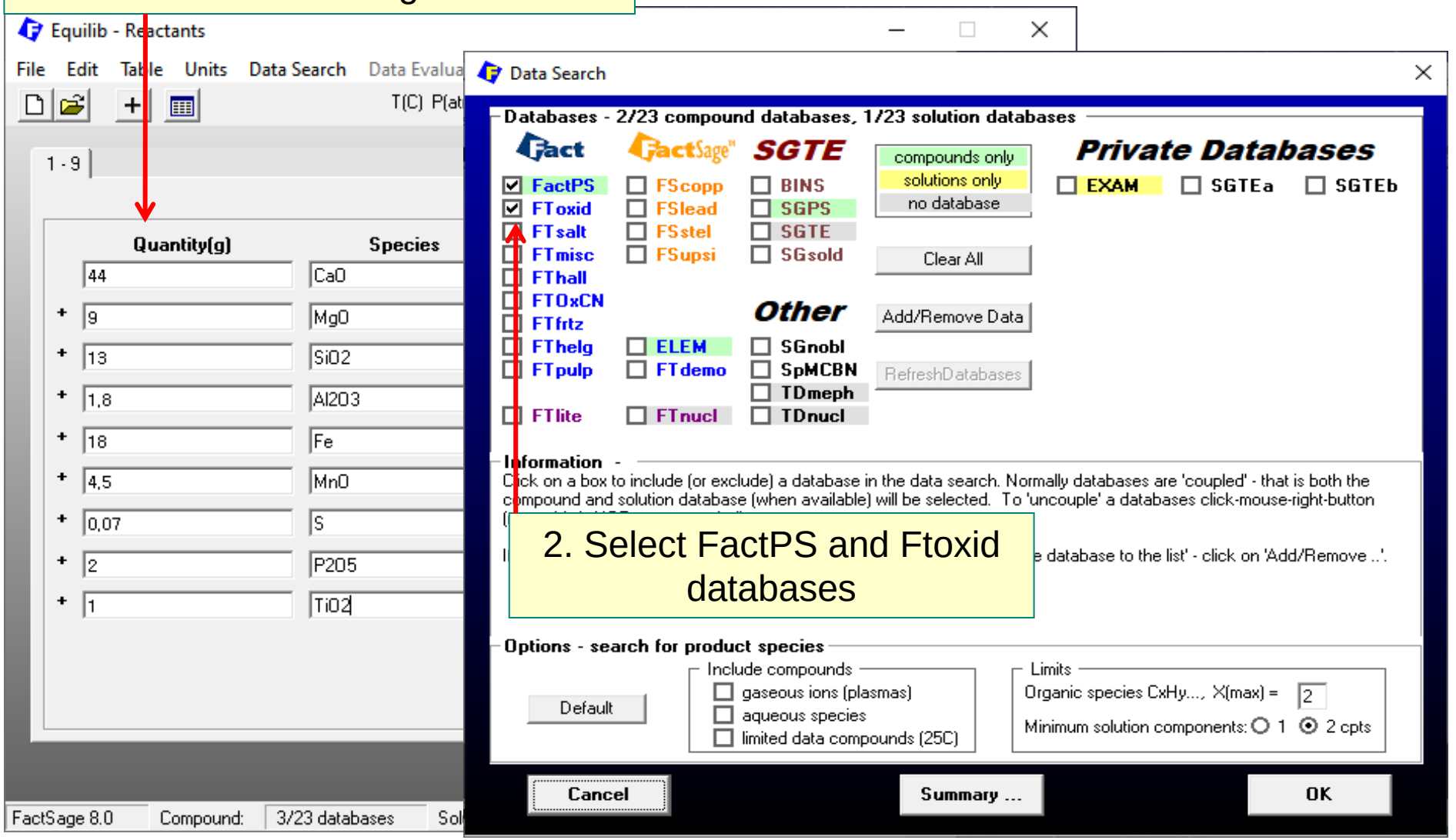
In the following slides, the sulphide capacity of four different slags will be calculated

Steelmaking Slag Parameters	BOF Slag		Ladle Furnace Slag	
	Type 1	Type 2	Type 1	Type 2
	Low-P Hot Metal	High-P Hot Metal	Al-Killed Steel	Si-Killed Steel
CaO	44.0	54.0	53.0	55.0
MgO	9.0	1.0	9.0	9.0
SiO2	13.0	14.0	5.0	20.0
Al2O3	1.8	1.0	30.0	12.0
Fe (total)	18.0	19.0	1.0	1.0
MnO	4.5	0.5	1.0	0.6
S	0.07	0.06	0.50	0.50
P2O5	2.00	3.50	0.05	0.05
TiO2	1.0	<0.5	<0.5	<0.5
Slag Basicity (CaO / SiO2)	3.4	3.9	10.6	2.8
Slag Basicity (CaO +MgO) / (SiO2+Al2O3)	3.6	3.7	1.8	2.0

Calculating Slag Sulphide Capacity

1. Enter the amount and species for the first slag

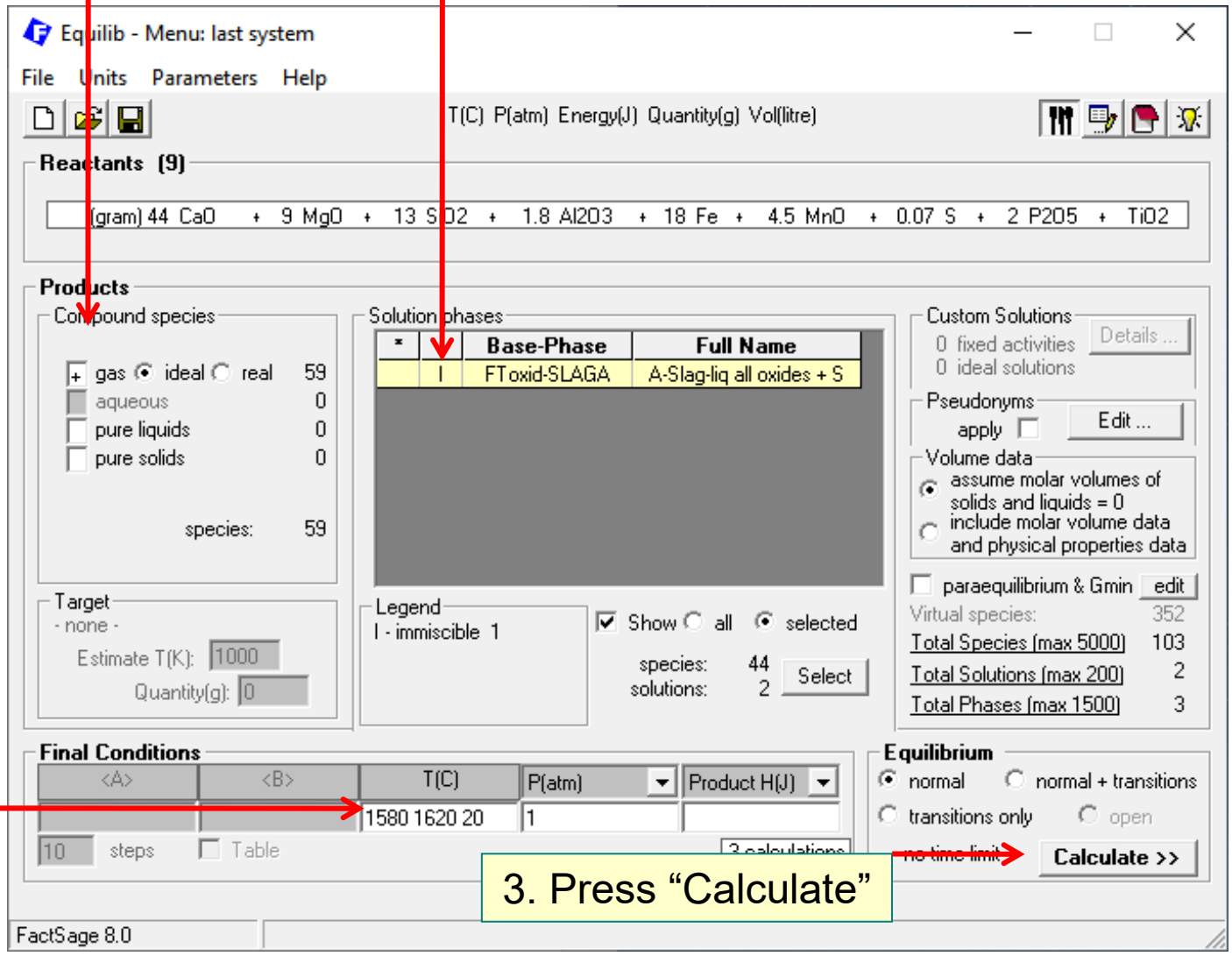
This example can be found in EquiCase2-13.dat



2. Select FactPS and Ftoxid databases

Calculating Slag Sulphide Capacity

1. Select gas and SlagA as possible products



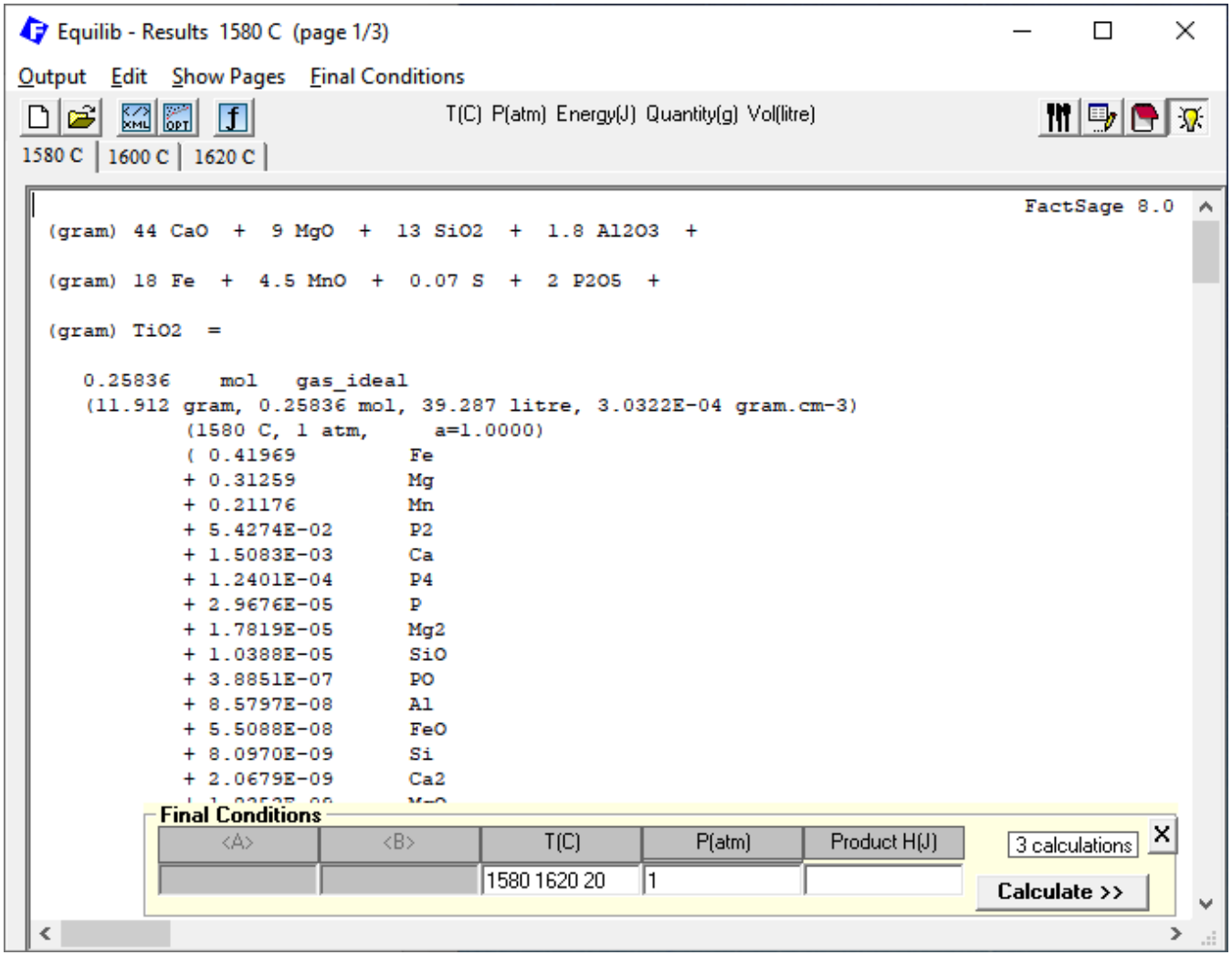
2. We will calculate the sulphide capacity at three temperatures: 1580, 1600 and 1620°C

3. Press “Calculate”

Calculating Slag Sulphide Capacity

It is now possible to calculate the sulphide capacity using these results.

In the next slides, two ways of calculating sulphide capacity will be demonstrated.

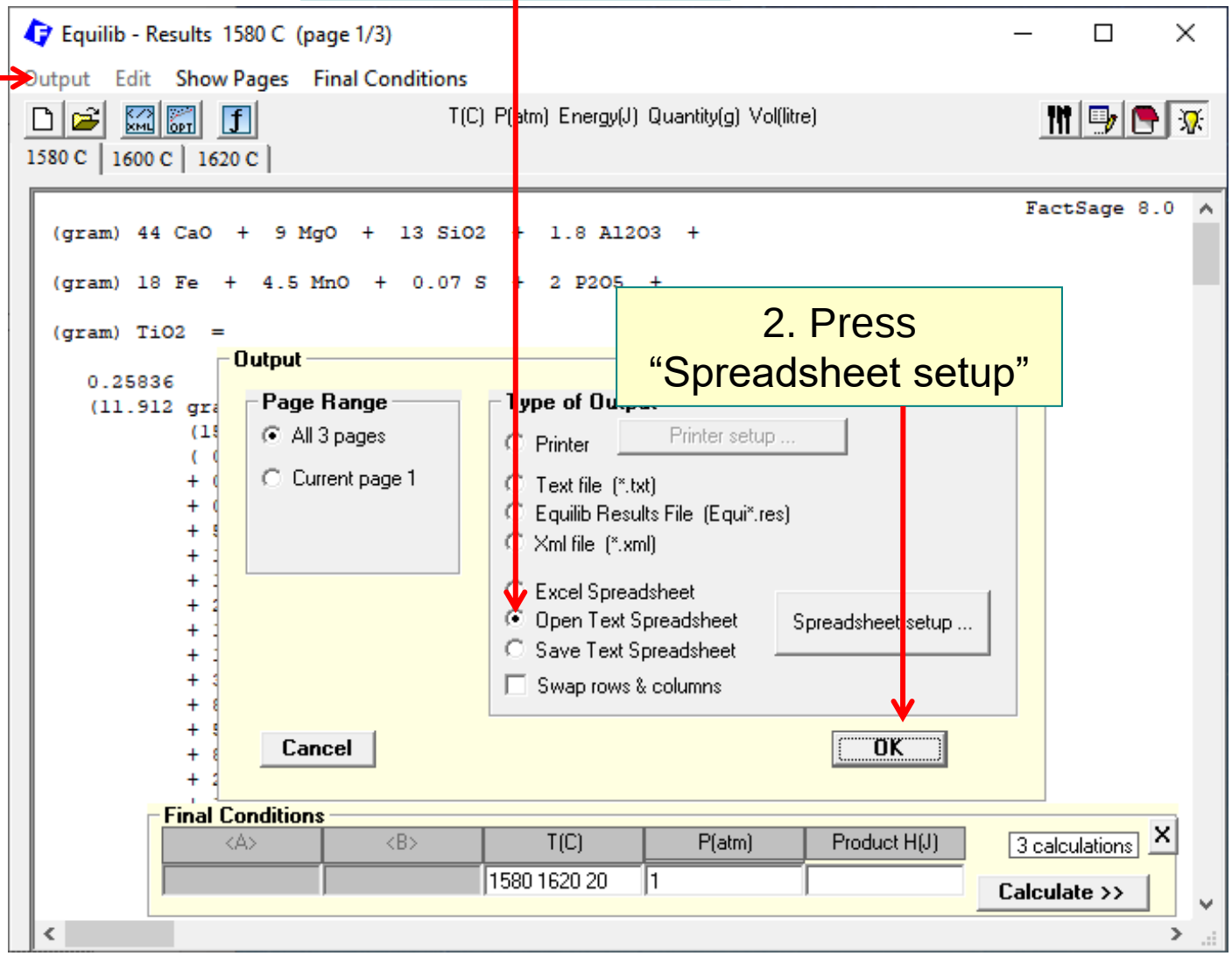


Calculating Slag Sulphide Capacity

The first way is to use Excel

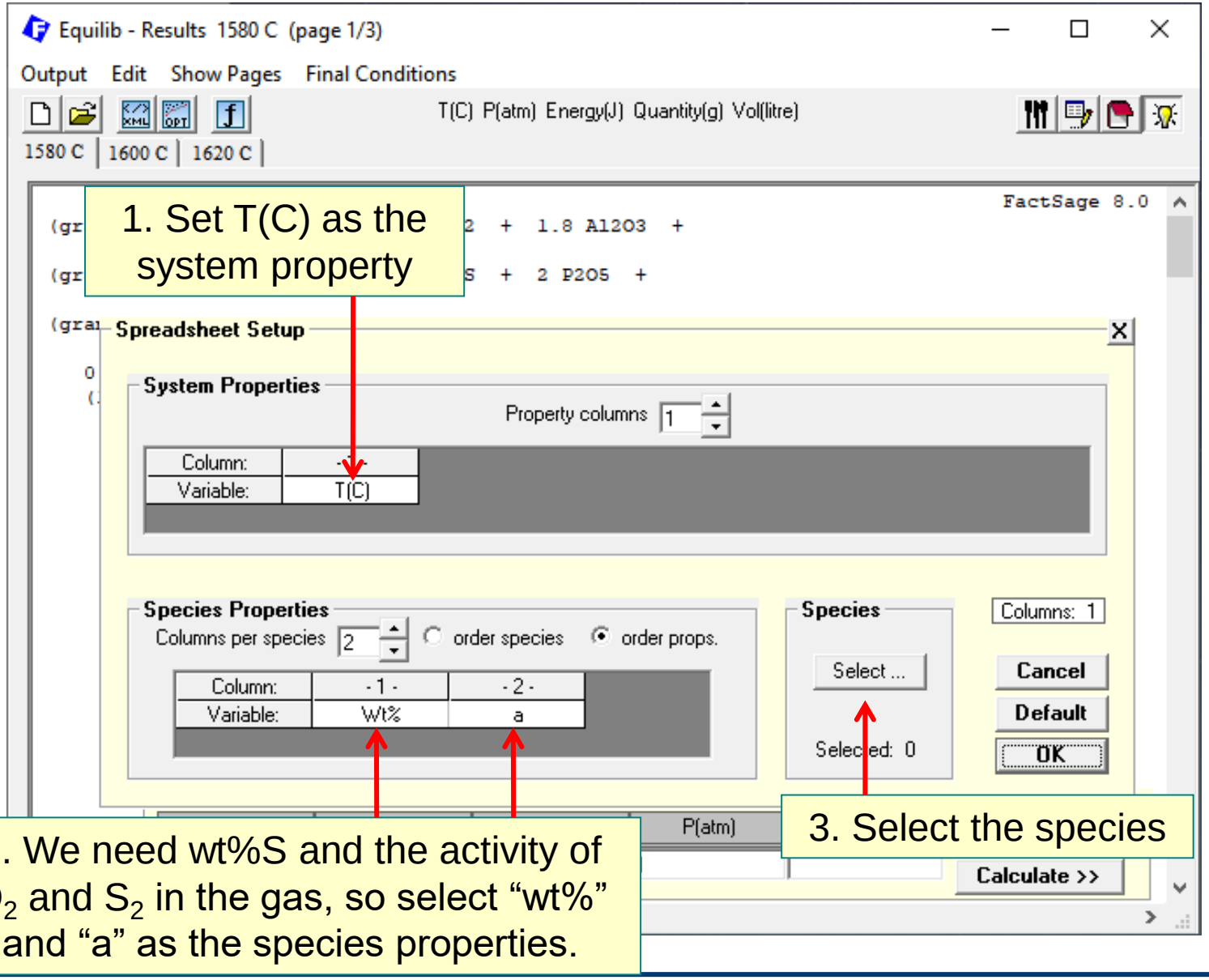
Press “Output”
→ “Save or Print As”

1. Save the results in a text spreadsheet



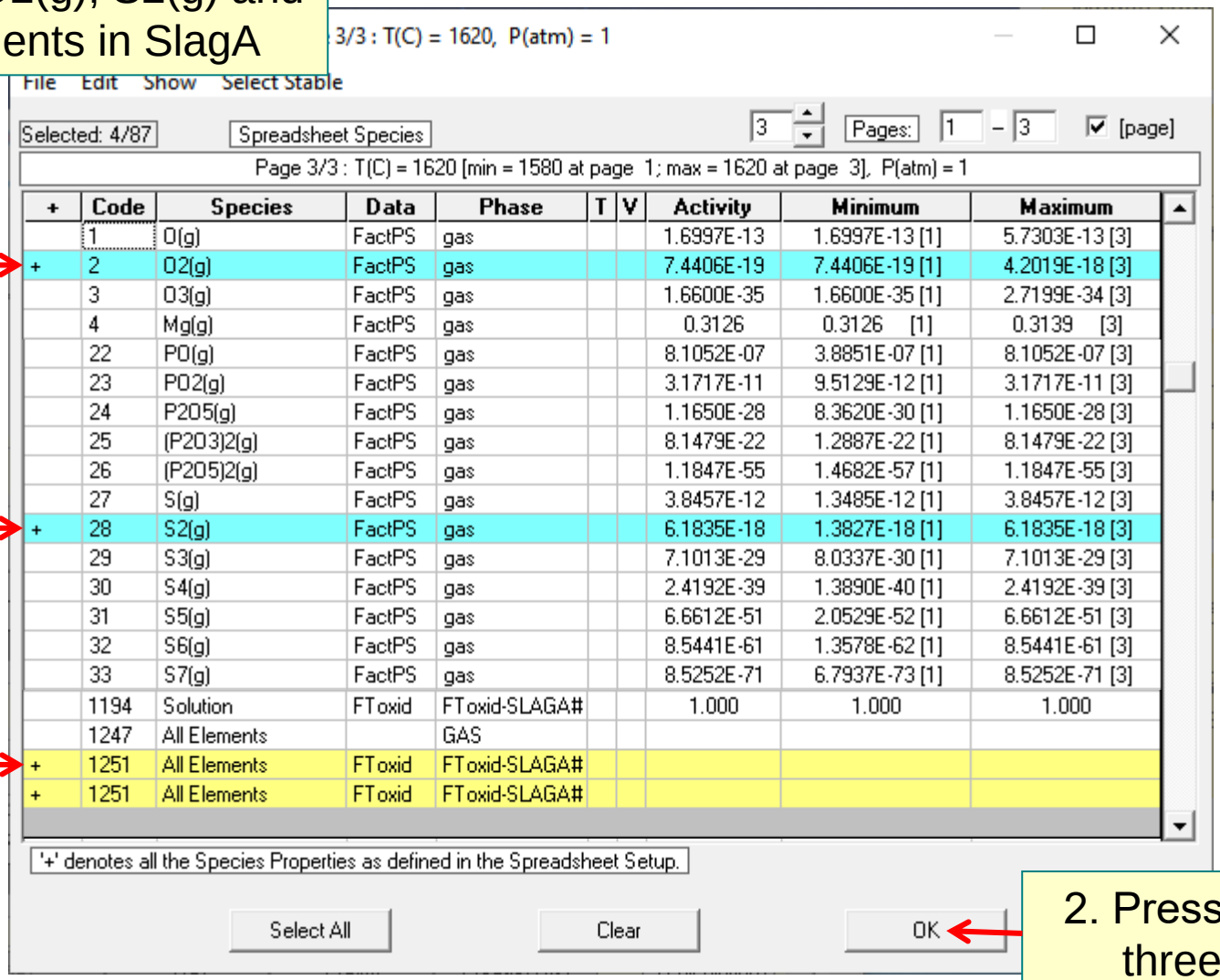
2. Press “Spreadsheet setup”

Calculating Slag Sulphide Capacity



Calculating Slag Sulphide Capacity

1. Select O2(g), S2(g) and All Elements in SlagA



+	Code	Species	Data	Phase	T	V	Activity	Minimum	Maximum
	1	O(g)	FactPS	gas			1.6997E-13	1.6997E-13 [1]	5.7303E-13 [3]
+	2	O2(g)	FactPS	gas			7.4406E-19	7.4406E-19 [1]	4.2019E-18 [3]
	3	O3(g)	FactPS	gas			1.6600E-35	1.6600E-35 [1]	2.7199E-34 [3]
	4	Mg(g)	FactPS	gas			0.3126	0.3126 [1]	0.3139 [3]
	22	PO(g)	FactPS	gas			8.1052E-07	3.8851E-07 [1]	8.1052E-07 [3]
	23	PO2(g)	FactPS	gas			3.1717E-11	9.5129E-12 [1]	3.1717E-11 [3]
	24	P2O5(g)	FactPS	gas			1.1650E-28	8.3620E-30 [1]	1.1650E-28 [3]
	25	(P2O3)2(g)	FactPS	gas			8.1479E-22	1.2887E-22 [1]	8.1479E-22 [3]
	26	(P2O5)2(g)	FactPS	gas			1.1847E-55	1.4682E-57 [1]	1.1847E-55 [3]
	27	S(g)	FactPS	gas			3.8457E-12	1.3485E-12 [1]	3.8457E-12 [3]
+	28	S2(g)	FactPS	gas			6.1835E-18	1.3827E-18 [1]	6.1835E-18 [3]
	29	S3(g)	FactPS	gas			7.1013E-29	8.0337E-30 [1]	7.1013E-29 [3]
	30	S4(g)	FactPS	gas			2.4192E-39	1.3890E-40 [1]	2.4192E-39 [3]
	31	S5(g)	FactPS	gas			6.6612E-51	2.0529E-52 [1]	6.6612E-51 [3]
	32	S6(g)	FactPS	gas			8.5441E-61	1.3578E-62 [1]	8.5441E-61 [3]
	33	S7(g)	FactPS	gas			8.5252E-71	6.7937E-73 [1]	8.5252E-71 [3]
	1194	Solution	FToxid	FToxid-SLAGA#			1.000	1.000	1.000
	1247	All Elements		GAS					
+	1251	All Elements	FToxid	FToxid-SLAGA#					
+	1251	All Elements	FToxid	FToxid-SLAGA#					

2. Press “OK” on all three screens

Calculating Slag Sulphide Capacity

1. All the needed results (and even more) appear in the spreadsheet.

Equilib Results

File Edit Swap rows and columns

T(C)	Wt%-O2(g)	Wt%-S2(g)	a-O2(g)	a-S2(g)	Wt%-Fe_FToxid-SLAGA#1	Wt%-Mn_FToxid-SLAGA#1	Wt%-Ti_FToxid-SLAGA#1	Wt%-Ca_FToxid-SLAGA#1	Wt%-S_FToxid-SLAGA#
1.5800000E+03	5.1637146E-17	1.9231229E-16	7.4406462E-19	1.3826999E-18	1.4663848E+01	5.8864892E-01	7.3577311E-01	3.8585457E+01	8.5934254E-02
1.6000000E+03	1.2396872E-16	4.1051196E-16	1.7854731E-18	2.9501184E-18	1.4653391E+01	6.0921013E-01	7.3574367E-01	3.8582714E+01	8.5930795E-02
1.6200000E+03	2.9188401E-16	8.6085431E-16	4.2018929E-18	6.1835344E-18	1.4642836E+01	6.2987870E-01	7.3571473E-01	3.8579942E+01	8.5927386E-02

2. Copy the results in Excel and delete the unnecessary columns

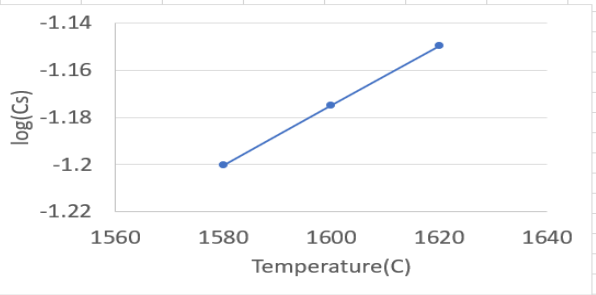
4. Plot log(Cs) versus temperature

AutoSave Off | Equilib.xls - Compatibility Mode - Excel | Search

File Home Insert Page Layout Formulas Data Review View Developer Help

SUMIFS | =LOG(D4*SQRT(B4/C4))

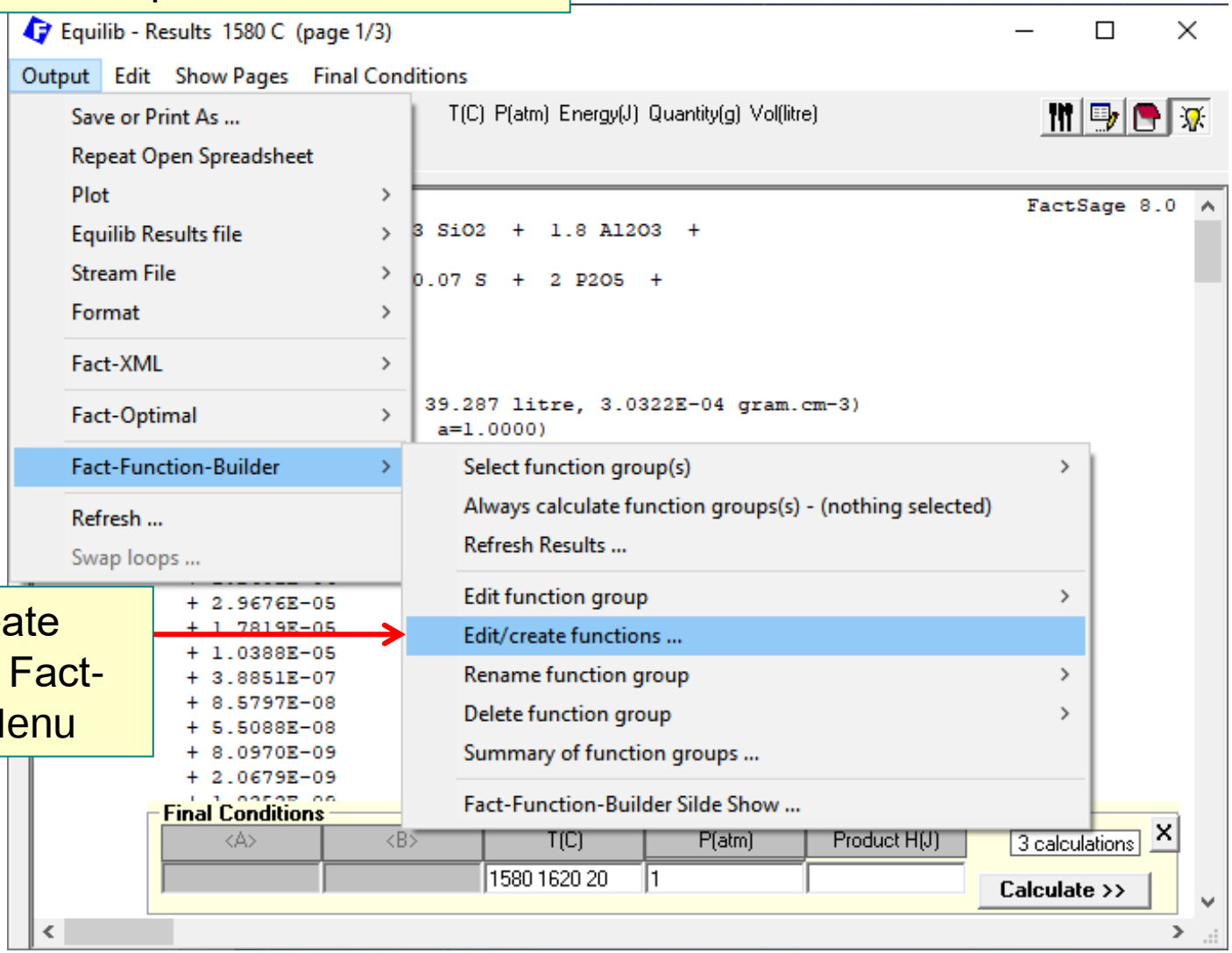
	A	B	C	D	E
1	T(C)	a-O2(g)	a-S2(g)	Wt%-S_FToxid-SLAGA#1	log(Cs)
2	1580.00	7.44E-19	1.38E-18	8.59E-02	-1.200392327
3	1600.00	1.79E-18	2.95E-18	8.59E-02	-1.174894238
4	1620.00	4.20E-18	6.18E-18	8.59E-02	SQRT(B4/C4))



3. Calculate the sulphide capacity in a separate column.

Calculating Slag Sulphide Capacity

Another way to plot the sulphide capacity is to use the function builder tool coupled with Fact-XML



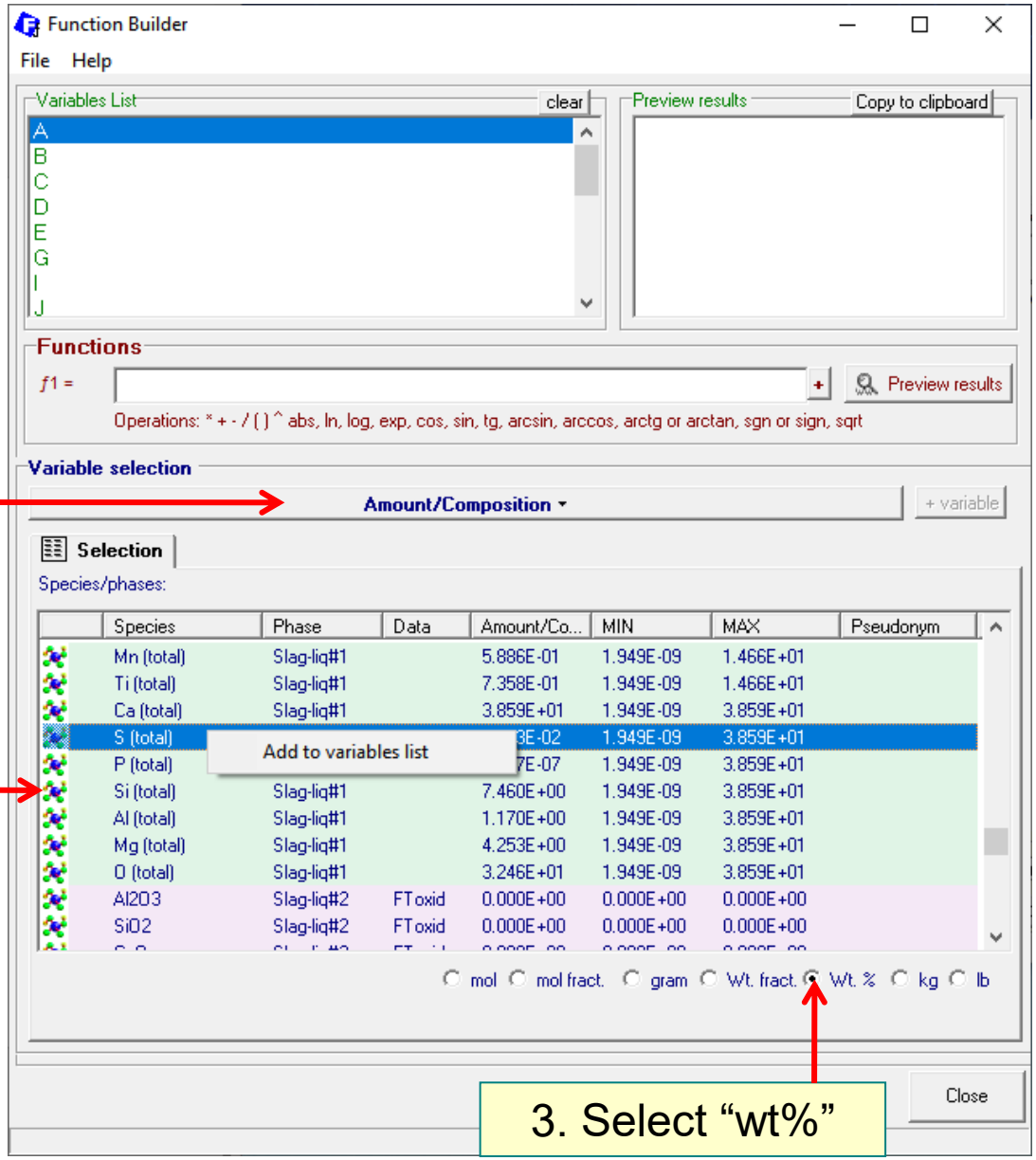
1. Press “Edit/Create functions” under the Fact-Function-Builder Menu

Calculating Slag Sulphide Capacity

1. We need to select wt%S as one variable

2. Select “Amount/Composition” under “Variable selection”

4. Right-click on S(total) in slag and add it to variables list



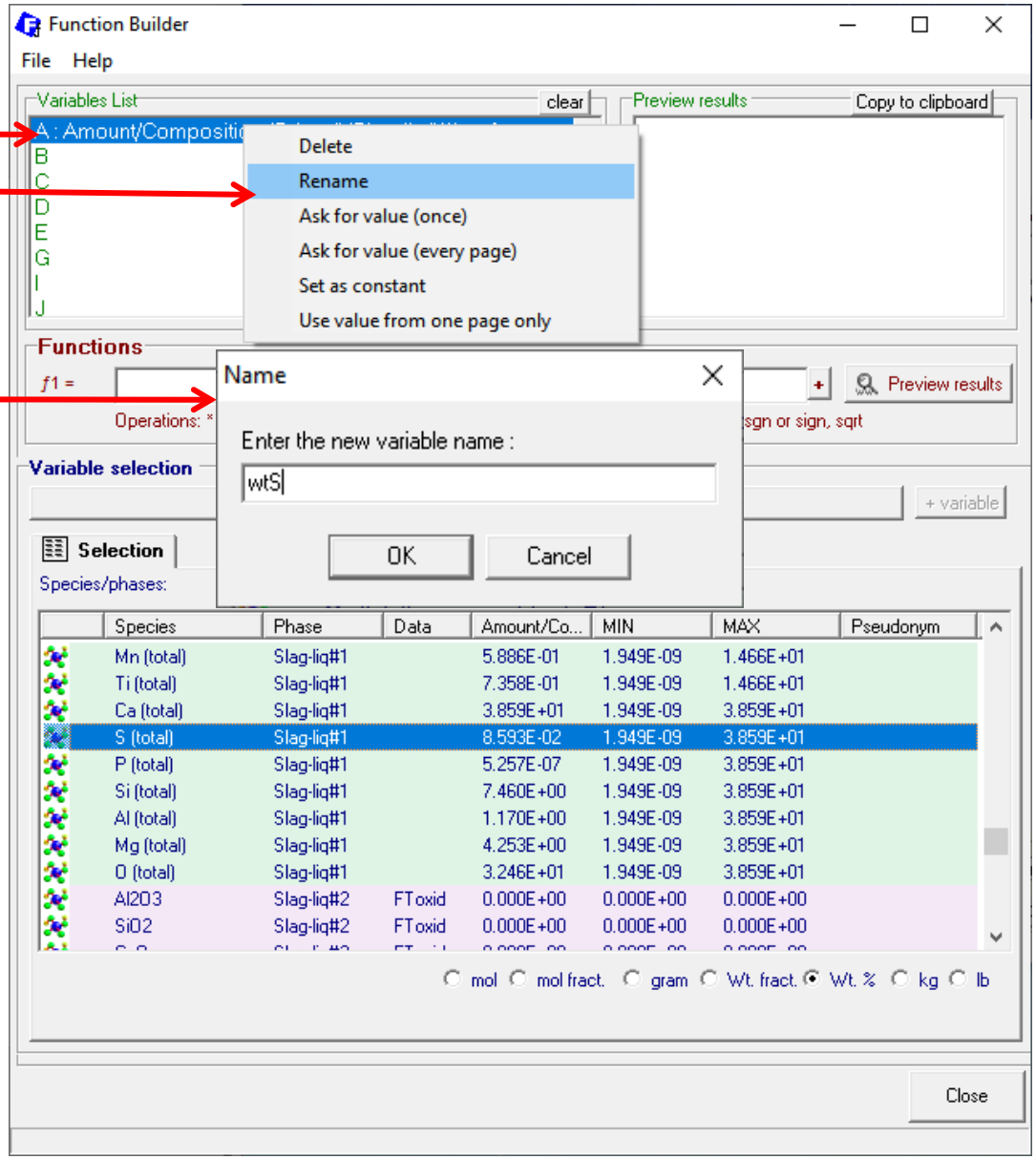
3. Select “wt%”

Calculating Slag Sulphide Capacity

1. The amount of S now appears in the variables list.

2. Right-click on the variable and rename it to “wtS”

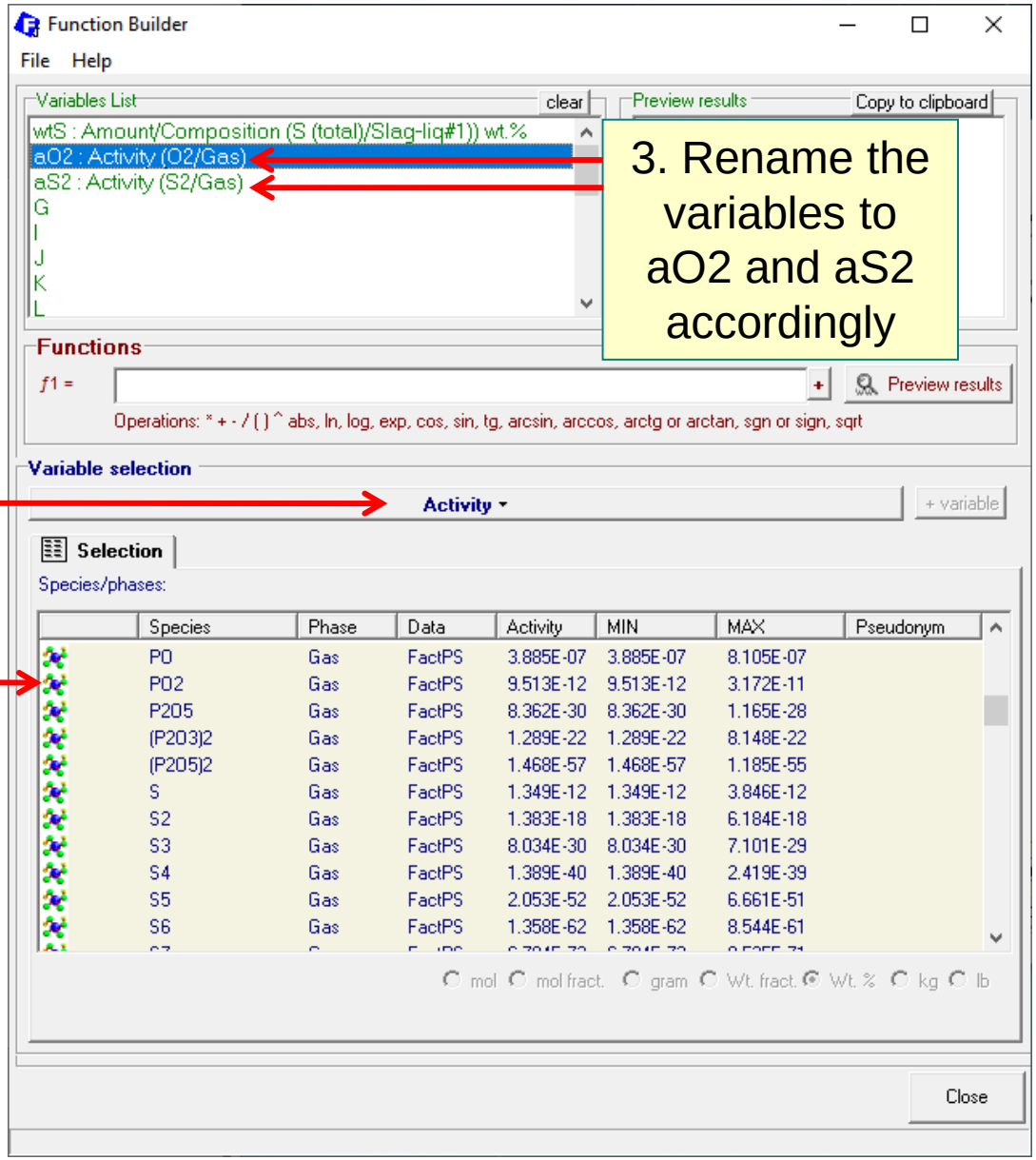
3. Partial pressure and activity of a gas is the same thing, so we need to select activity of O_2 and S_2 in the gas as the two other variables.



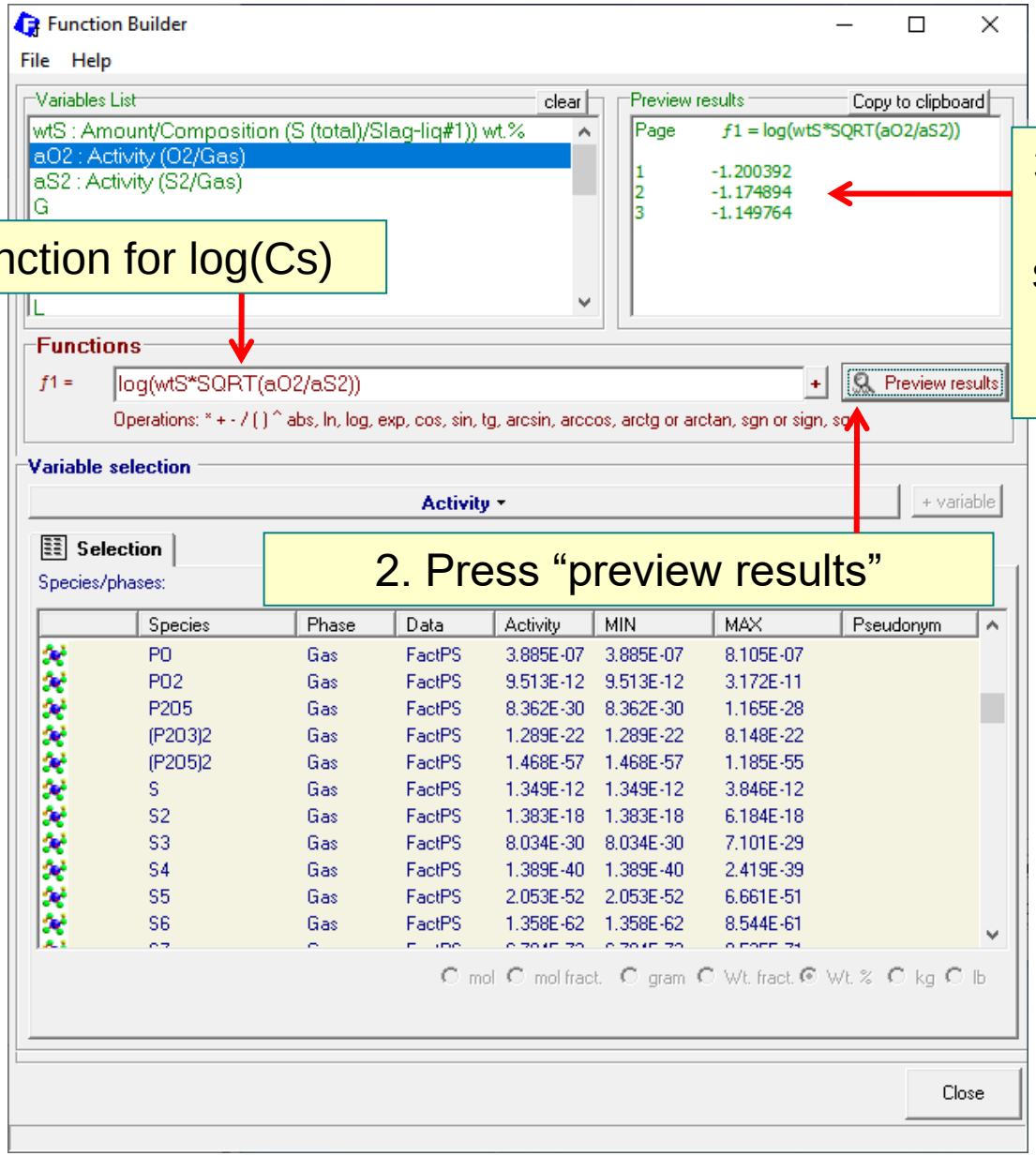
Calculating Slag Sulphide Capacity

1. Select “Activity” under “Variable Selection”

2. Right-click on the O2 and S2 and add them to the variable list



Calculating Slag Sulphide Capacity



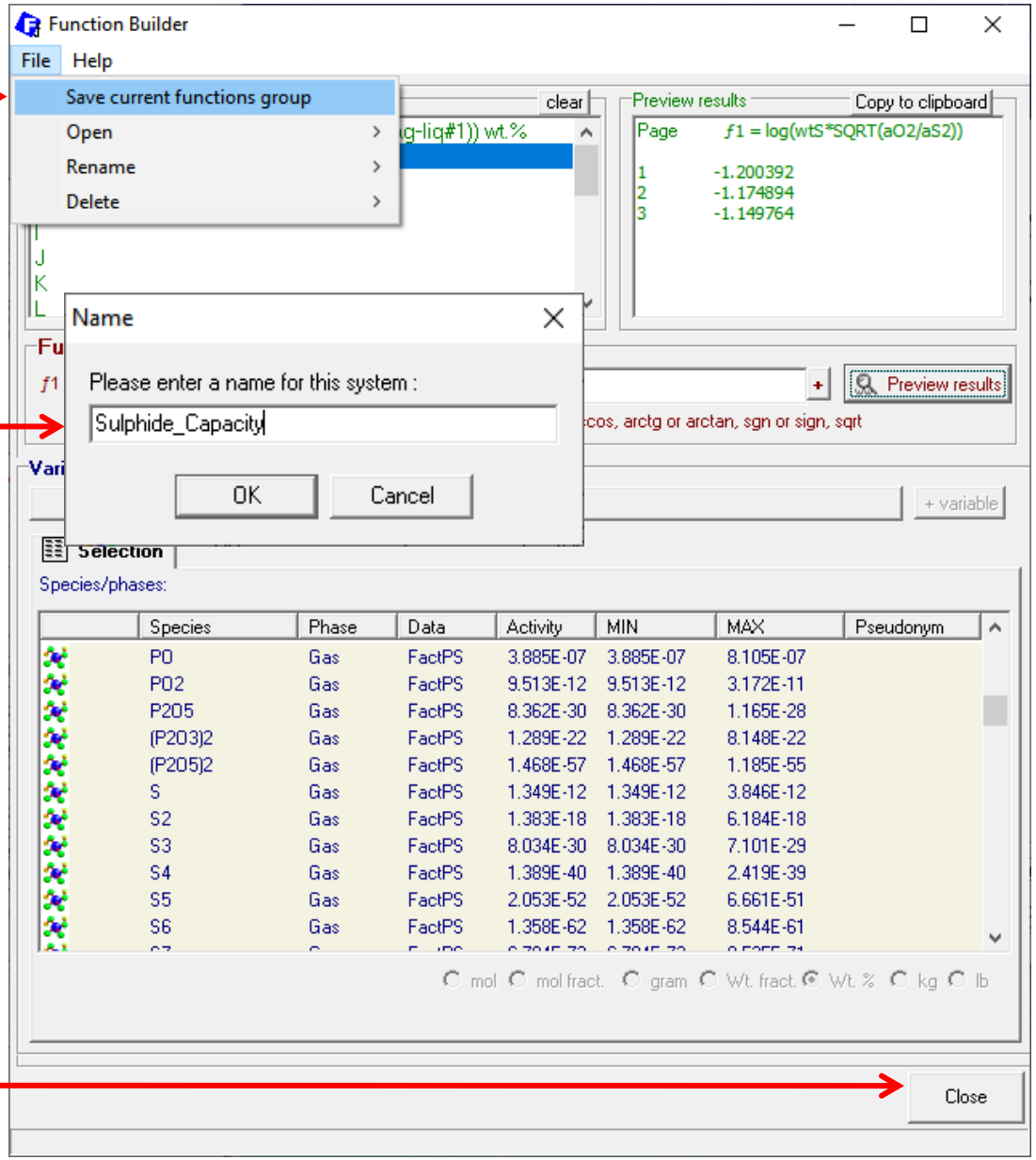
1. Enter the function for log(Cs)

2. Press “preview results”

3. Note that the results are the same as for the Excel calculation

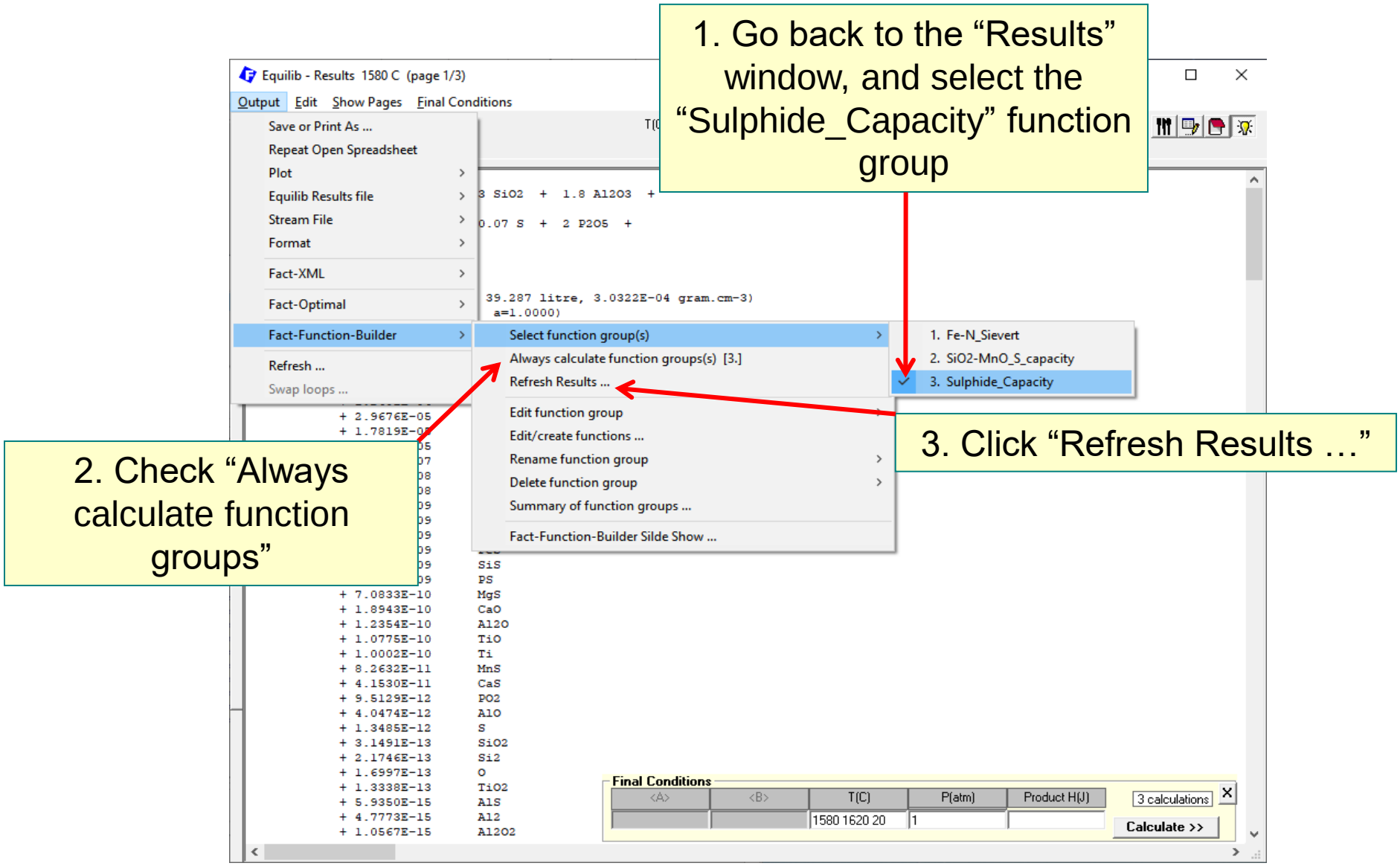
Calculating Slag Sulphide Capacity

1. Save the function as “Sulphide_Capacity”



2. Close the window

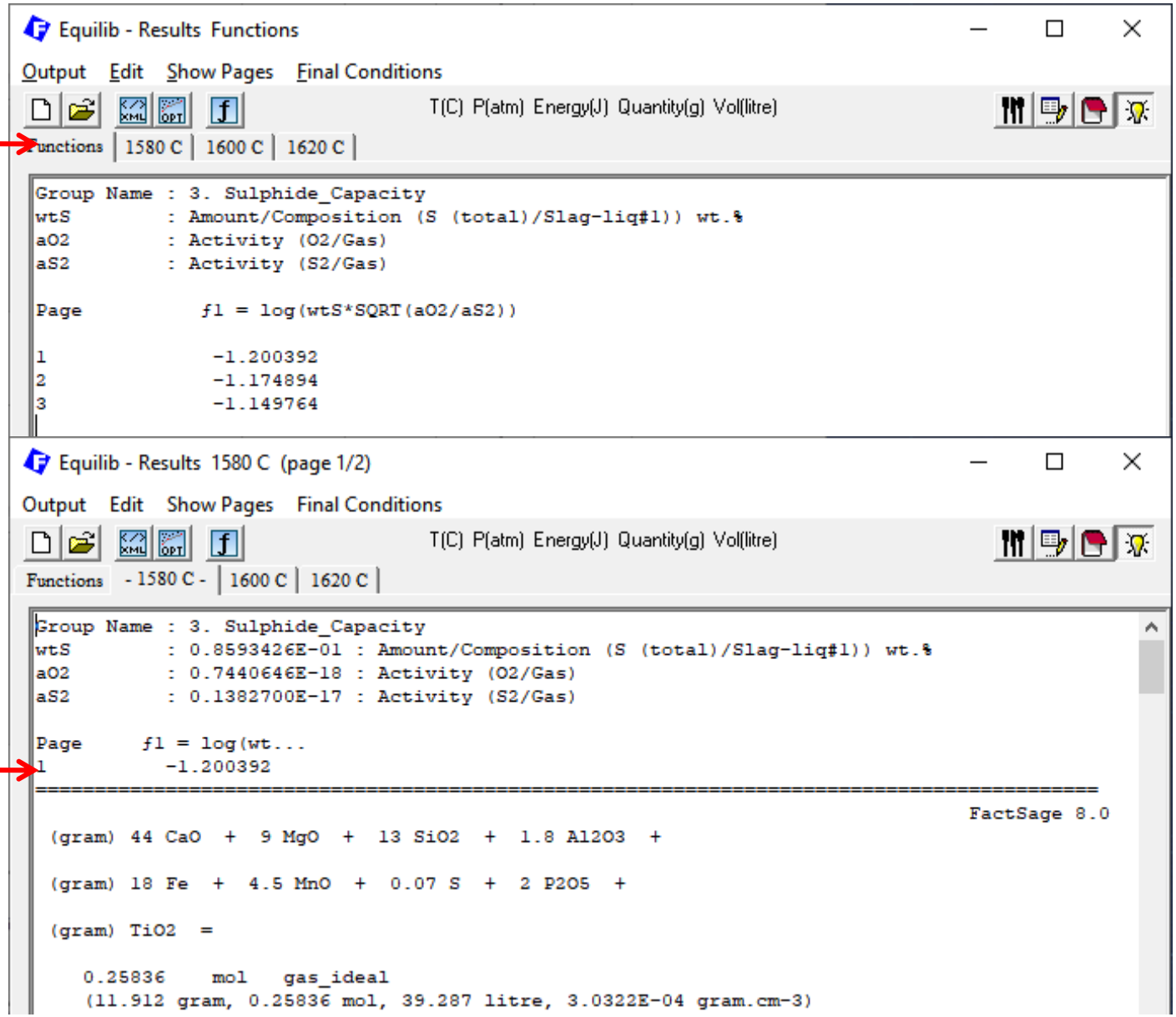
Calculating Slag Sulphide Capacity



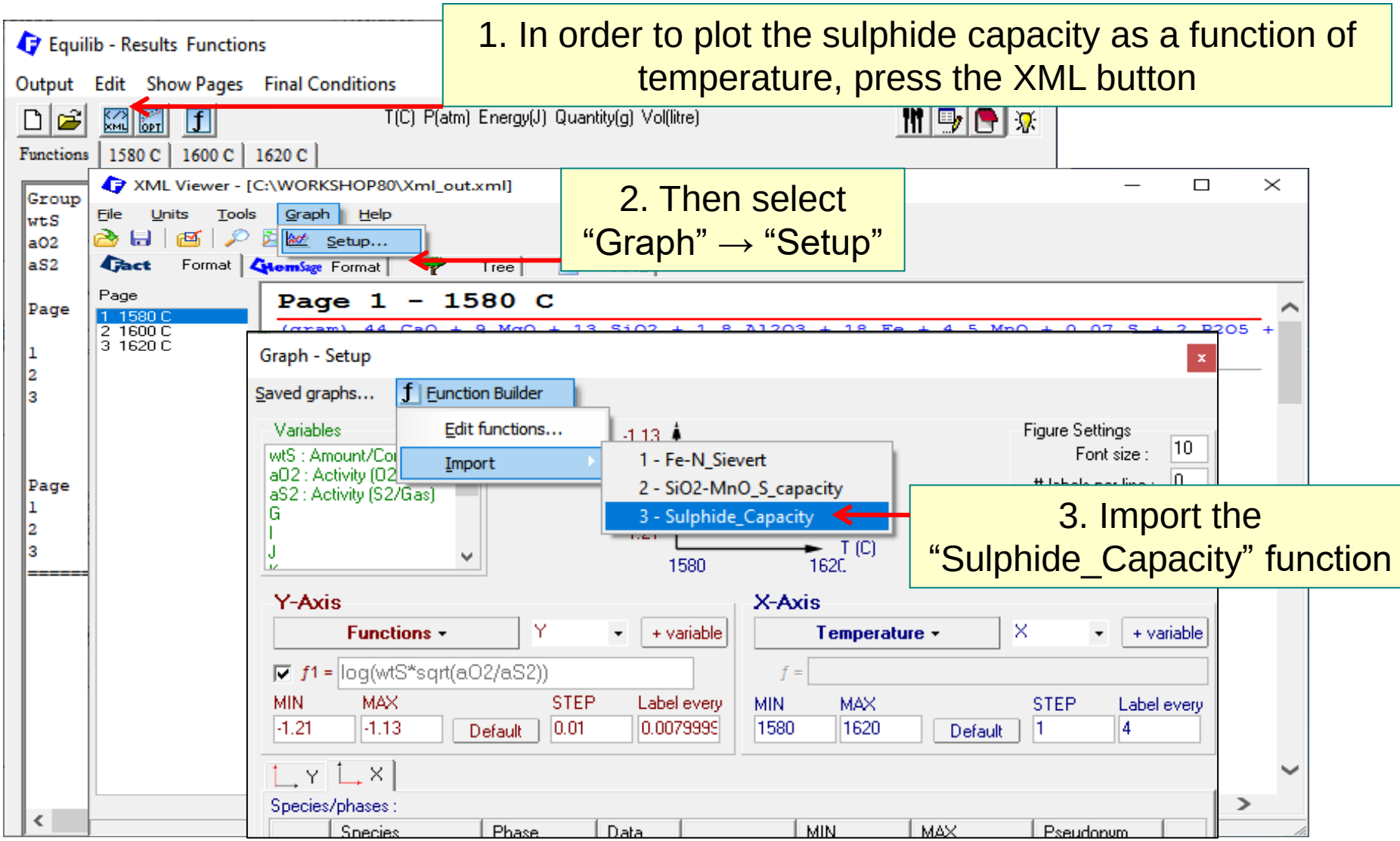
Calculating Slag Sulphide Capacity

1. A separate "Functions" tab will appear with the results of the calculations

2. Each tab will have the information on the function along with the calculated equilibrium.



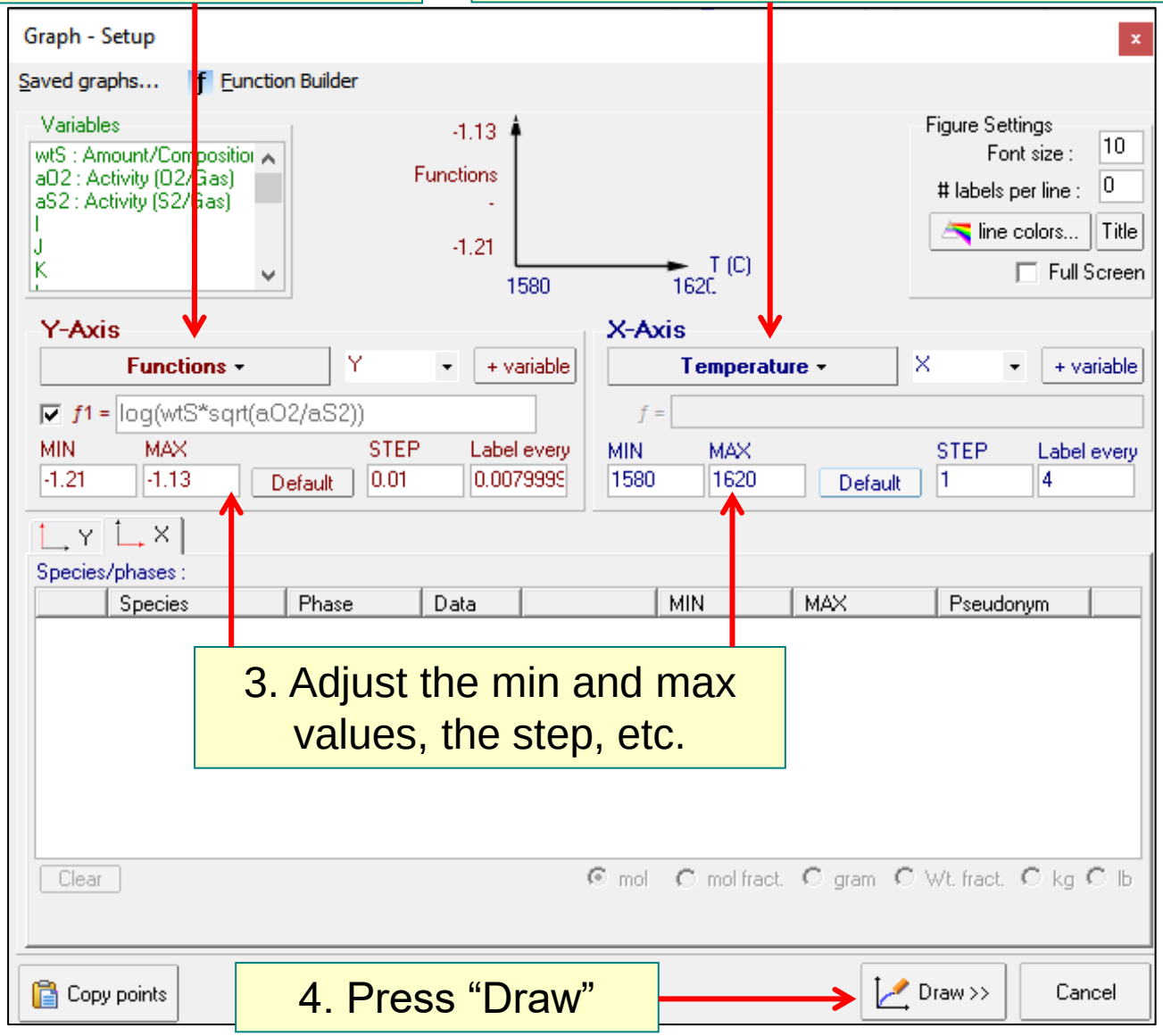
Calculating Slag Sulphide Capacity



Calculating Slag Sulphide Capacity

1. Select “Functions” as the Y-Axis

2. Select “Temperature” as the X-axis

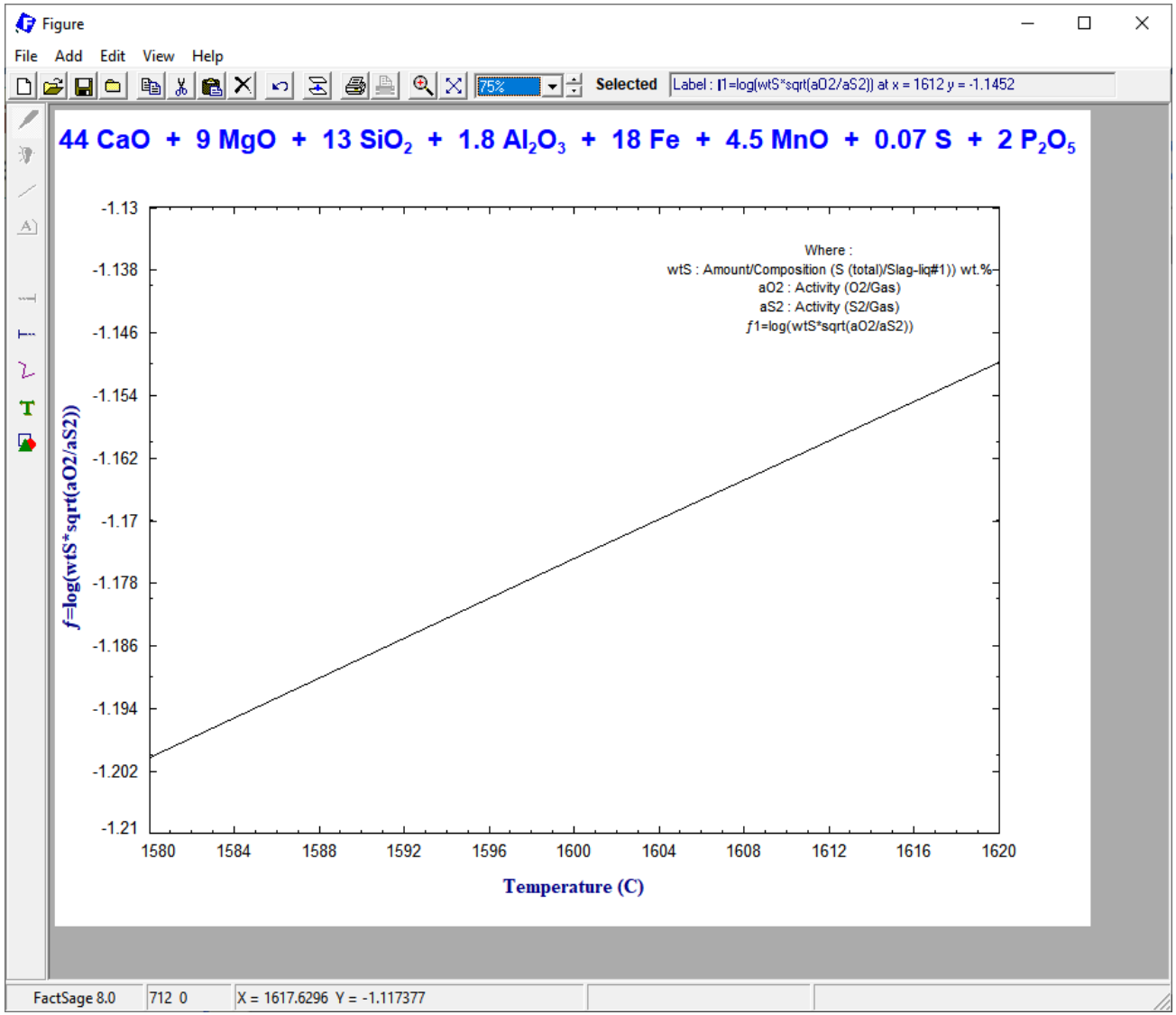


3. Adjust the min and max values, the step, etc.

4. Press “Draw”

Calculating Slag Sulphide Capacity

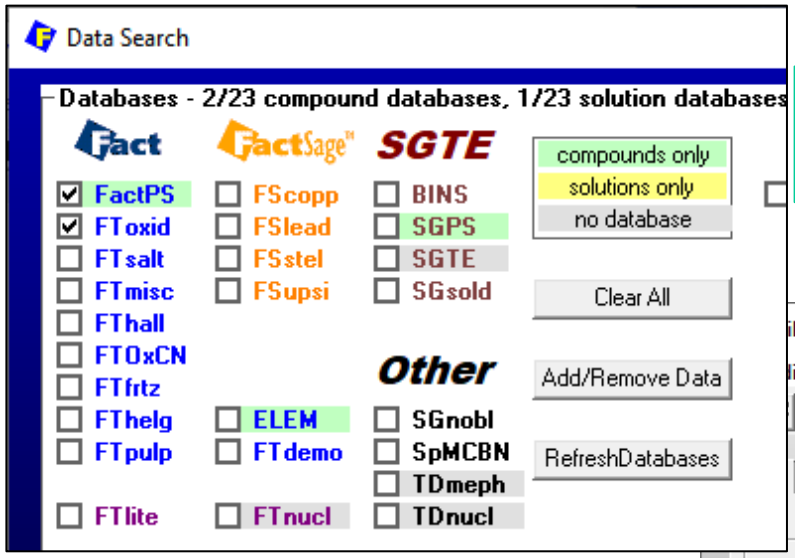
The figure is then obtained



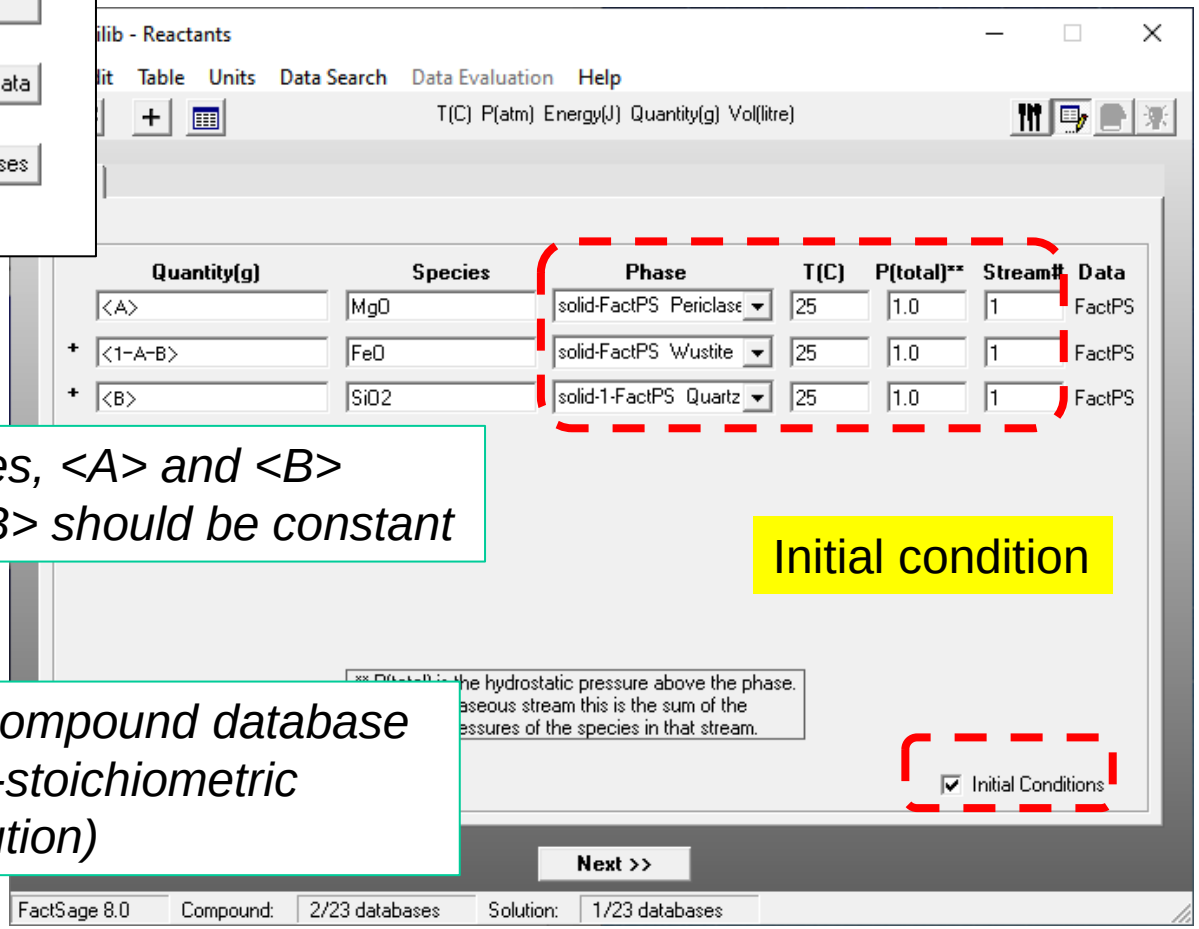
Slag cooling and heating (Enthalpy diagram)

- When slag forms from pure oxides, a certain amount of heat (enthalpy) is needed.
- When slag is cooled down, a certain amount of heat should be extracted.
- FactSage Phase diagram: Enthalpy diagram

Heat required to form and increase temperature of slag



$\Delta H = H_{final} - H_{initial}$
So initial conditions(phase,T,P) should be defined

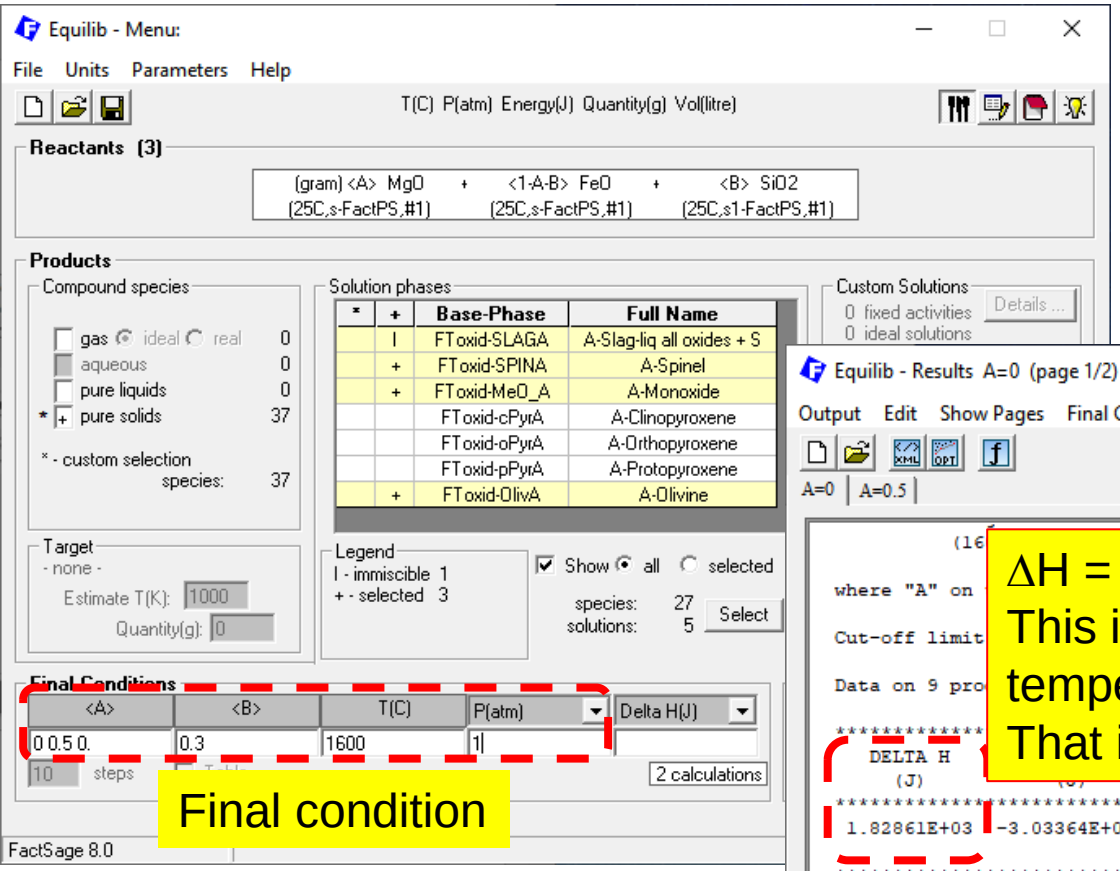


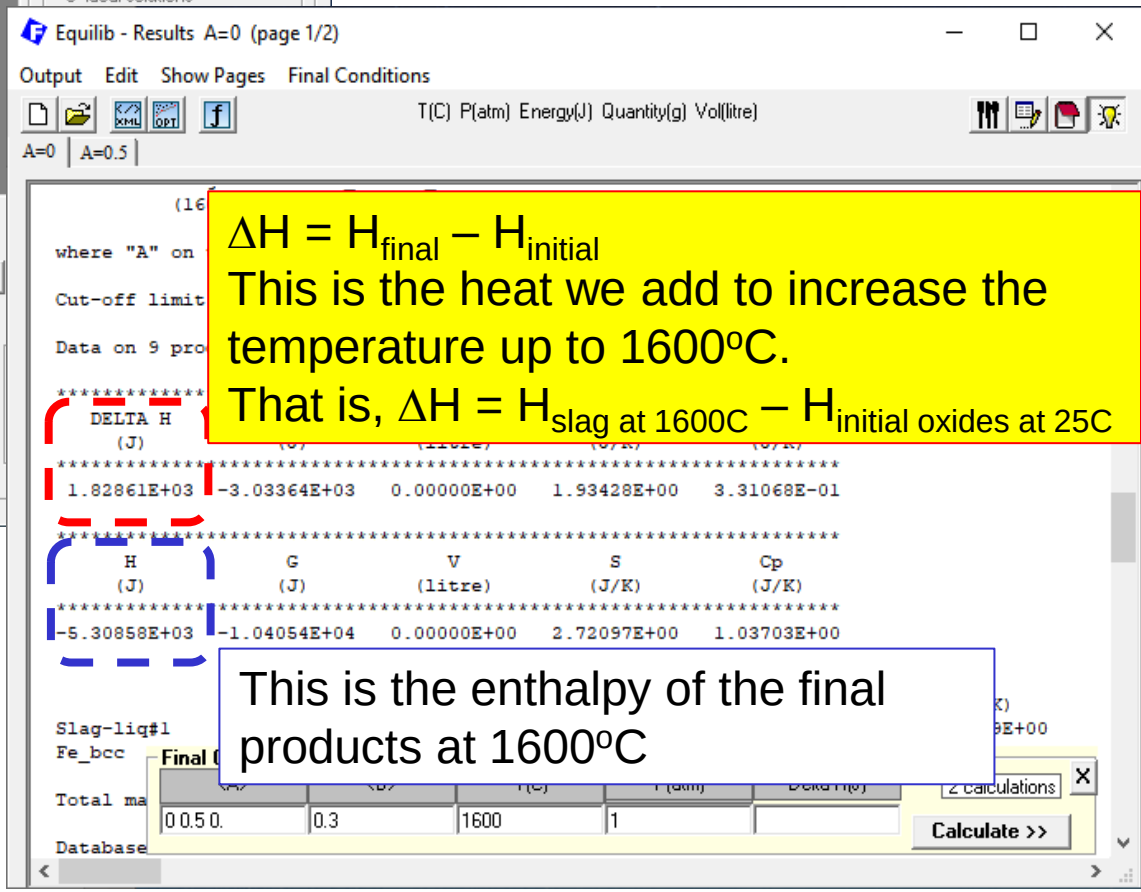
FactSage can used two variables, <A> and <B>
<A> can be really varied and <B> should be constant

Initial condition

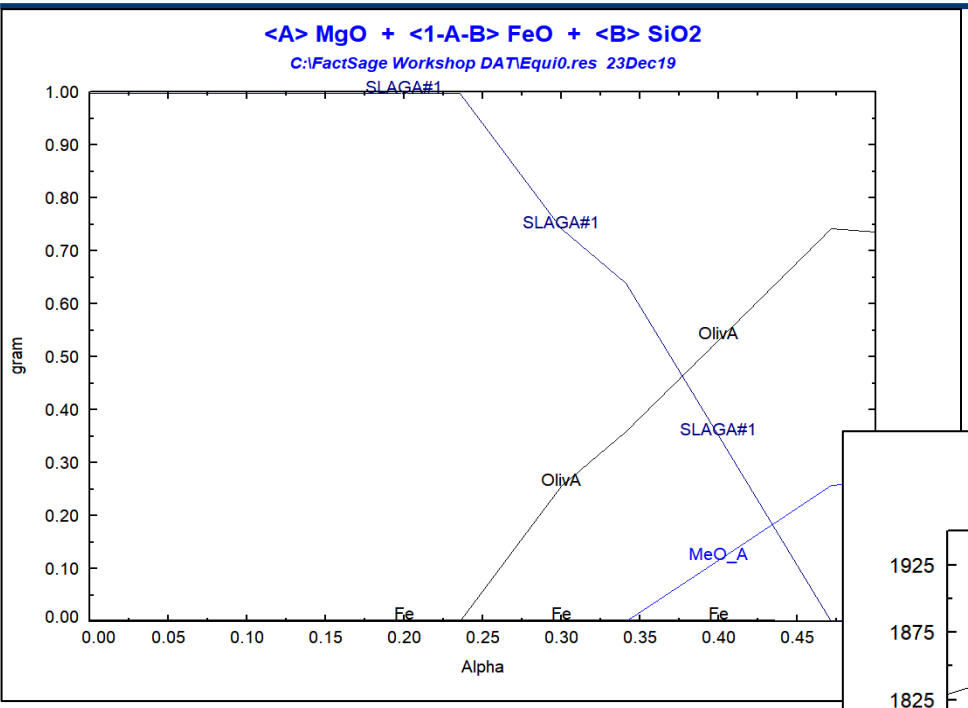
Pure FeO(s) is not in FToxid compound database (Strictly speaking, FeO is non-stoichiometric compound so it is in MeO solution)

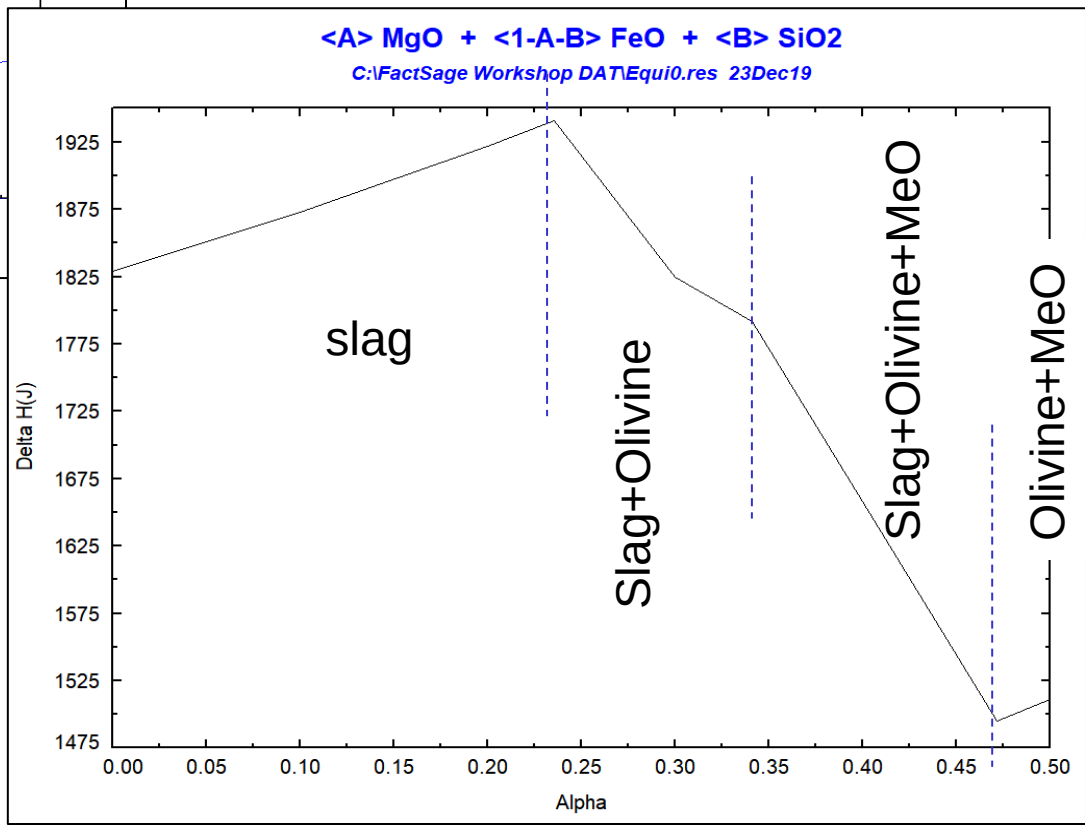
Heat required to form slag and increase the temperature of slag



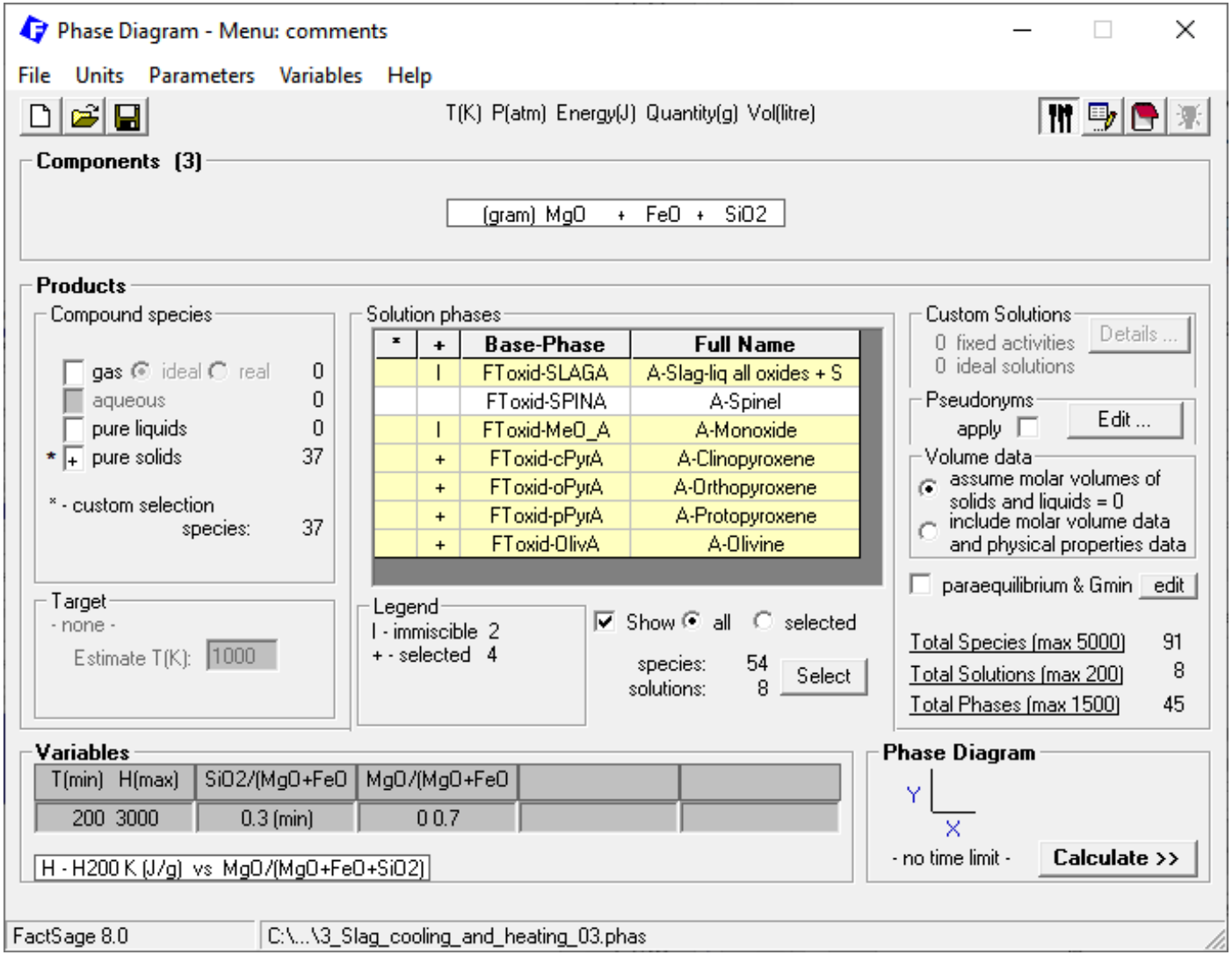


Heat required to form slag and increase the temperature of slag

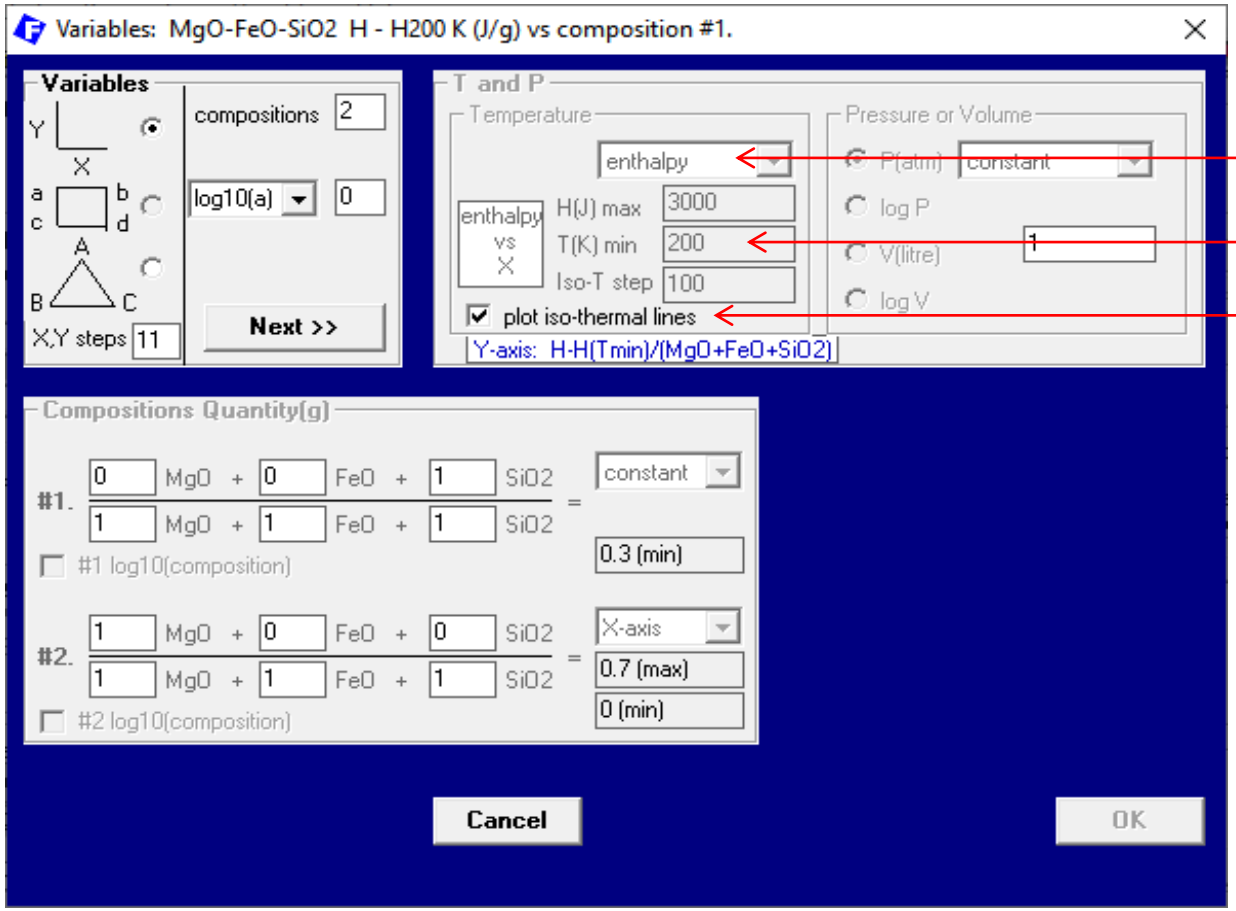




Enthalpy diagram: phase change with ΔH



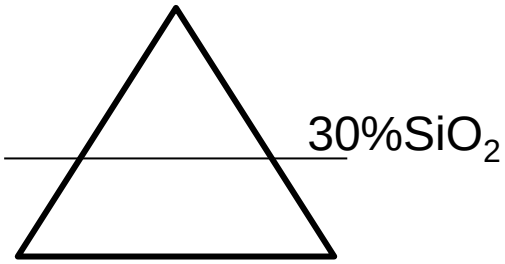
Enthalpy diagram: phase change with ΔH



Enthalpy diagram option

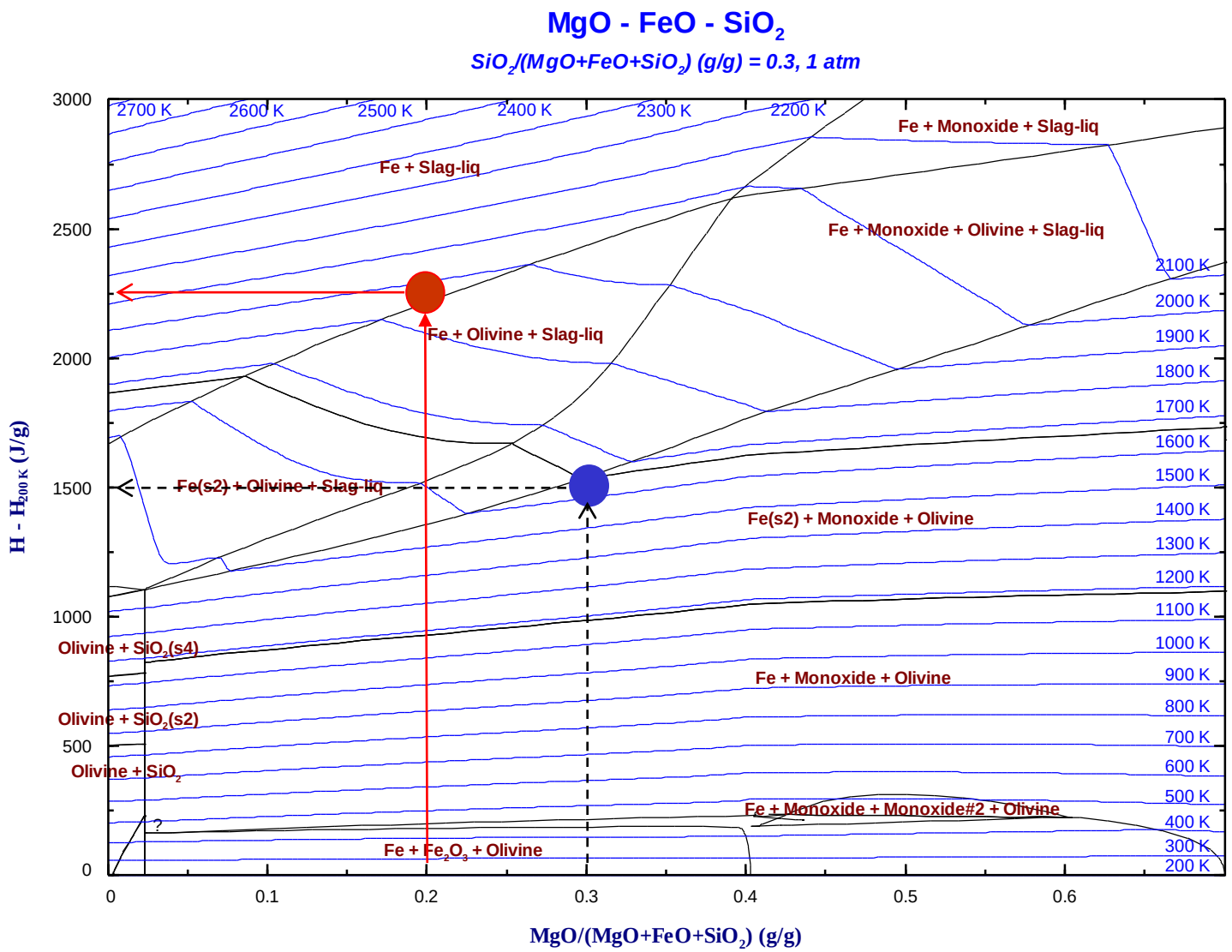
$T_{initial}$

Iso-Temperature



- Only X-Y type diagram allowed.
- Y axis should be Enthalpy ($H-H_{Tmin}$).
- $H_{initial}$ (H_{Tmin}) is the enthalpy of products stable at T_{min}. *For example, Fe_2SiO_4 (fayalite_olivine) and SiO_2 are stable at 0% MgO and 30% SiO_2 instead of FeO and SiO_2.*

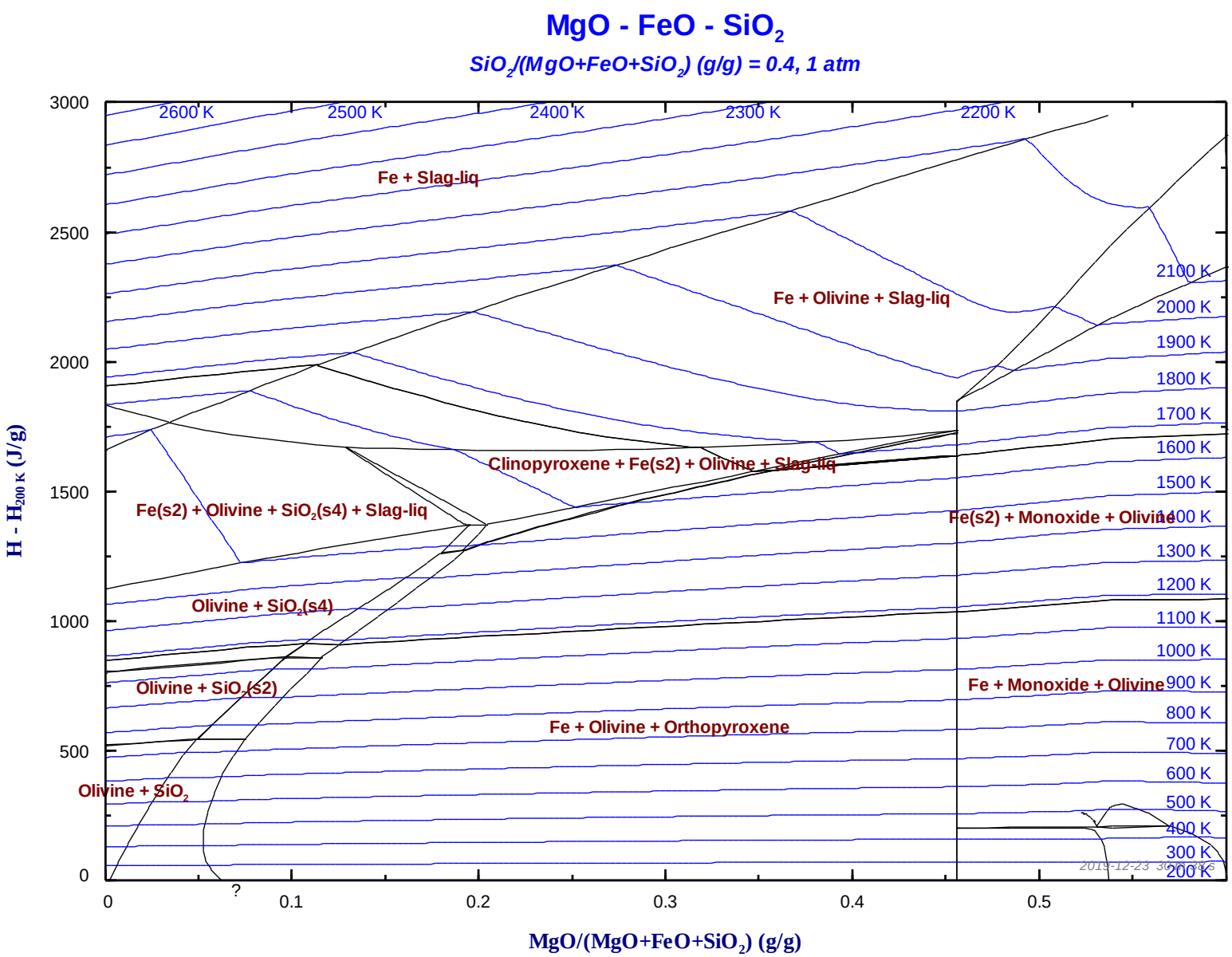
Enthalpy diagram: phase change with ΔH



If we heat the mixture of (Monoxide + olivine) at 30 wt % MgO and 30 wt % SiO2 from 25 °C by 1500 J/g, the mixture becomes mixture of (liquid slag + olivine) at about 1425 °C.

If we increase the temperature of the mixture of (Monoxide + olivine) at 20 wt % MgO and 30 wt % SiO2 from 25 °C to 1625 °C, liquid slag is forming and the amount of heat required for this is about 2250 J/g.

Enthalpy diagram: phase change with ΔH



Application: Addition of new compound and solution (user defined) in calculations

MnCr2O4-MnAl2O4 ideal solid solution

- New stainless steel production: high Mn stainless steel 400 grade. High MnO formation in AOD / VOD refining process

- MnCr2O4-MnAl2O4 inclusion formation in Mn and Cr containing steels

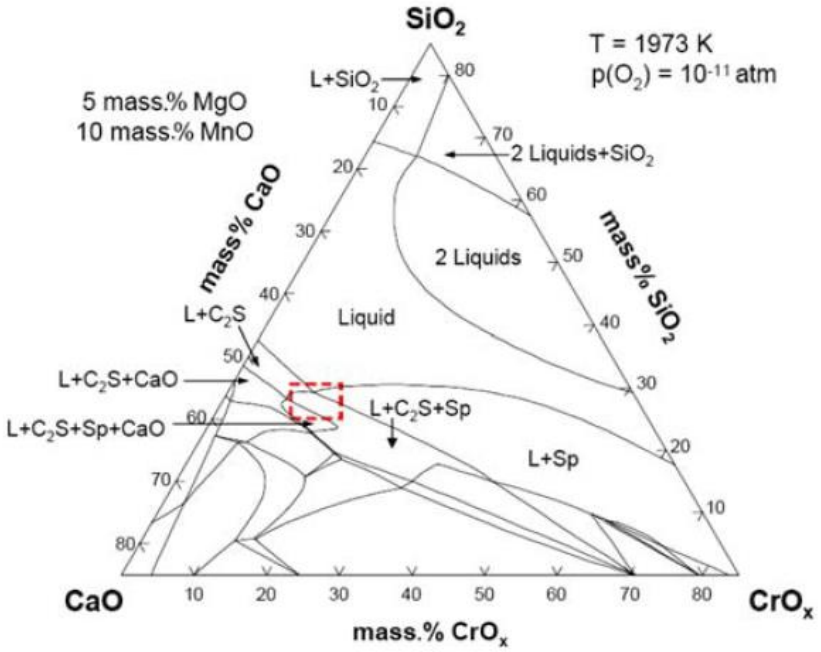
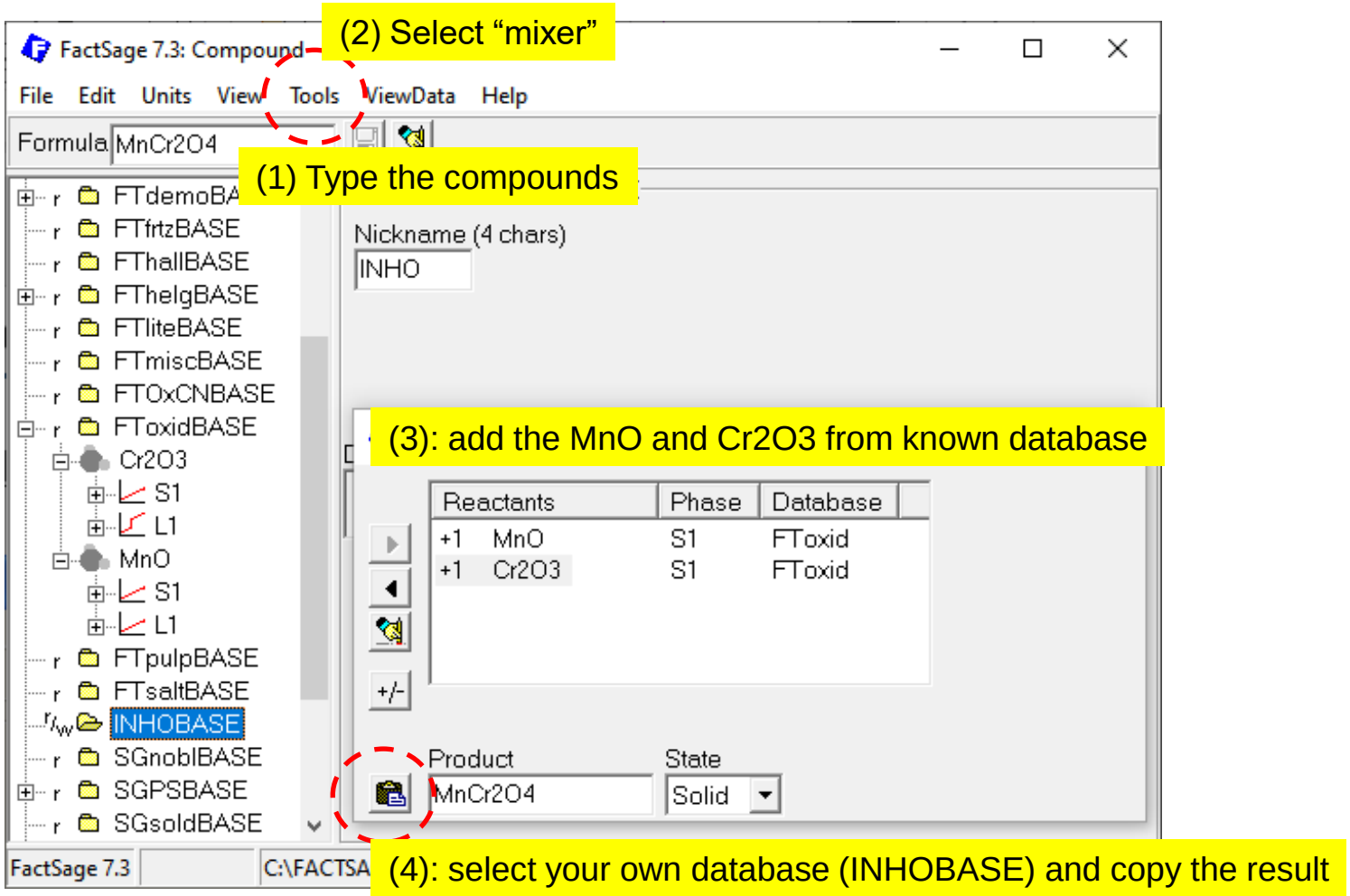


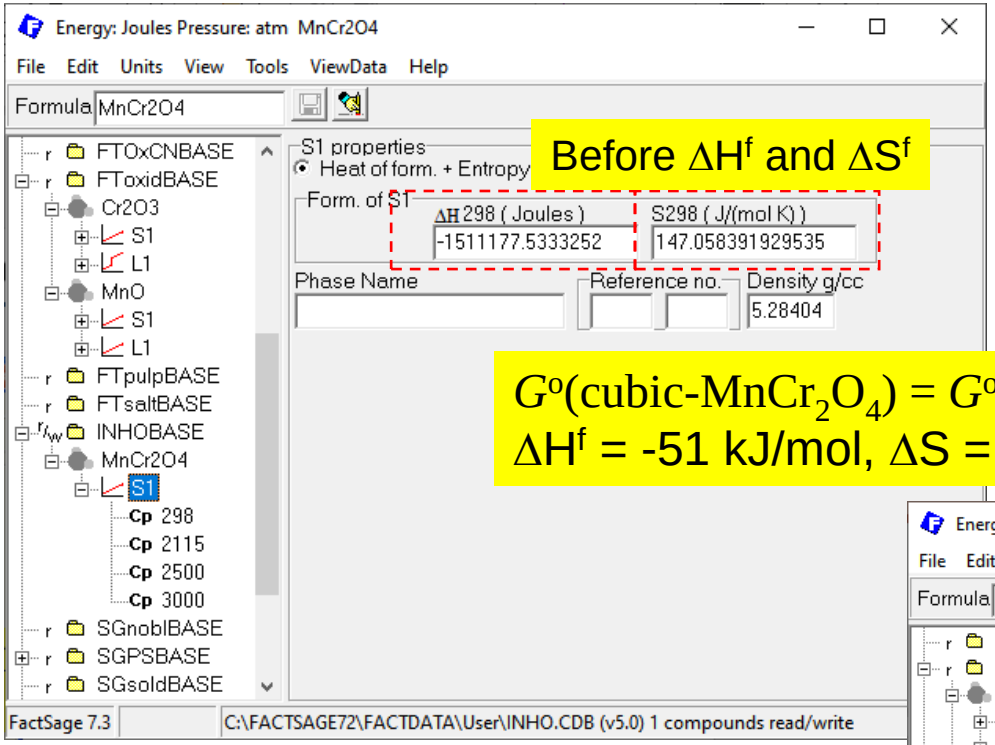
Fig. 1. Computed phase diagram of the CaO-SiO_2-CrO_x-5 mass.%MgO-10 mass.%MnO system at 1973 K under the oxygen partial pressure, $pO_2 = 10^{-11}$ atm.

User Compound Database

Creating user compound database: MnCr2O4 from MnO and Cr2O3



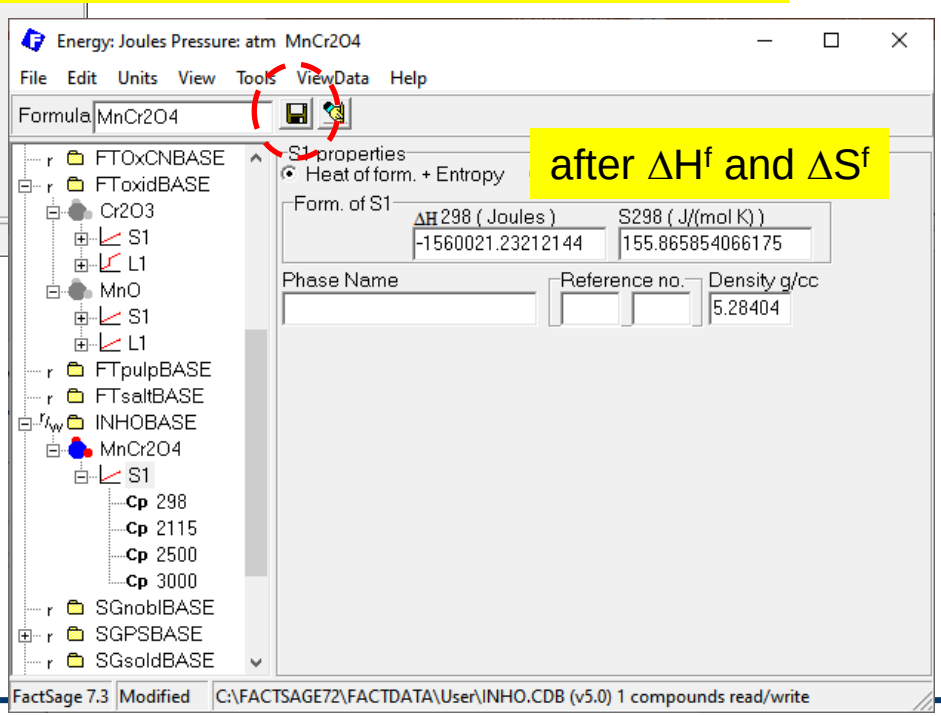
User Compound Database



Before ΔH^f and ΔS^f

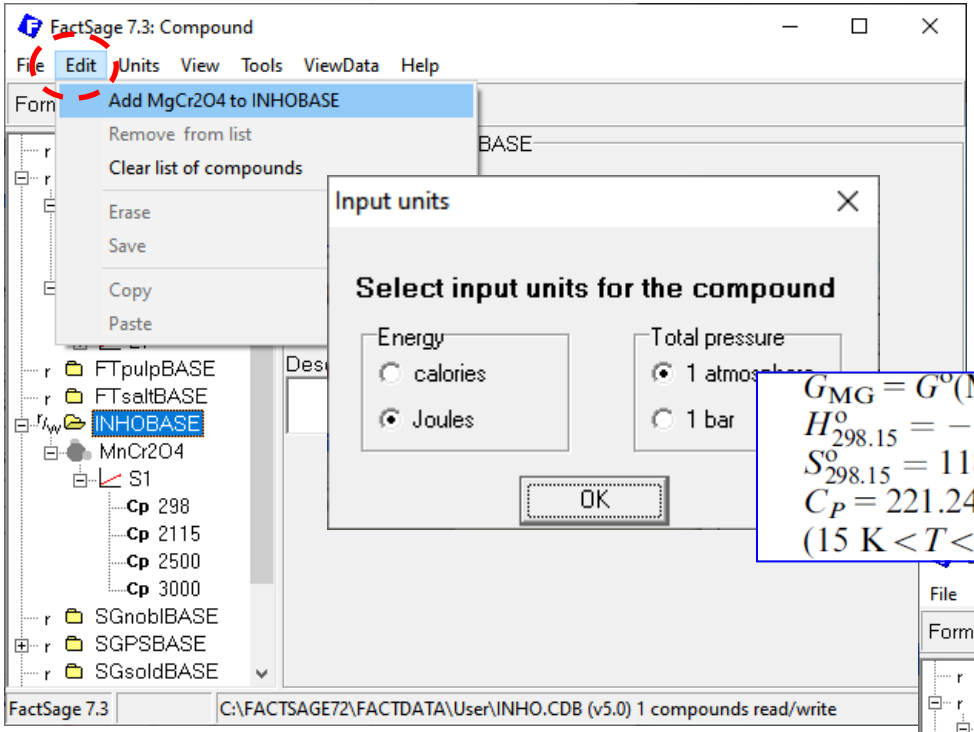
$$G^o(\text{cubic-}MnCr_2O_4) = G^o(MnO) + G^o(Cr_2O_3) + \Delta H^f - T\Delta S^f$$

ΔH^f = -51 kJ/mol, ΔS = 0 J/mol-K



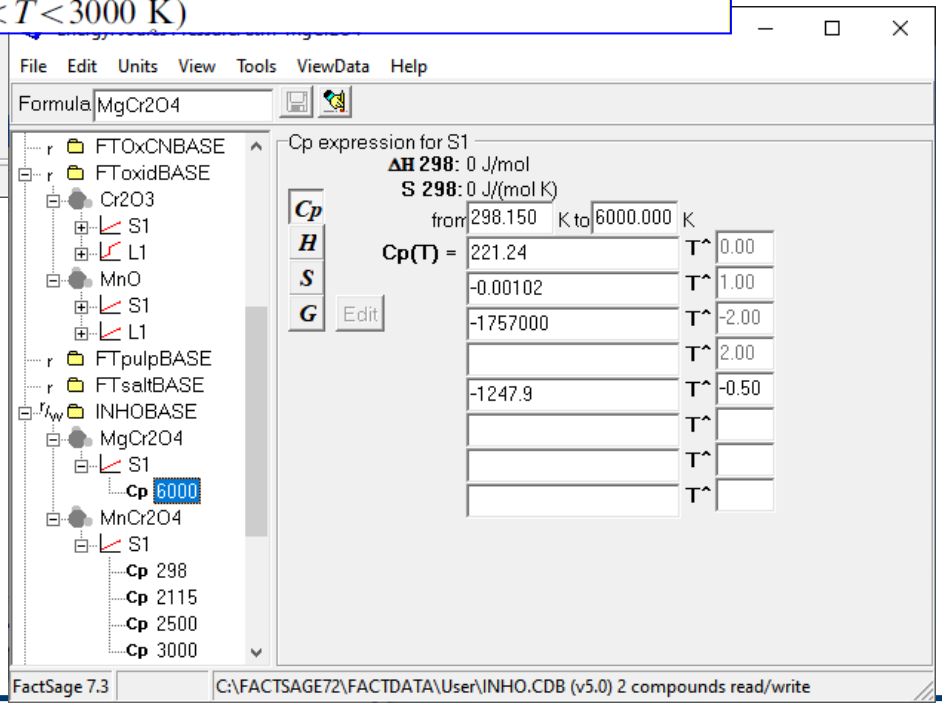
after ΔH^f and ΔS^f

User Compound Database



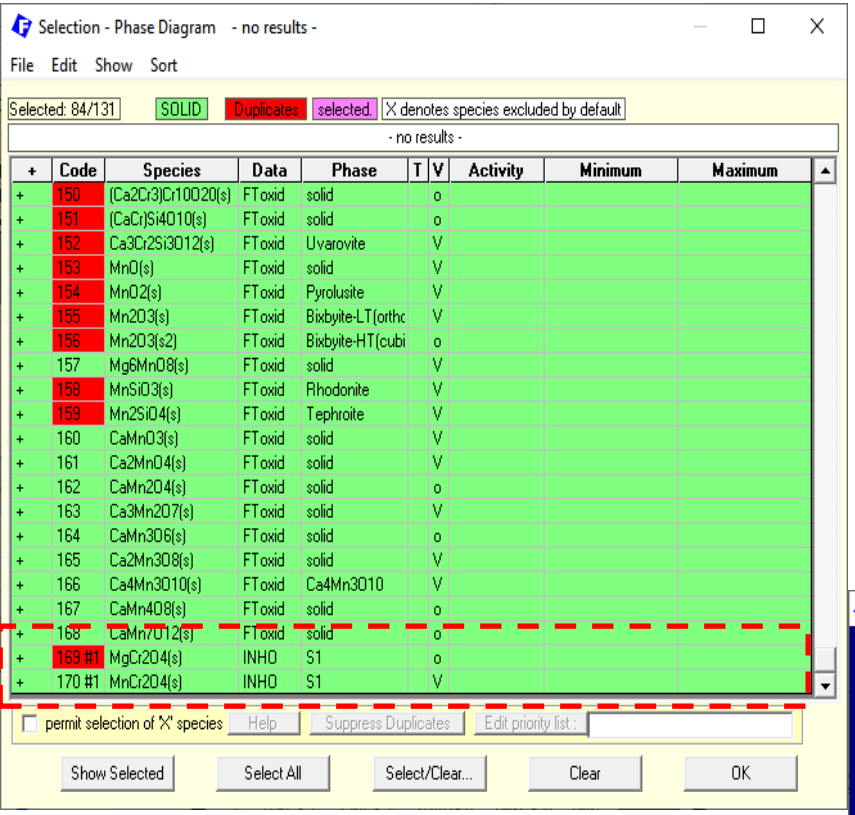
Creating user compound database: $MgCr_2O_4$ from H_{298}, S_{298} and Cp

$G_{MG} = G^o(MgCr_2O_4)^+$:
$H^o_{298.15} = -1769907.76$
$S^o_{298.15} = 118.300$
$C_P = 221.24 - 0.001020T - 1.757(10^6)T^{-2} - 1247.9T^{-0.5}$
$(15\ K < T < 3000\ K)$



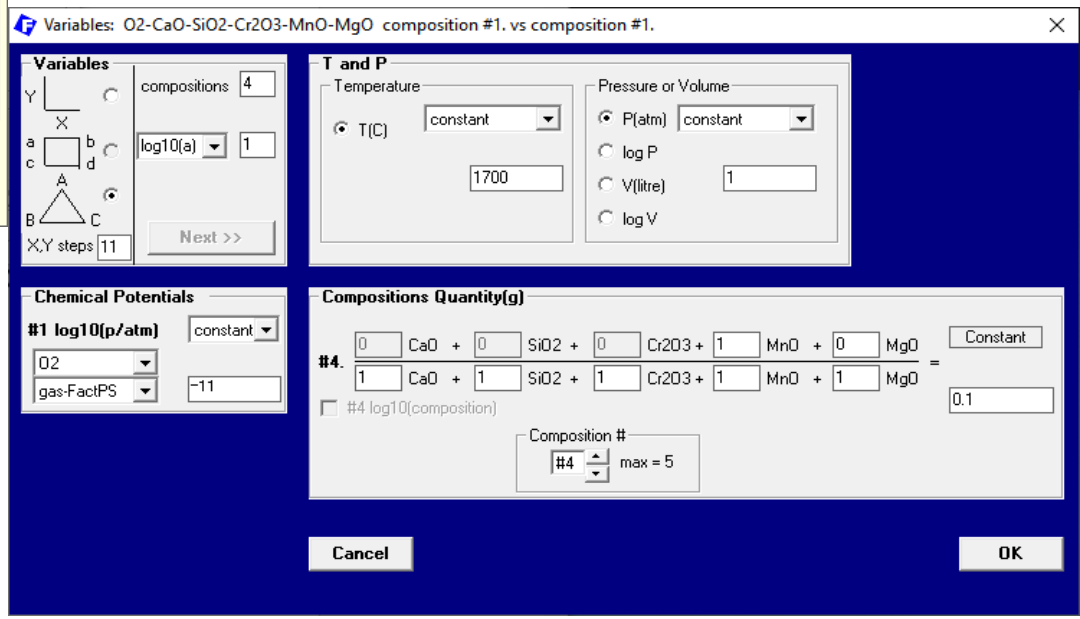
Add ΔH298, S298 and Cp, respectively →

Ideal Solution between compounds



MnCr2O4-MgCr2O4 ideal sol'n: (Mg,Mn)Cr2O4

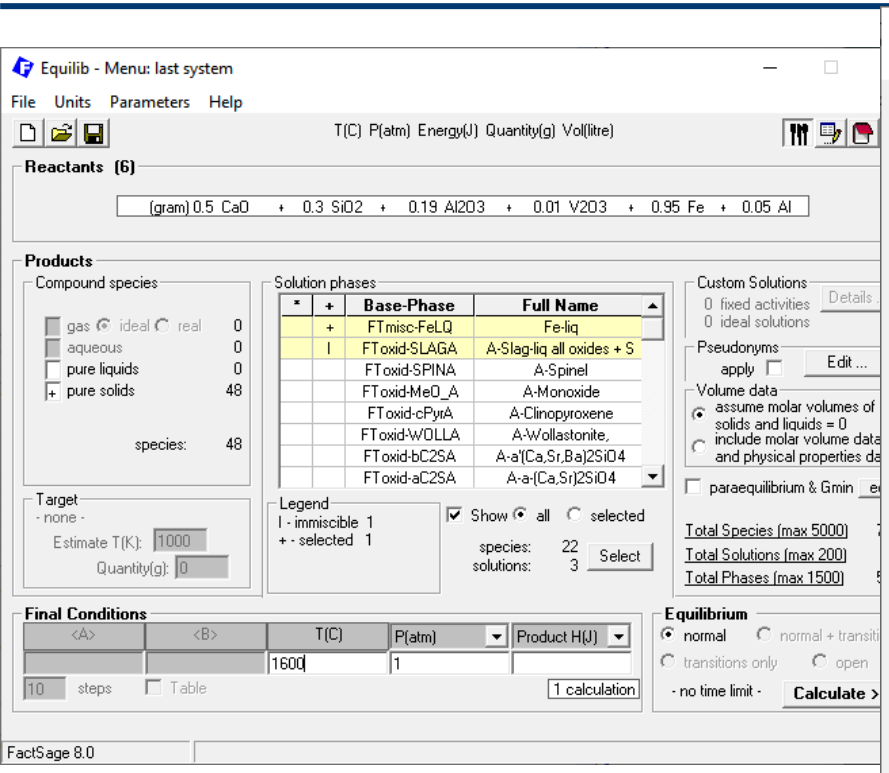
→ Both MnCr2O4 and MgCr2O4 are selected as ideal solution #1 with 0 activity coefficients

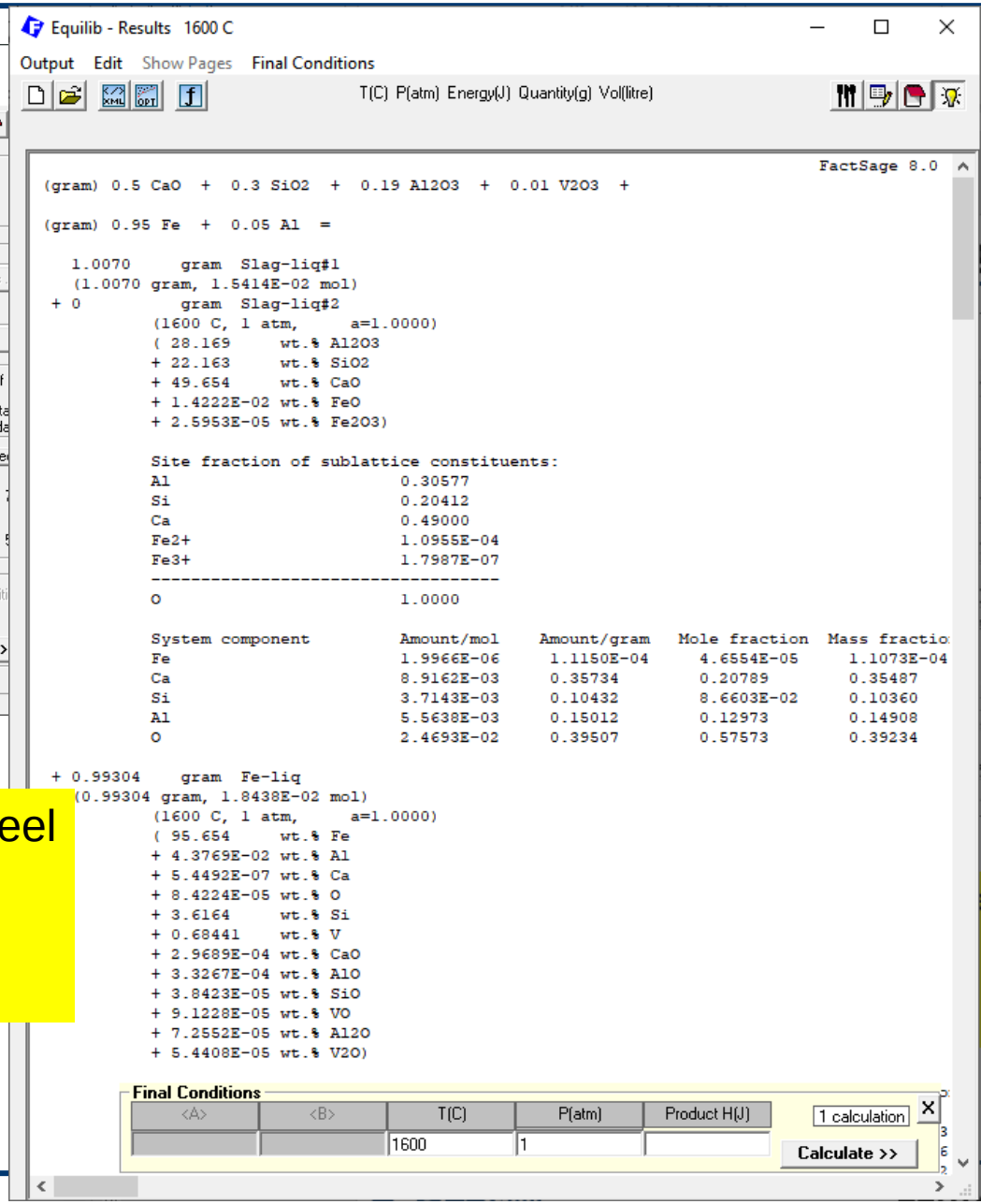


Application: Addition of new component in slag

V2O3 into molten slag for V distribution calculations
(Henrian Solution)

New component in slag: Henrian activity coefficient

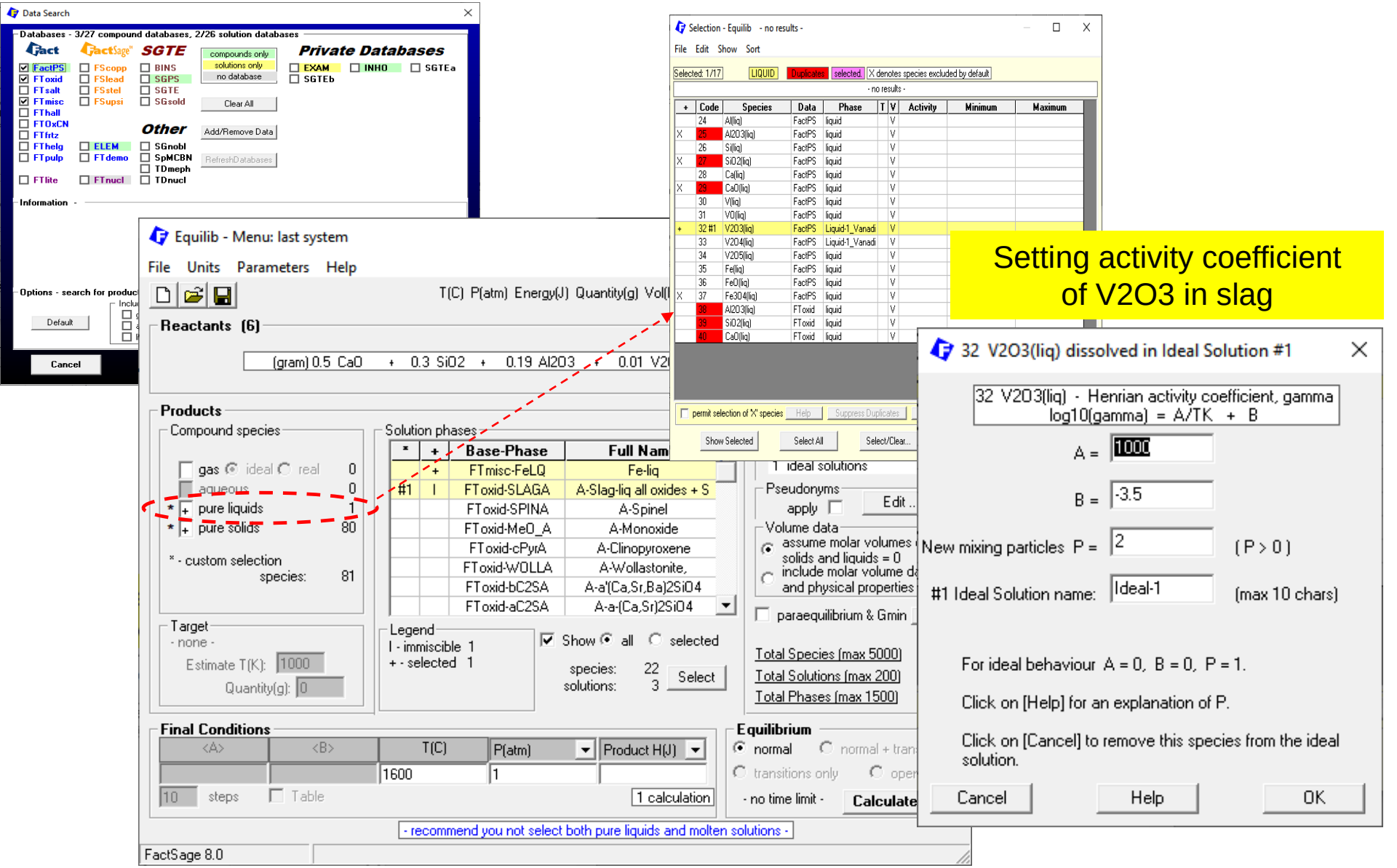




V2O3 containing slag // Liquid Fe-Al steel

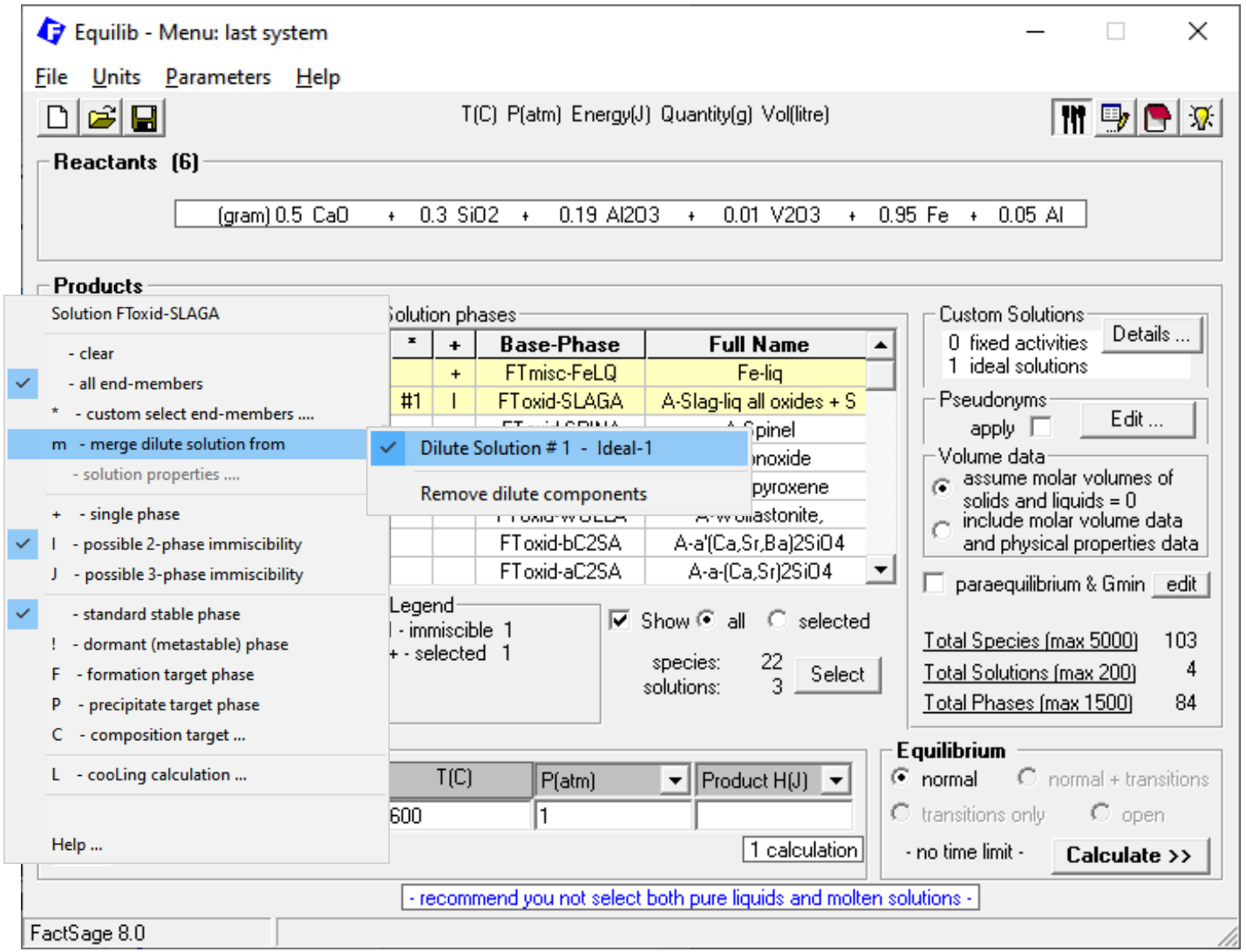
→ All V go to liquid Fe ??
(because no V oxide in slag yet)

New component in slag: Henrian activity coefficient

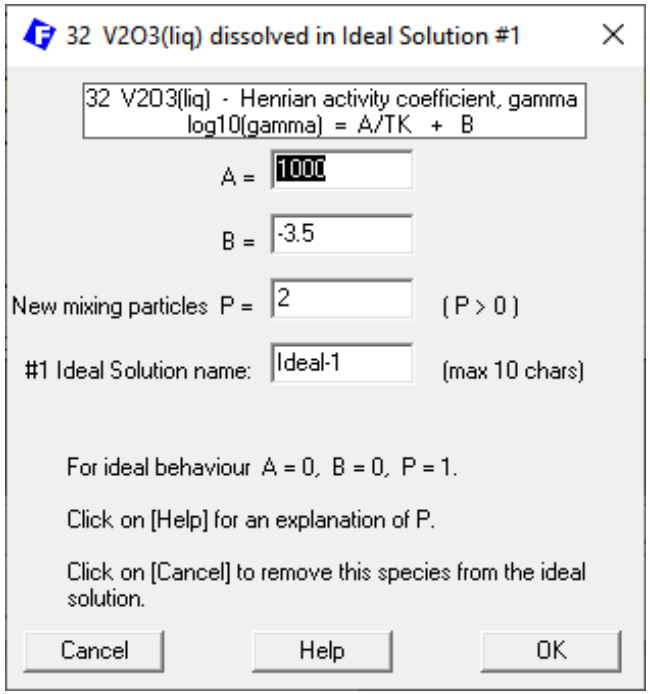


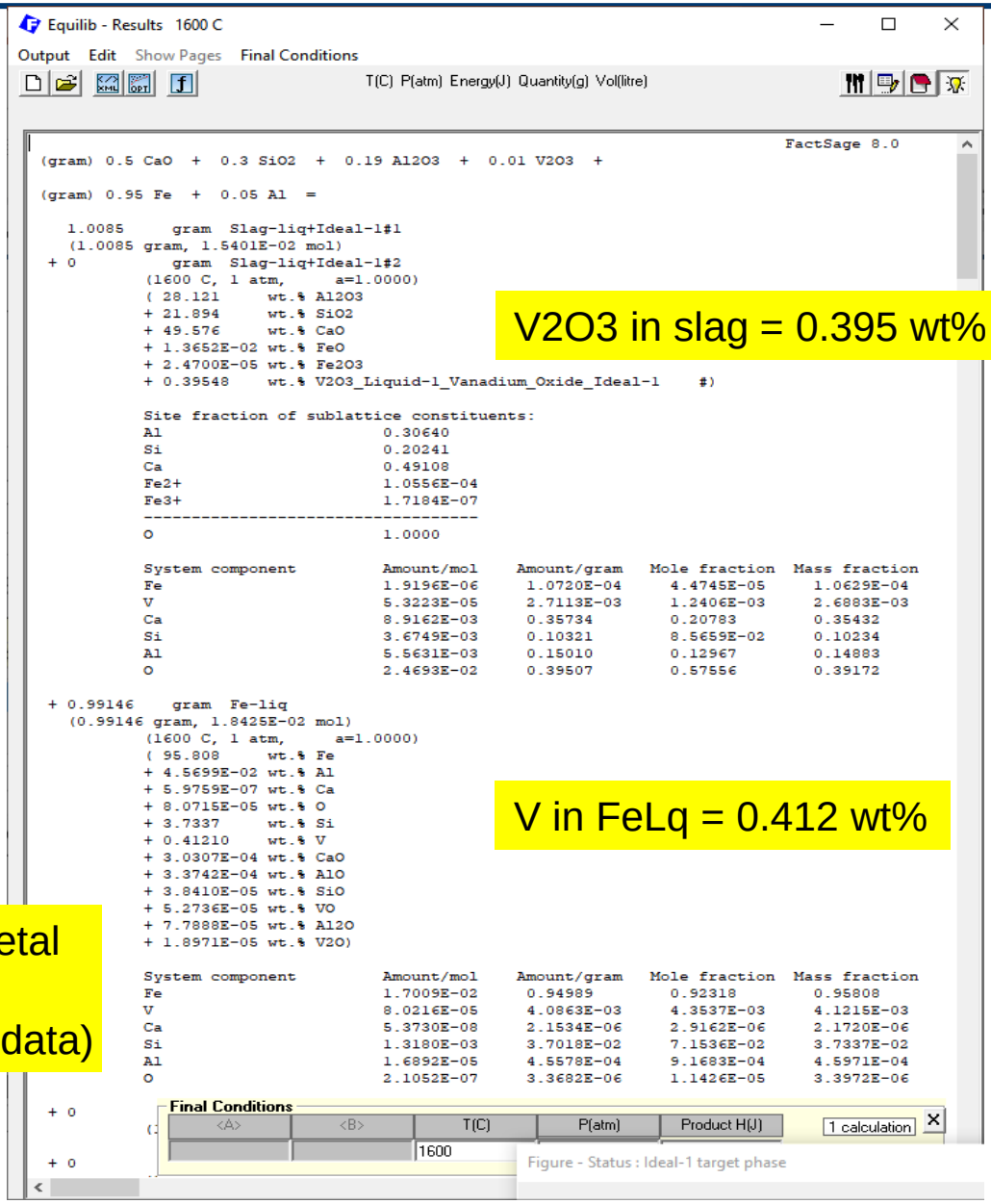
Setting activity coefficient of V2O3 in slag

New component in slag: Henrian activity coefficient



New component in slag: Henrian activity coefficient





V2O3 in slag = 0.395 wt%

V in FeLq = 0.412 wt%

The distribution of V between slag and metal can be varied depending on the activity coefficient. (evaluated from experimental data)

Vanadium Partition Coefficient In Steel/Slag Melts based on literature data (BOF condition)

FINAL REPORT for MIME572

By Jonathan Spring

Undergraduate student
McGill University

More details can be found in:
http://in-ho-group.snu.ac.kr/?page_id=398

Background

- Partition coefficients used to purify/quantity solute concentration in steel/slag
- Partition coefficient, L_v, = (wt% V) / [wt% V]
- No known expression to predict vanadium distribution coefficient

Henry's Law

- We are dealing with dilute solutions
  - (V_2O_3) ~ 3 wt%
- $2\,\underline{V} + 3\,\underline{O} = V_2O_3$
- $K_{eq} = A_{V2O3} / (A_{\underline{V}}^2 * A_{\underline{O}}^3)$
- Activity = $\gamma_{V2O3} x_{V2O3}$
- $\log_{10}(\gamma_{V2O3}) = A/T + B$

V distribution coefficient between steel and slag

Literature Search

- Found ~ 20 articles with data on vanadium partition coefficients in slag/steel melts
- 3 of those contained tables of raw data with slag compositions (Zhang, Shin and Inoue) and 2 were performed at similar temperatures (Shin and Inoue). These 2 were used initially.
- Shin's article dealt with slag containing Al2O3. His experiments were performed without proper control of the oxygen partial pressure and the partition coefficients for V he found were drastically different than in Inoue's article. His results are therefore unreliable. Furthermore, the initial V partition coefficient model had trouble fitting Shin's data. It was decided after my presentation to redo the model using only Inoue's data.
- Total data points: 63

V distribution coefficient between steel and slag

- 1550 °C: 15 data points
- 1600 °C: 28 data points
- 1650 °C: 18 data points
- Slag
  - x SiO_2
  - x CaO
  - x FeO
  - x Fe_2O_3
  - x MgO
- L_v for each data point

V distribution coefficient between steel and slag

Data from Inoue's Article

	Slag (wt%)						
T (C)	(CaO)	(SiO2)	(FeO)	(Fe2O3)	(MgO)	(V)	Lv
1650	27	28	21	2	19	1	410.1
1650	19	22	36	4	16	1	751.4
1650	29	15	36	6	10	1	1087.6
1650	8	13	52	4	22	1	850.6
1650	25	7	47	11	8	2	1510.0
1650	17	3	58	12	7	2	1439.3
1650	1	4	71	6	16	1	1142.9
1650	1	15	50	3	29	1	705.9
1650	19	28	29	2	20	1	522.1
1650	28	22	30	4	13	1	761.7
1650	37	14	31	8	8	2	1174.2
1650	21	13	46	6	11	2	937.9
1650	31	7	40	13	7	2	1495.1
1650	0	1	82	6	8	2	1006.2
1650	1	7	71	5	14	1	900.7

The amount of V in the slag was not considered. The same fixed amount of V was used for all equilibrium calculations and the subsequent calculation of Lv.

Ref: R. Inoue and H. Suito, Trans. ISIJ, vol. 22, p 705 (1982).

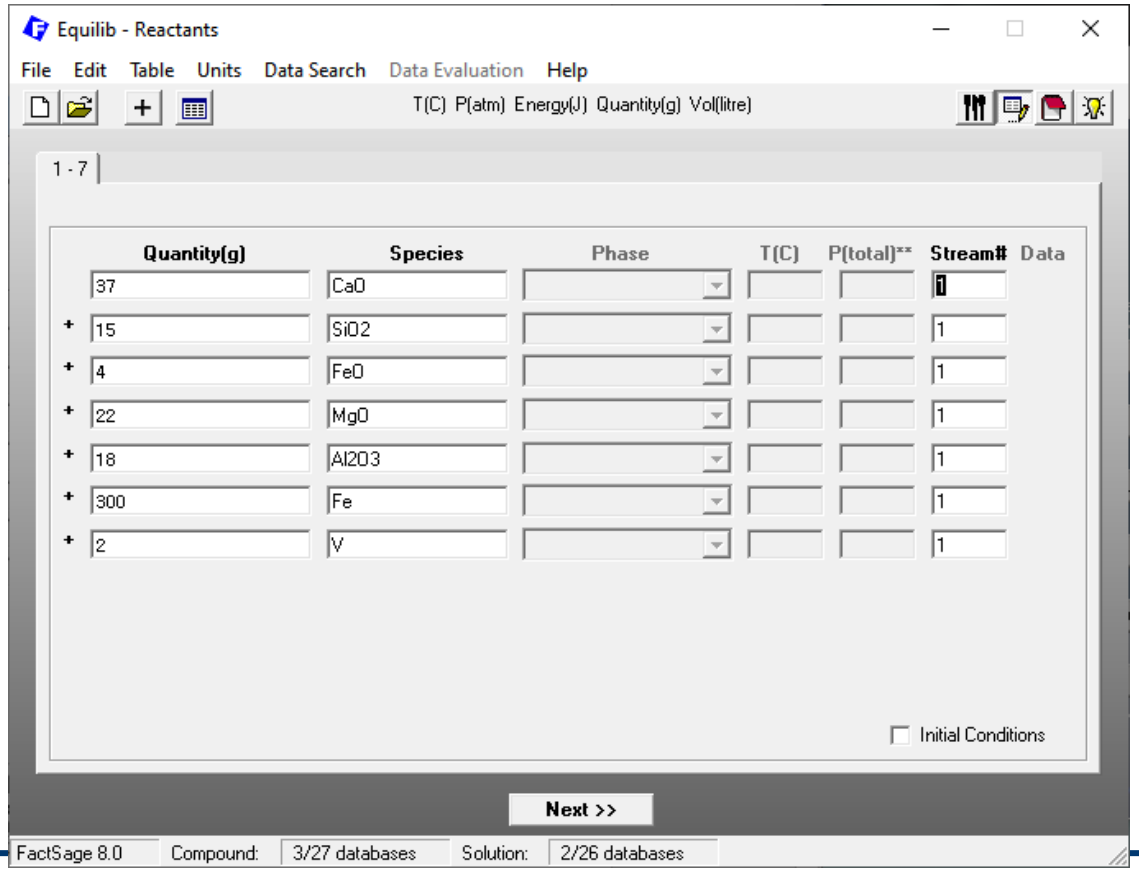
V distribution coefficient between steel and slag

- Databases: FToxid, Ftmisc (FeLQ), FactPS
- Equilibrium

100 g
- x SiO_2
- x CaO
- x FeO
- x Fe_2O_3
- x MgO

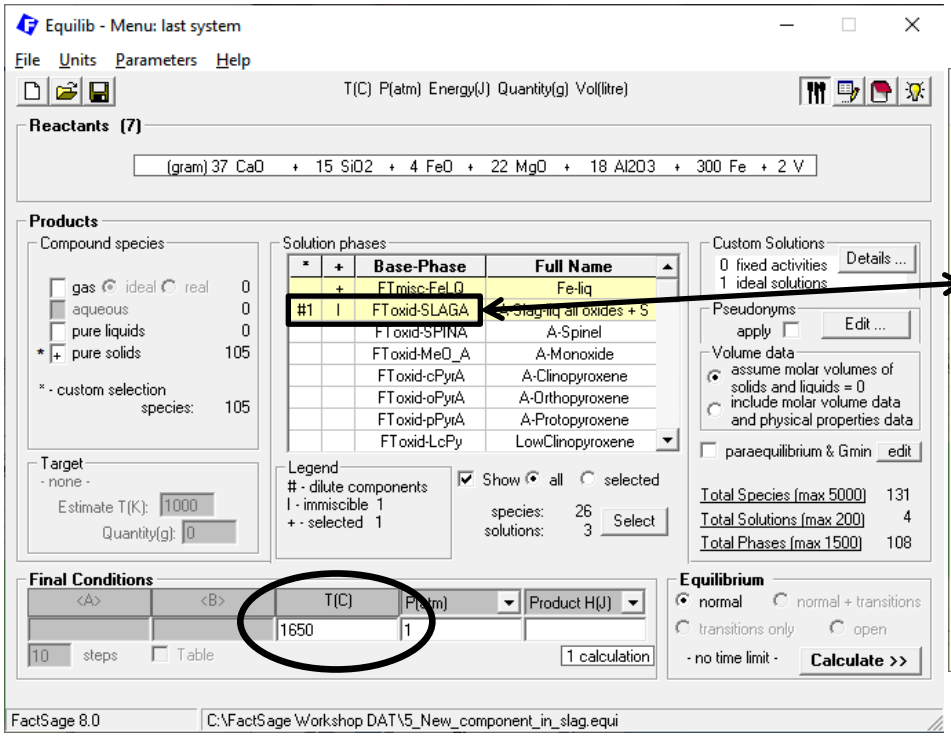
- 300 g Fe
- 2 g V

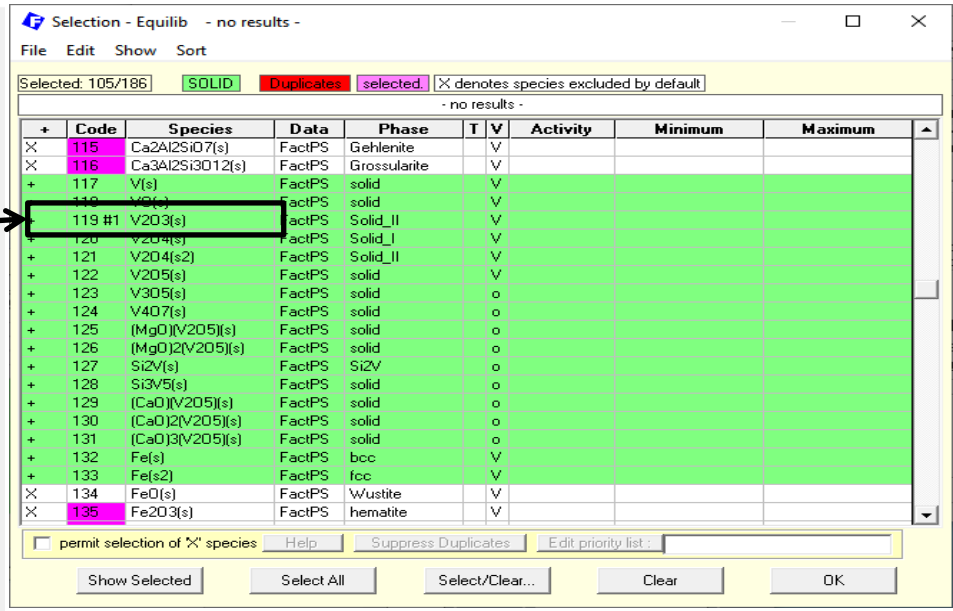
3:1 metal to slag ratio



V distribution coefficient between steel and slag

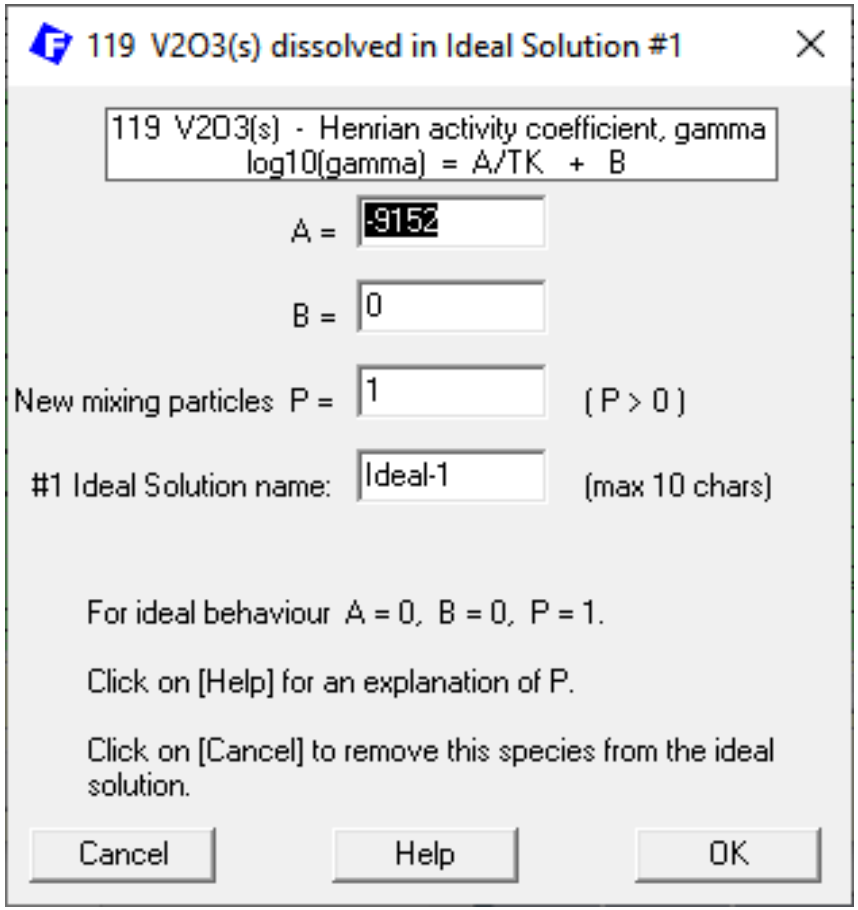
- Assume V in slag exists as V_2O_3

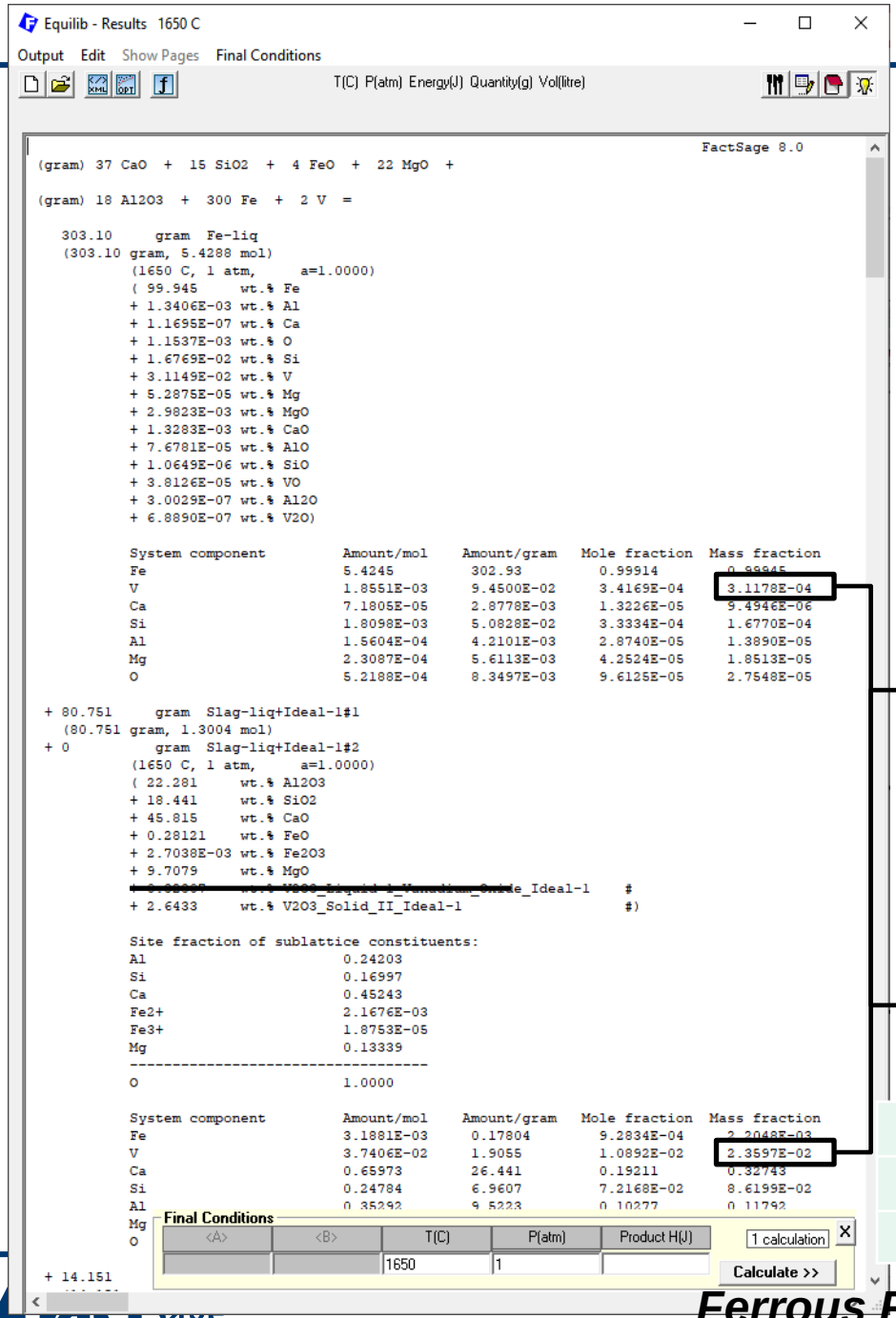




Solid V2O3 was considered because solid V2O3 is stable at these temperatures.

- Change “A” value, “B” assumed to be 0





- Calculate equilibrium
- Calculate L_v
- Compare to measured L_v
- Go back and try new "A" value
- Trial and error
- More negative "A" value creates a smaller Lv

$$L_v = \frac{(\text{Wt\% V})}{[\text{Wt\% V}]} = 75.68$$

	Slag (wt%)					
T (C)	(CaO)	(SiO2)	(Fe2O3)	(MgO)	(FeO)	Lv
1650	37	15	18	22	4	12.6

V distribution coefficient between steel and slag

"A" Value to Activity Coefficient

	Slag (wt%)								
T (C)	(CaO)	(SiO2)	(FeO)	(Fe2O3)	(MgO)	(V)	Lv	A	Ɣ
1650	27	28	21	2	19	1	410.1	-1025	0.29
1650	19	22	36	4	16	1	751.4	-1200	0.24
1650	29	15	36	6	10	1	1087.6	-2175	0.07
1650	8	13	52	4	22	1	850.6	-1100	0.27
1650	25	7	47	11	8	2	1510.0	-2750	0.04
1650	17	3	58	12	7	2	1439.3	-2300	0.06
1650	1	4	71	6	16	1	1142.9	-1300	0.21
1650	1	15	50	3	29	1	705.9	-750	0.41
1650	19	28	29	2	20	1	522.1	-1000	0.30
1650	28	22	30	4	13	1	761.7	-1475	0.17

$\log_{10}(Ɣ_{V2O3}) = A/T + B$

$\log_{10}(Ɣ_{V2O3}) = -1025/1923$

$Ɣ_{V2O3} = 10^{(-1025/1923)}$

$Ɣ_{V2O3} = 0.293$

A more negative "A" value indicates a smaller activity coefficient.

V distribution coefficient between steel and slag

- The regression using slag basicity, $A = aCaO/SiO_2 + bMgO/SiO_2 + c(FeO + Fe_2O_3)$, was discarded because the fit was not as good as for the regression using each slag component.
- The regression using each slag component was poor nonetheless. Another regression, using all slag components and the slag temperature, was introduced.
- Option #1

  $A = aCaO + bSiO_2 + c(FeO + Fe_2O_3) + dMgO$
- Option #2 (Option #1 including temperature)

  $A = aT(K) + bCaO + cSiO_2 + d(FeO + Fe_2O_3) + eMgO$
- Option #3 (Option #2 including Constant)

  $A = aT(K) + bCaO + cSiO_2 + d(FeO + Fe_2O_3) + eMgO +$ Constant

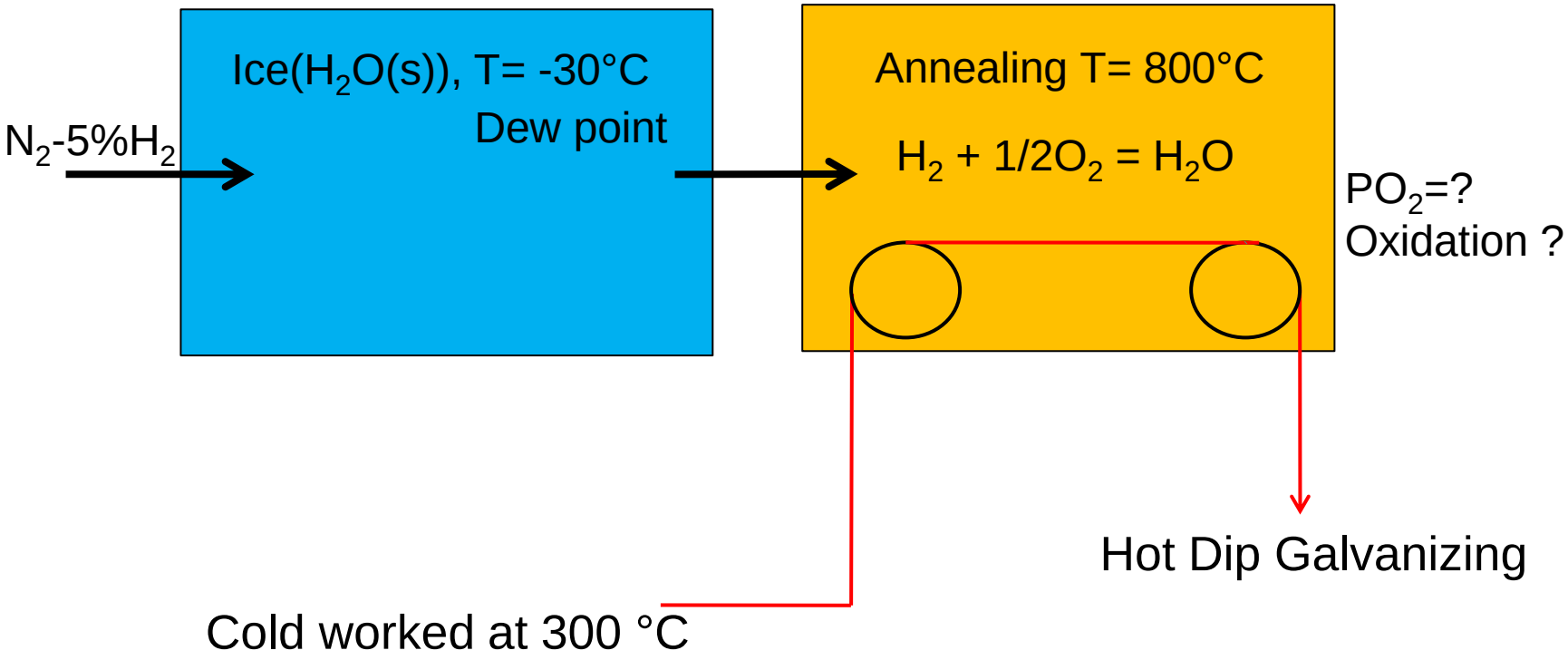
V distribution coefficient between steel and slag

- Regression #3 is best
  - Slope of Measured vs Predicted “A” and Measured vs Predicted Lv is closest to 1
  - Smaller residuals
  - Residuals are randomly distributed
- A = - 7 * Temperature (K) - 51 * wt% CaO + 133 * wt% SiO_2 + 31 * (wt% FeO + wt% Fe_2O_3) - 37 * wt% MgO + 10,100
- Need to test against more data!

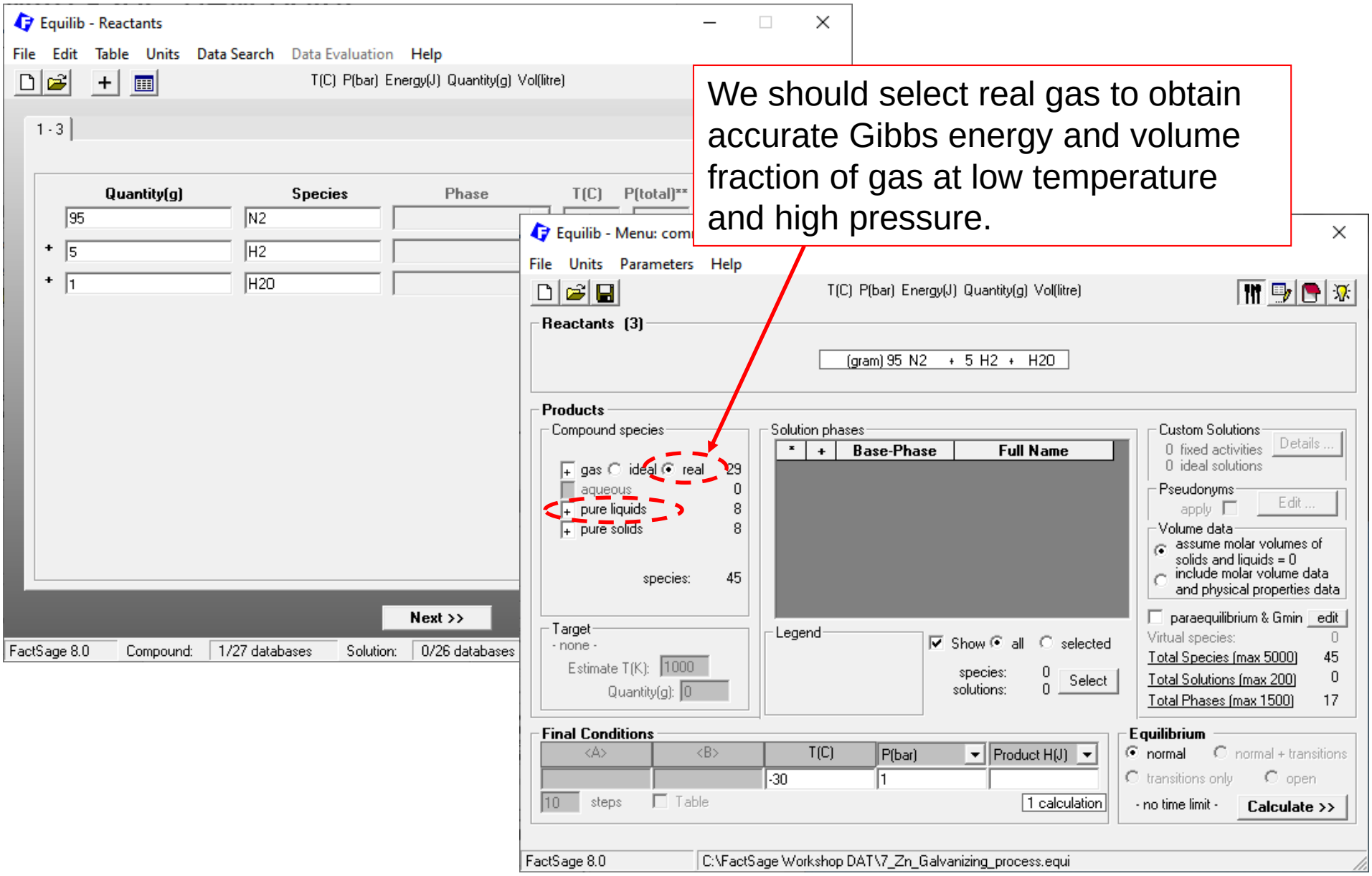
Zn Galvanizing process

Reduction furnace: selective oxidation
Galva-Annealing: Zn melting and oxidation

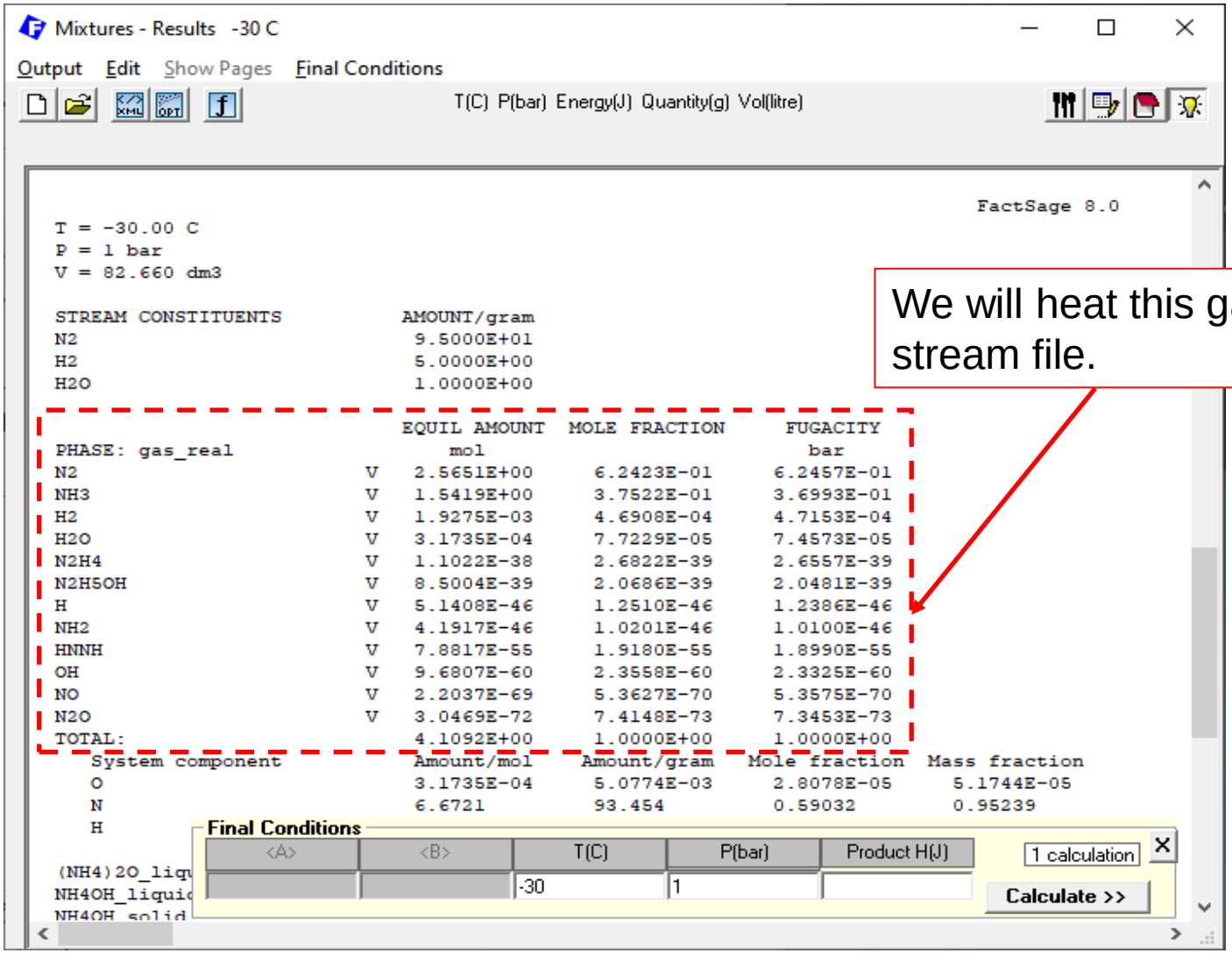
Oxygen partial pressure control using Dew-point control



N2-H2 gas with -30C dew point

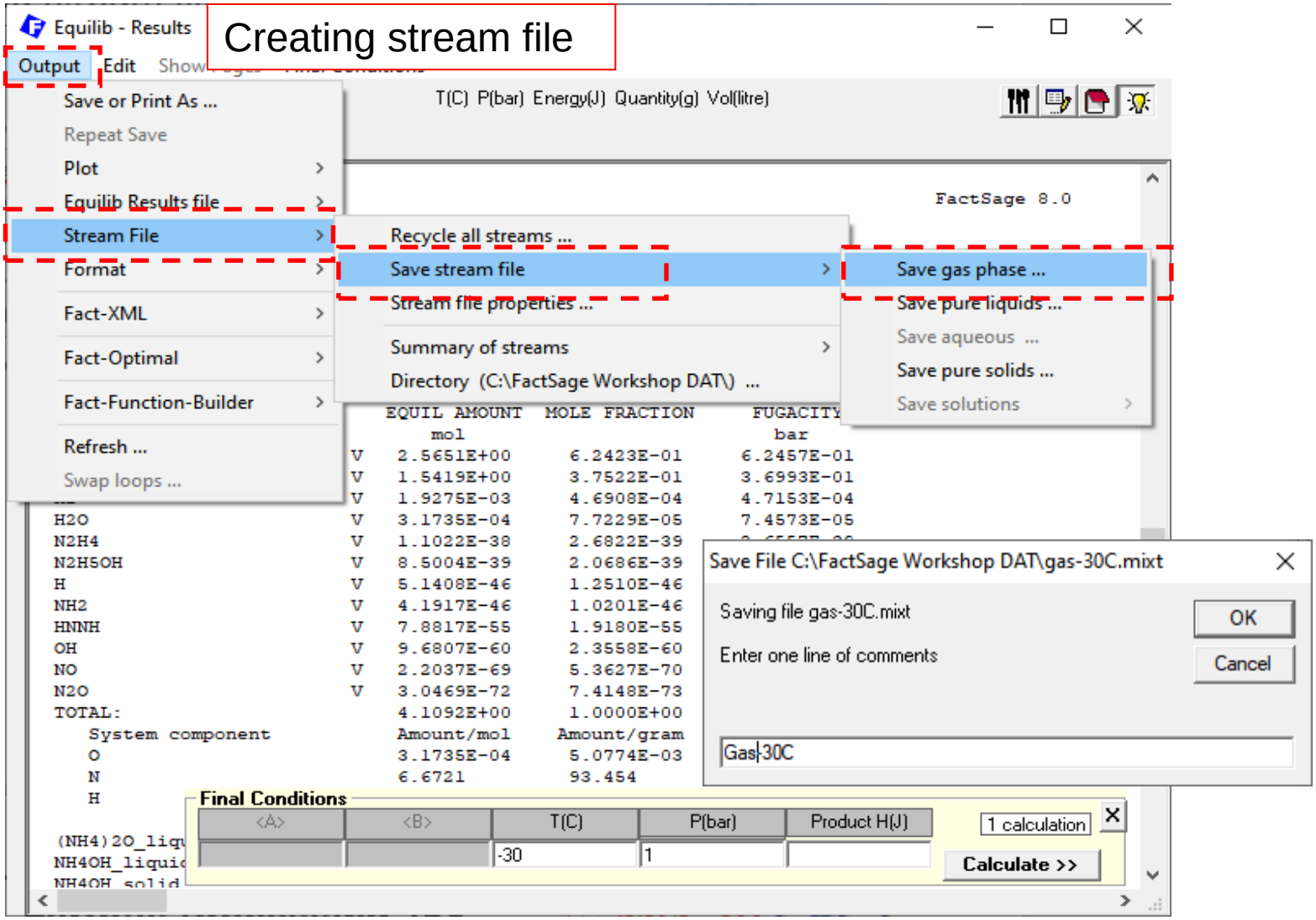


N2-H2 gas with -30C dew point

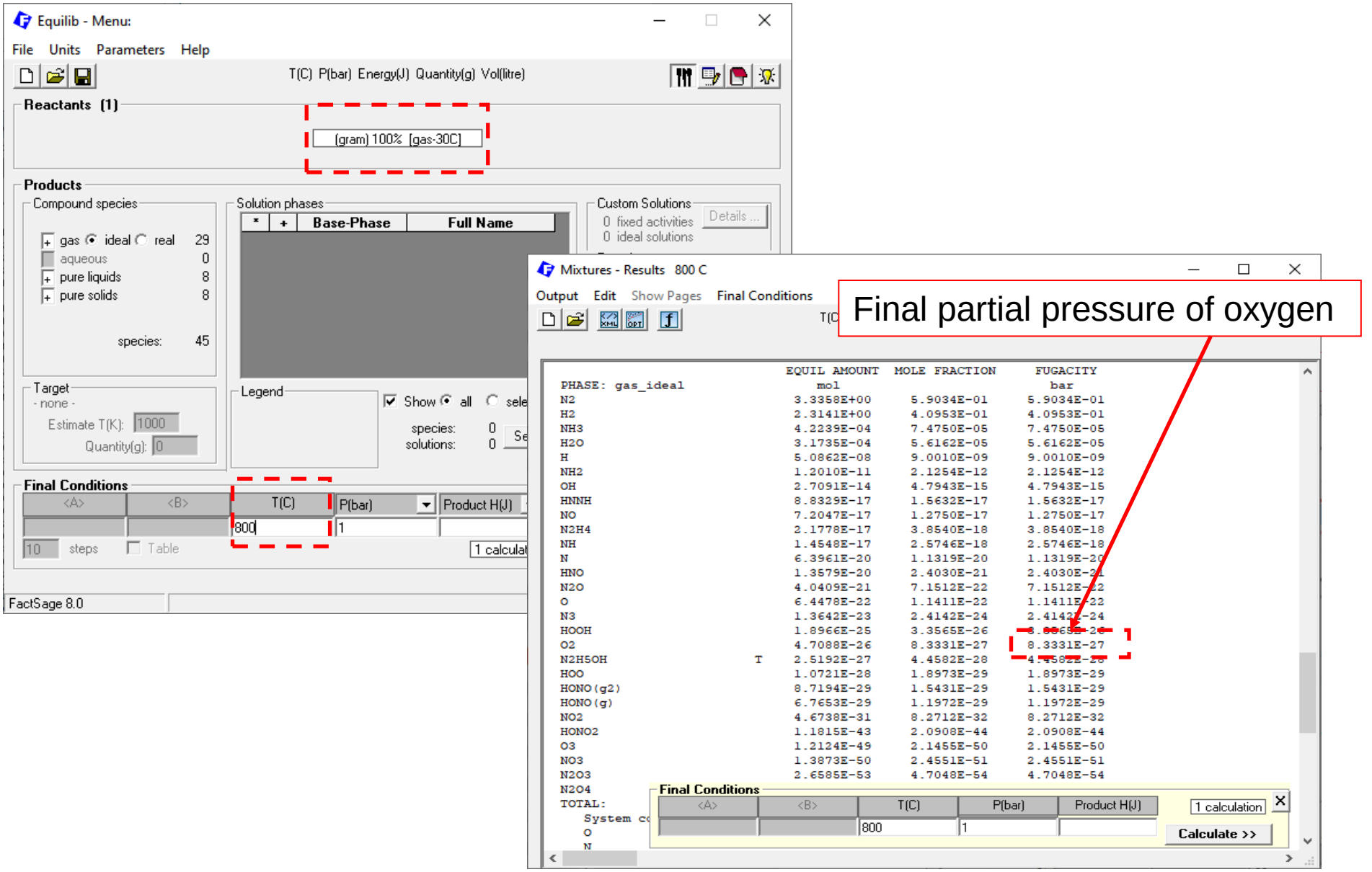


We will heat this gas at 800°C using stream file.

N2-H2 gas with -30C dew point

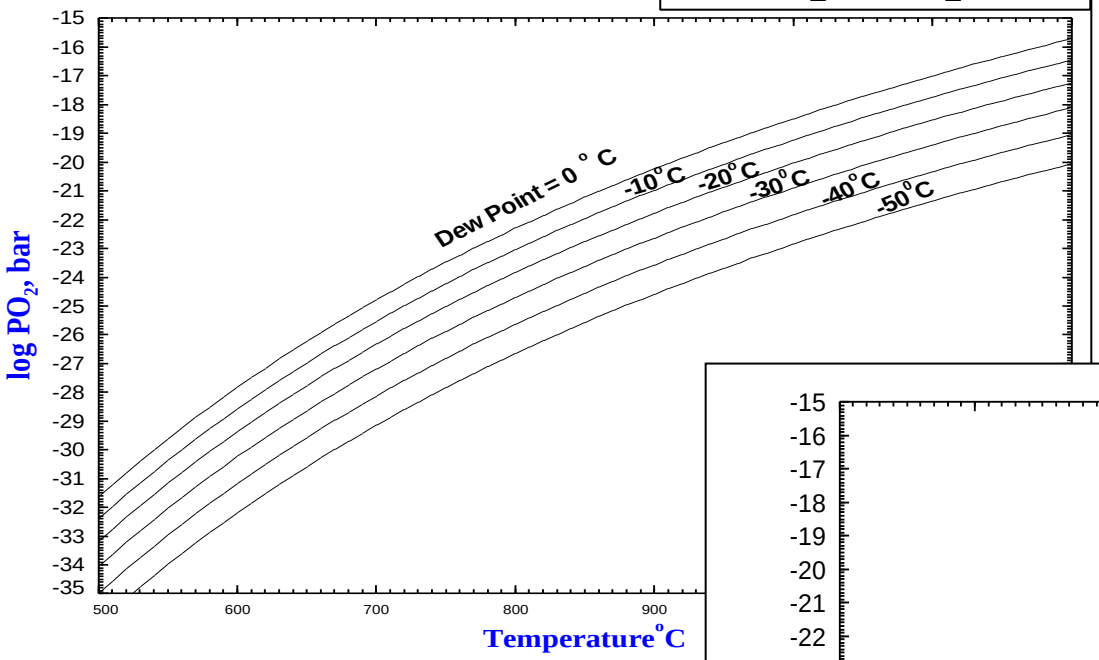


N2-H2 gas with -30°C dew point → 800°C

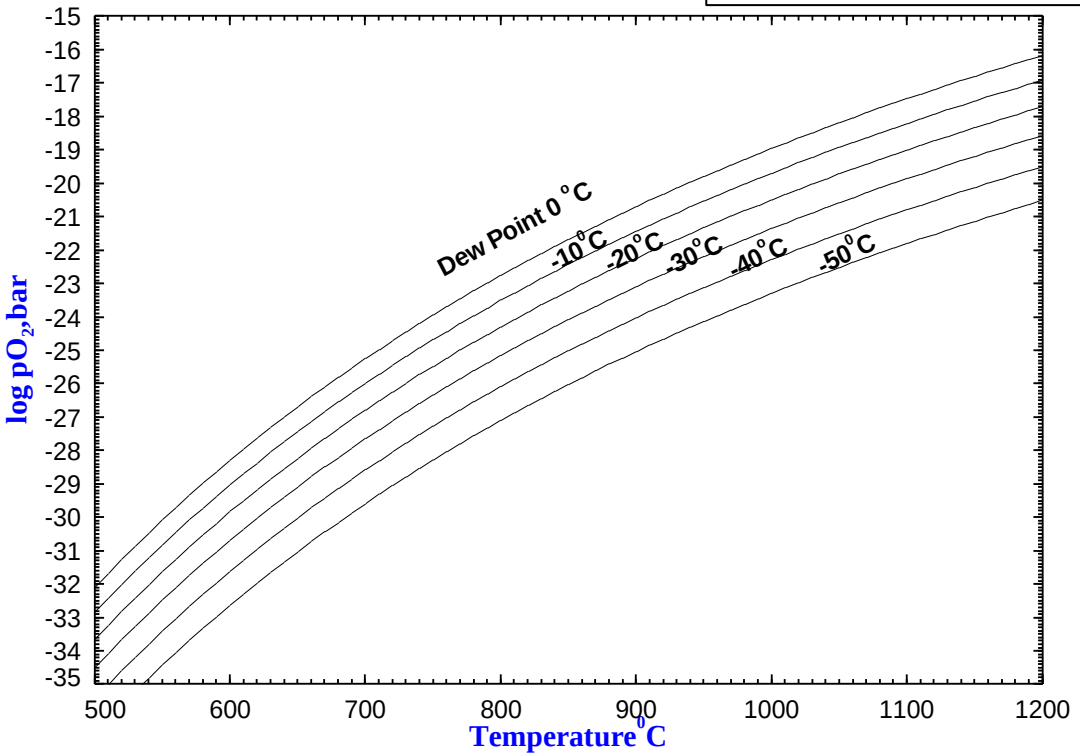


Dew points – PO_2/T Relationship

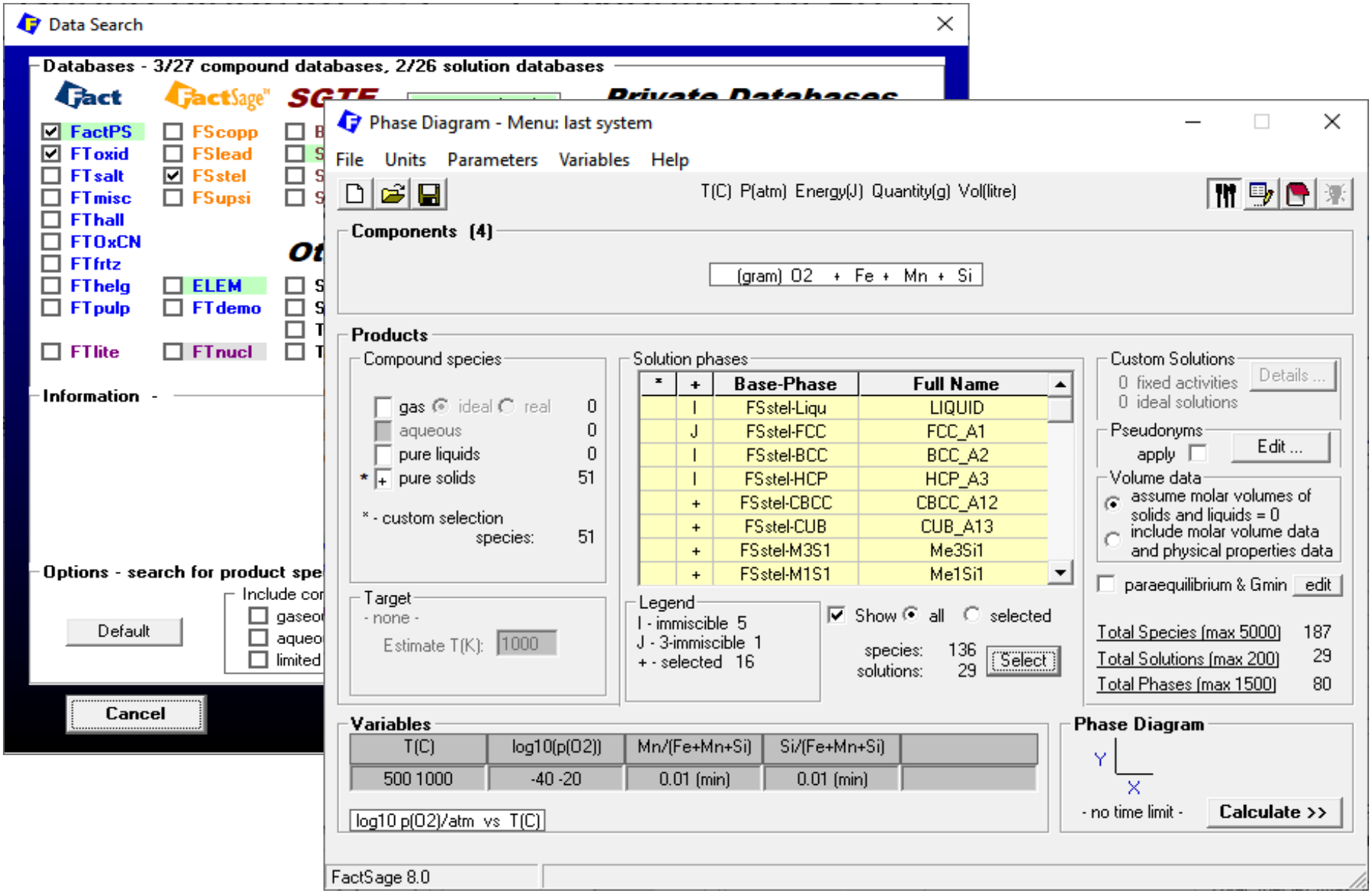
95%N_2,5%H_2



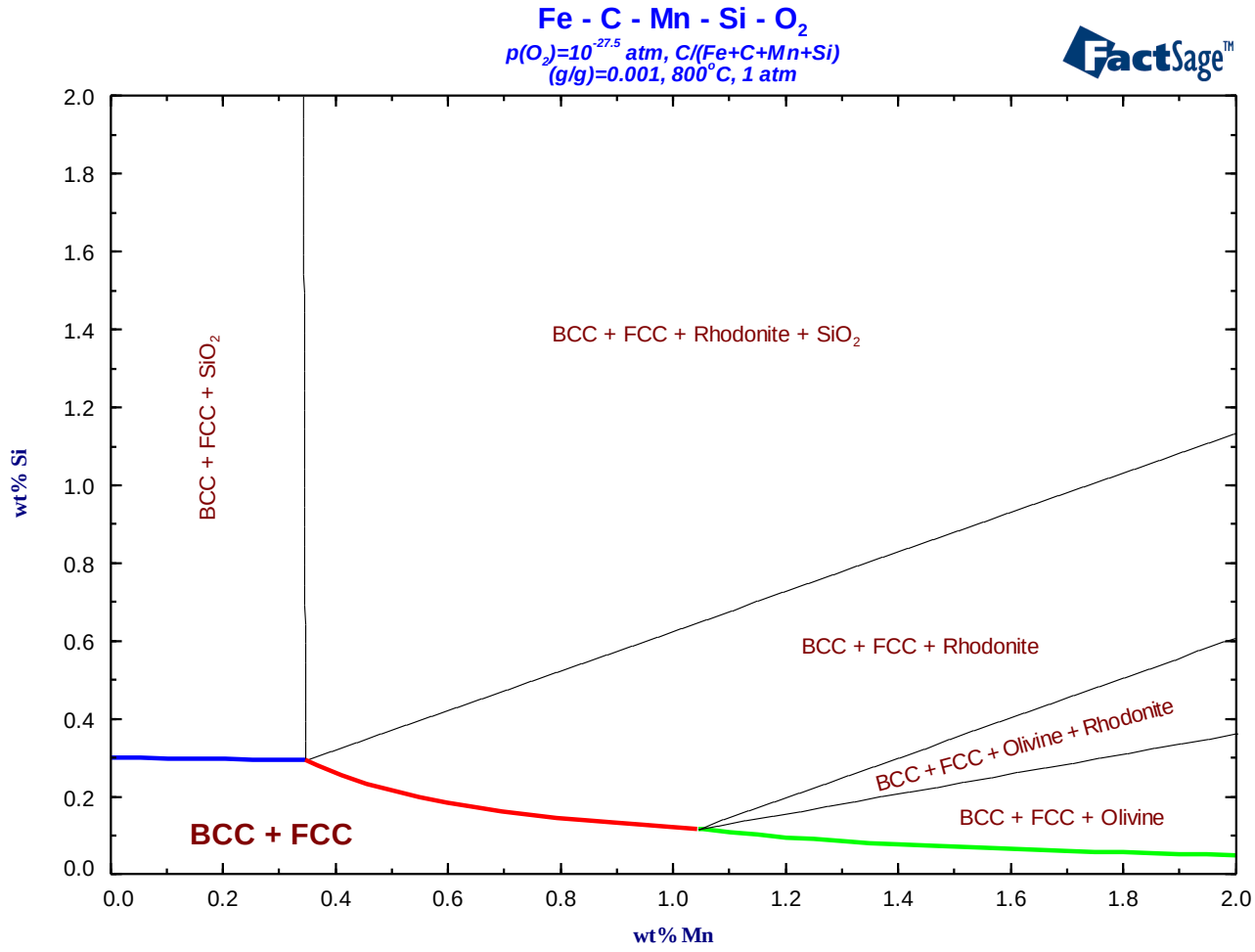
90%N_2,10%H_2



Phase diagram PO_2 – T: Oxidation of Fe-1%Mn-1%Si



Primary oxide formation diagram

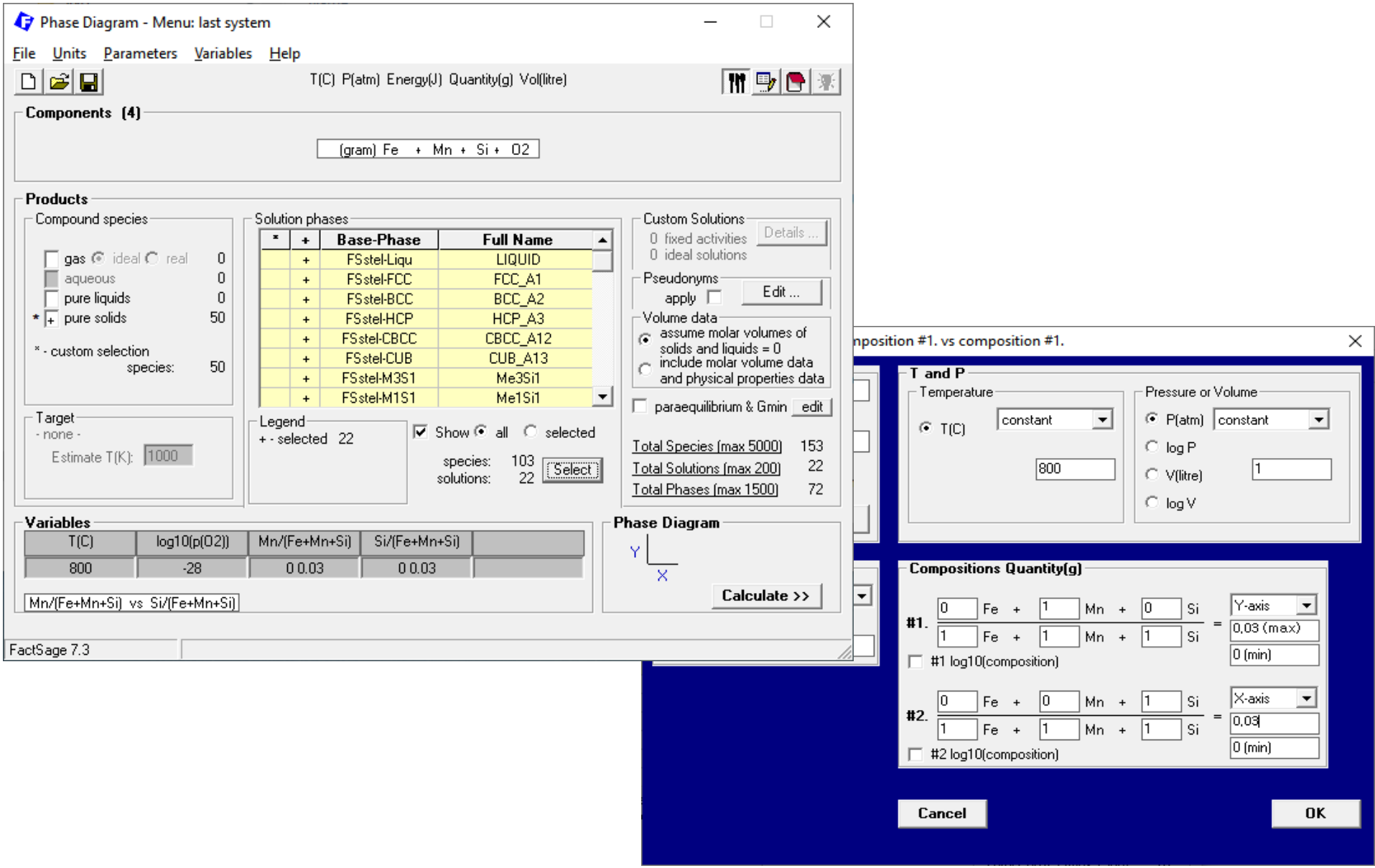


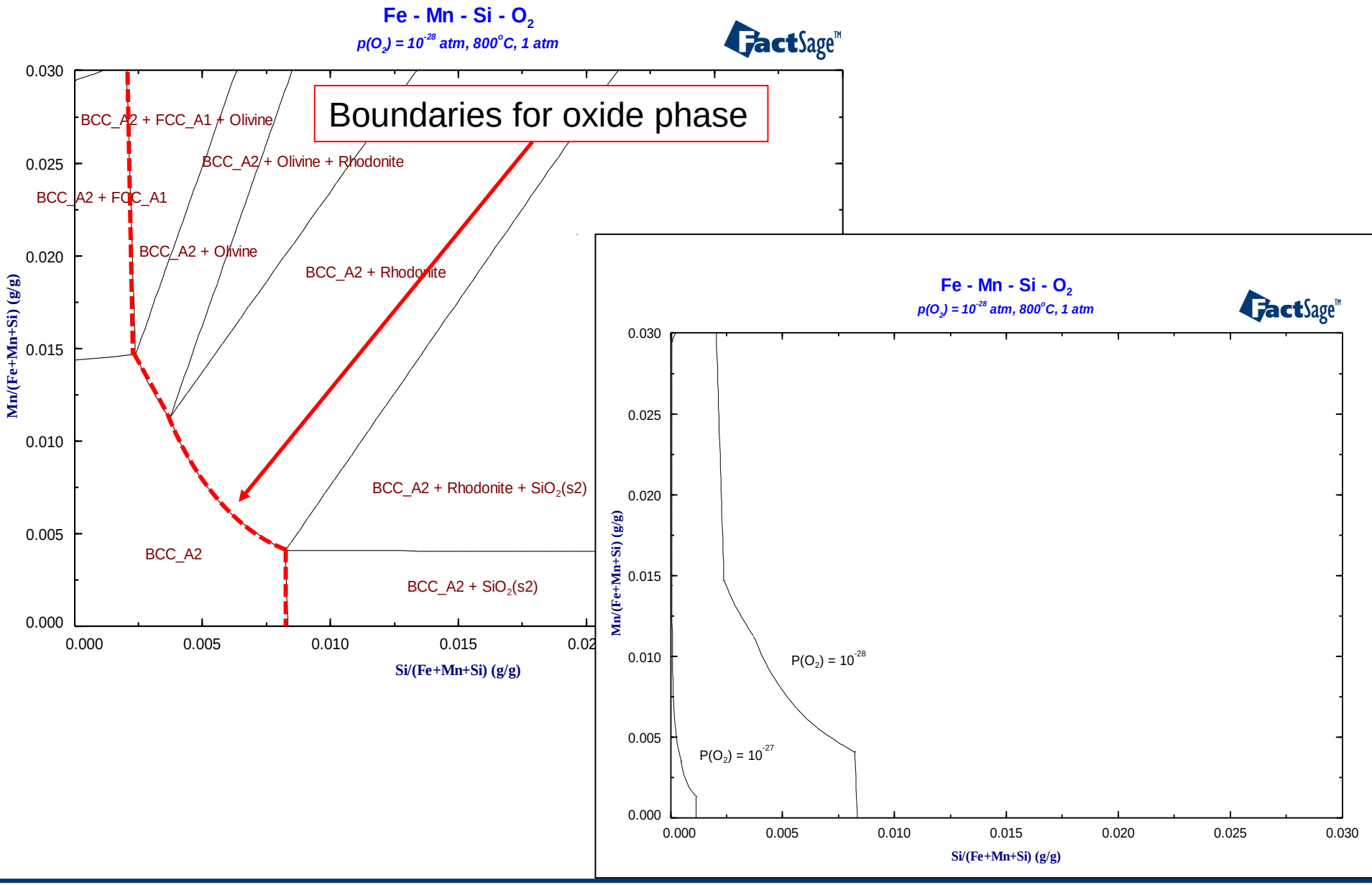
Drawing of the diagram:

1) Collect all blue/red/green lines at different PO2 and superimpose them in one diagram.

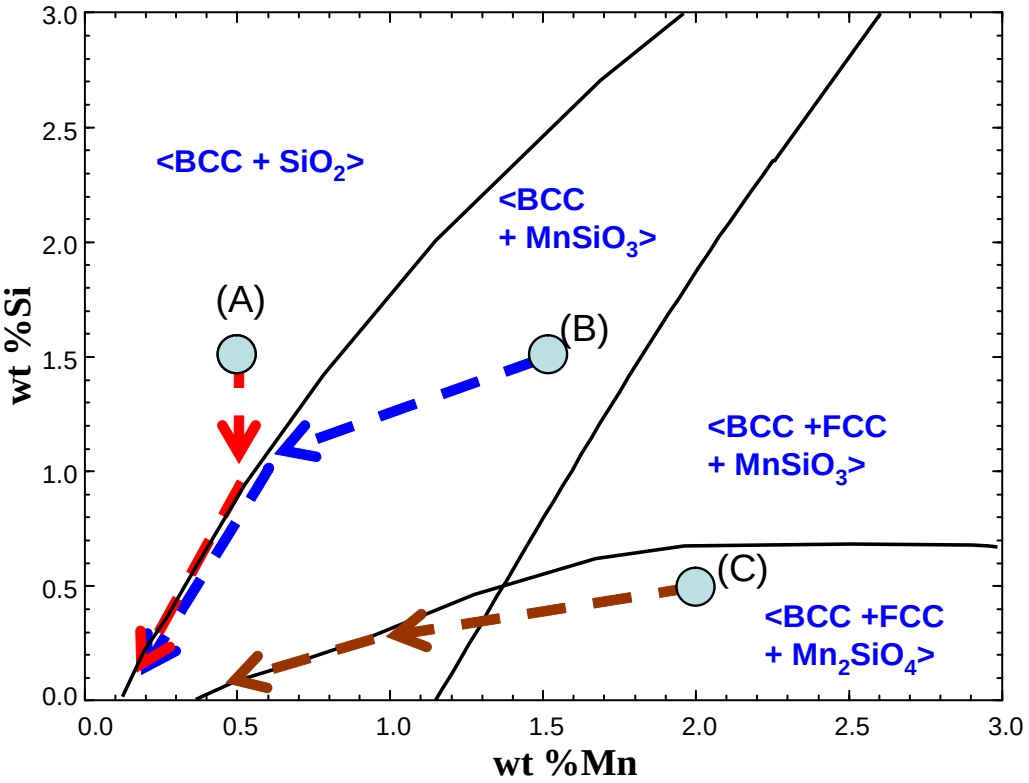
2) The boundary of each color line (different phase) is the phase boundary of the primary oxide phase in the diagram.

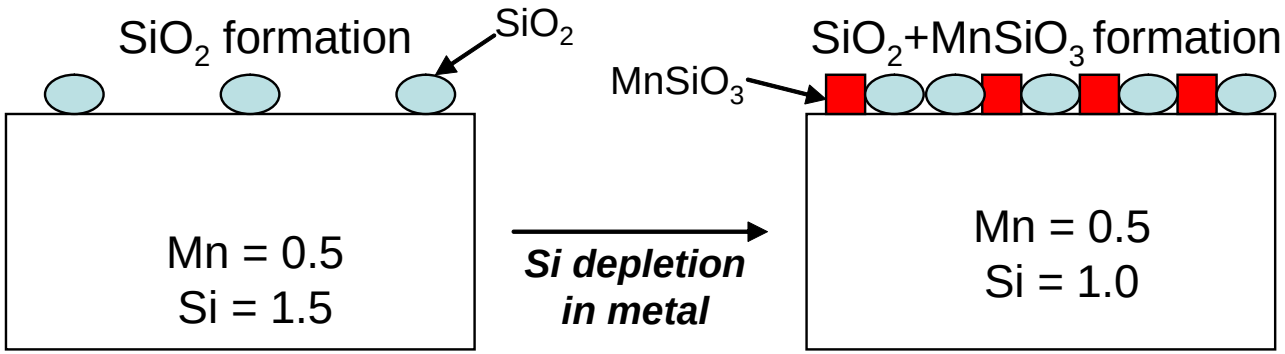
Fe-Mn-Si at $PO_2=10^{-28}$atm, T=800°C




Fe - Mn - Si - O2
p(O2) = 10-28 atm, 800°C, 1 atm
FactSage™
Boundaries for oxide phase
BCC_A2 + FCC_A1 + Olivine
BCC_A2 + Olivine + Rhodonite
BCC_A2 + FCC_A1
BCC_A2 + Olivine
BCC_A2 + Rhodonite
BCC_A2 + Rhodonite + SiO2(s2)
BCC_A2
BCC_A2 + SiO2(s2)
Mn/(Fe+Mn+Si) (g/g)
Si/(Fe+Mn+Si) (g/g)
0.000
0.005
0.010
0.015
0.020
0.025
0.030
Fe - Mn - Si - O2
p(O2) = 10-28 atm, 800°C, 1 atm
FactSage™
P(O2) = 10-28
P(O2) = 10-27
Mn/(Fe+Mn+Si) (g/g)
Si/(Fe+Mn+Si) (g/g)

Primary and Secondary Oxidations



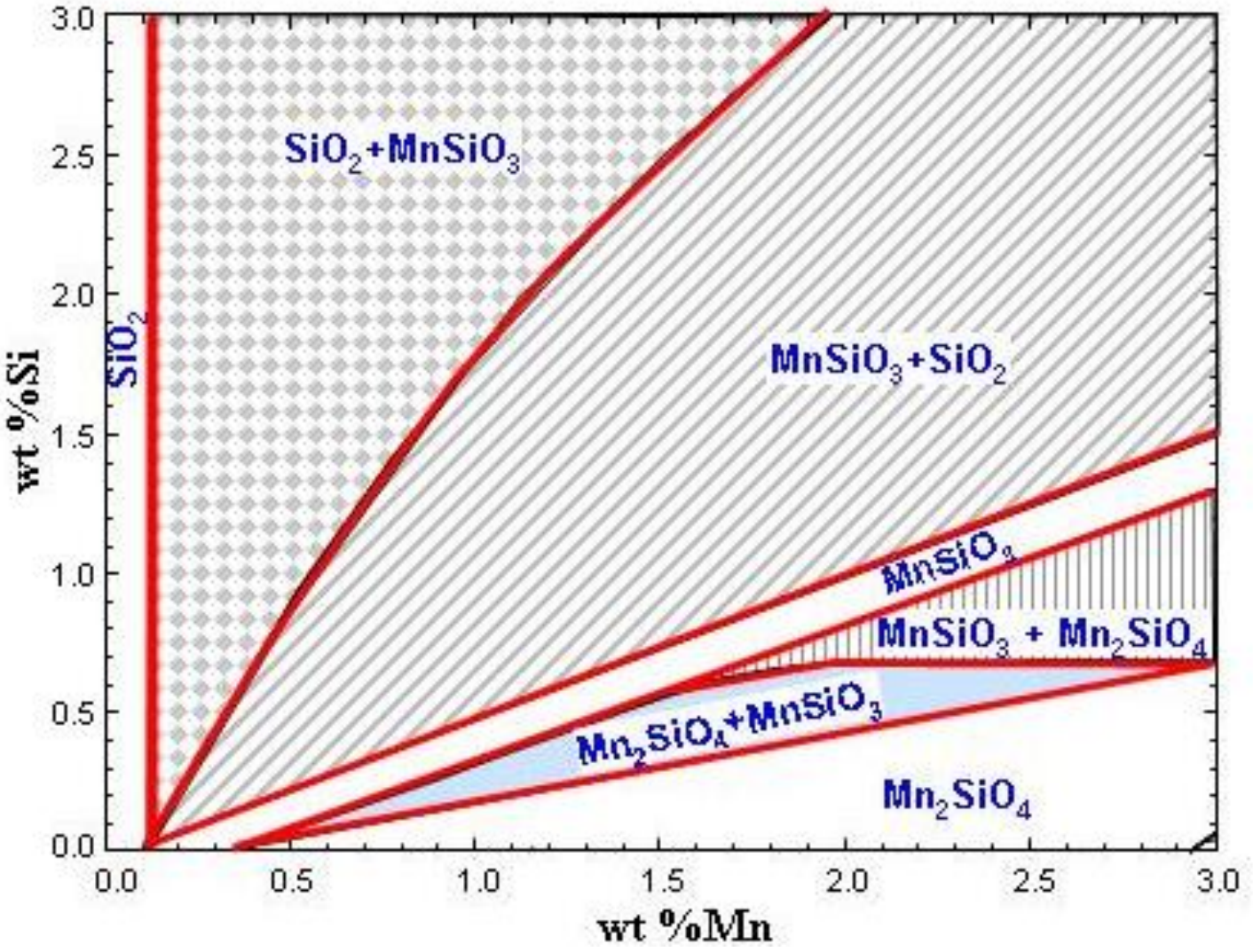


Primary oxidation

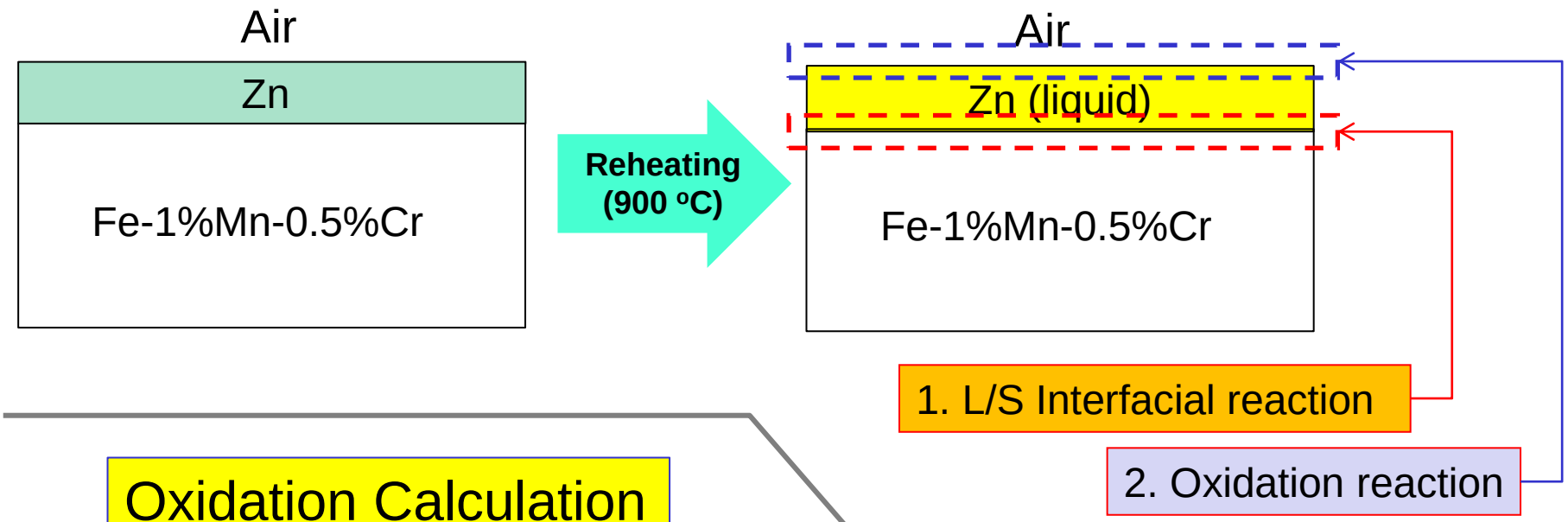
Secondary oxidation

Oxidation phase diagram

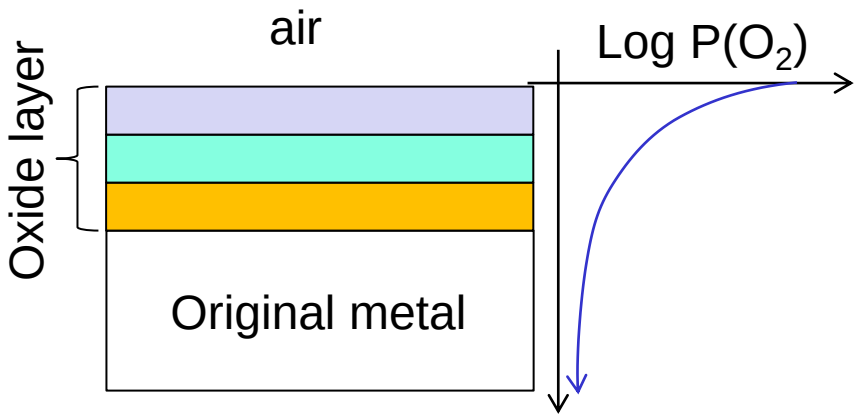
Oxidation phase diagram of the Fe-0.002%C-Mn-Si steel at 800°C



Remelting and oxidation of Zn galvanized steel

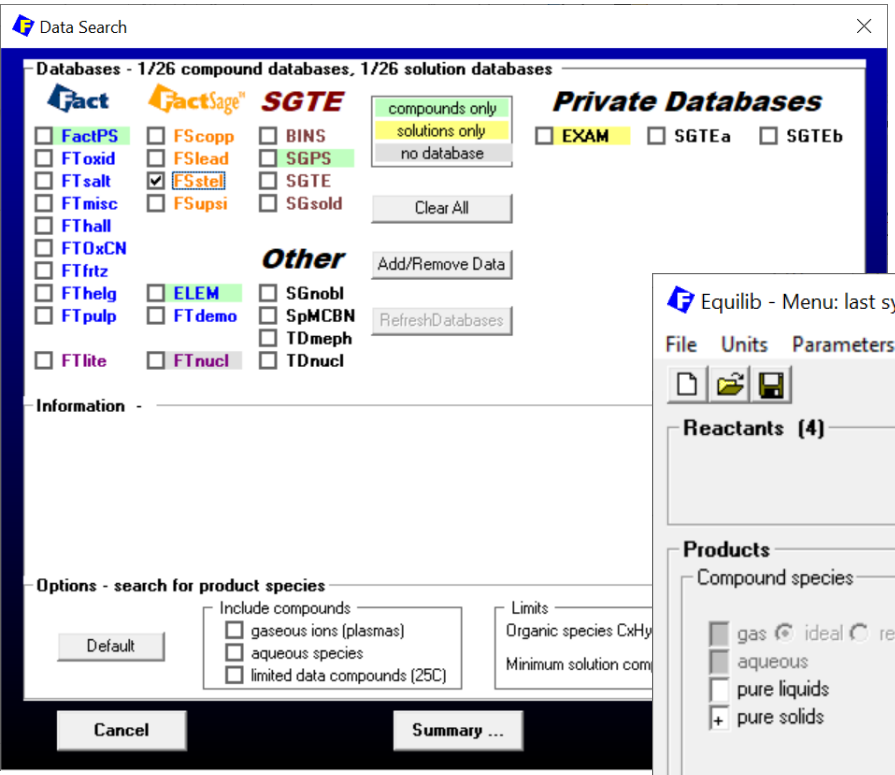


Oxidation Calculation

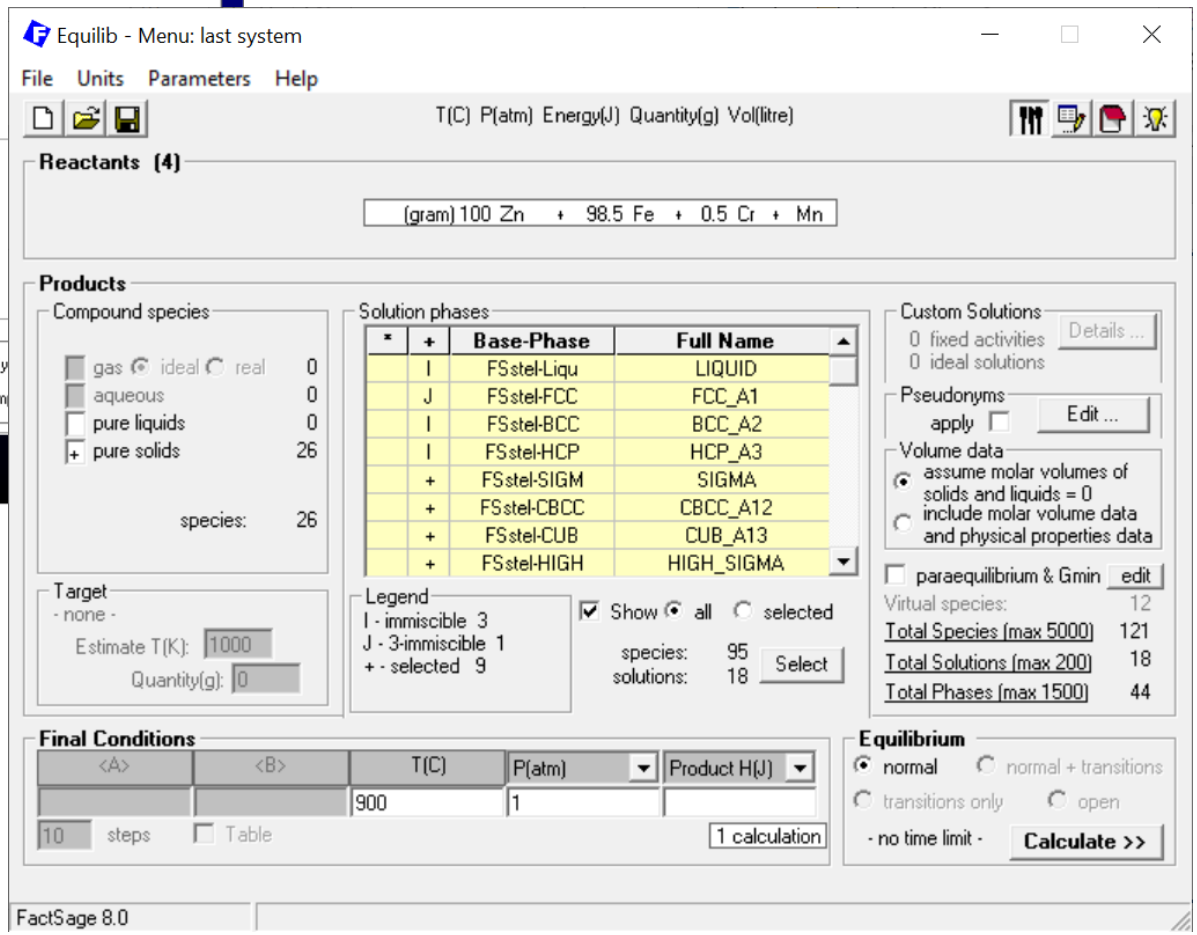


By controlling the partial pressure, different layer oxides can be calculated. But the partial pressure is not linearly decreasing with depth of oxide layer. So this type of calculation shows quantitative oxidation behavior

Interface reaction between liquid Zn and steel

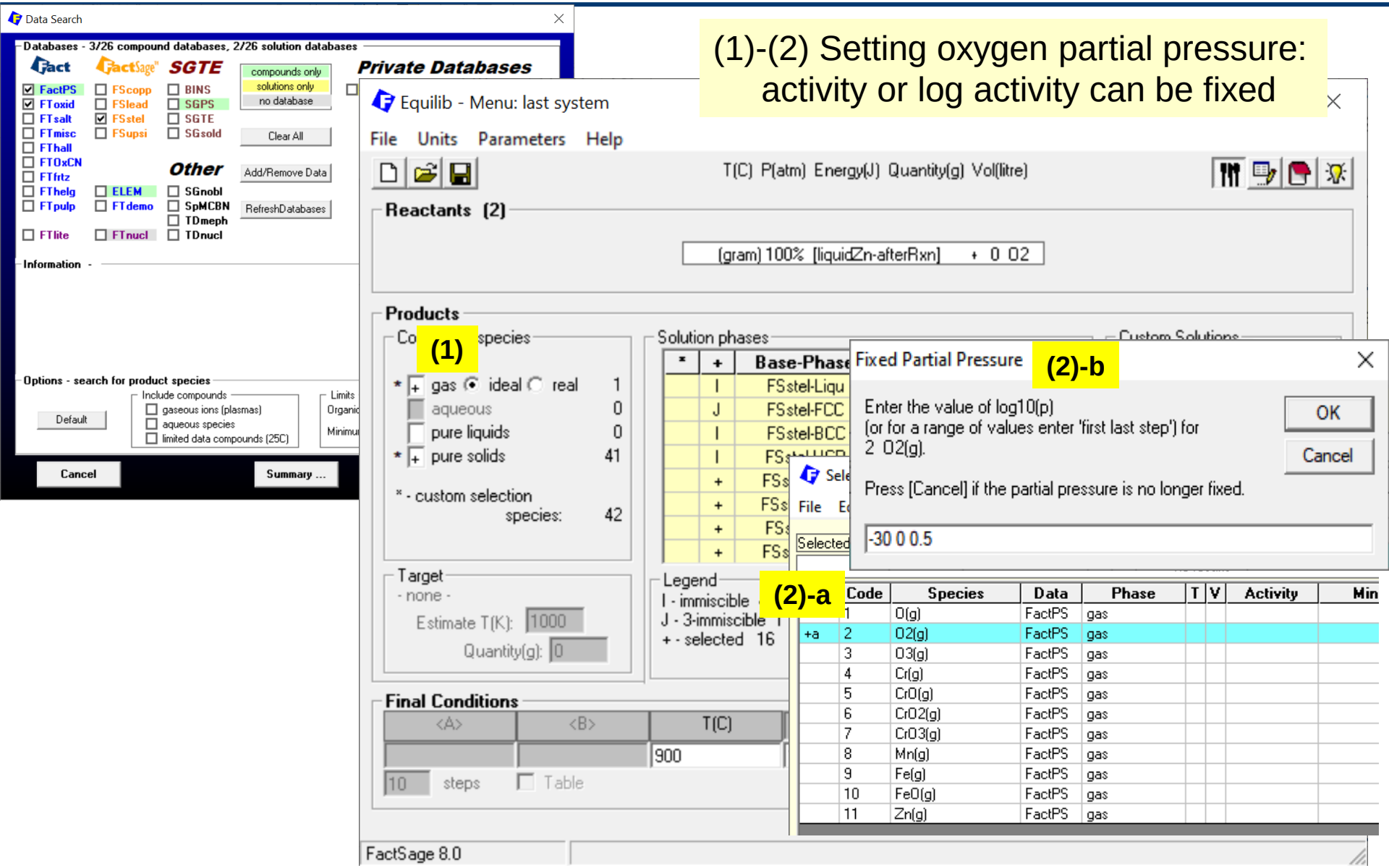


FSStel database contains reasonable Zn bath data for Zn-galvanizing (Zn-Al-Fe-Mg-Si).

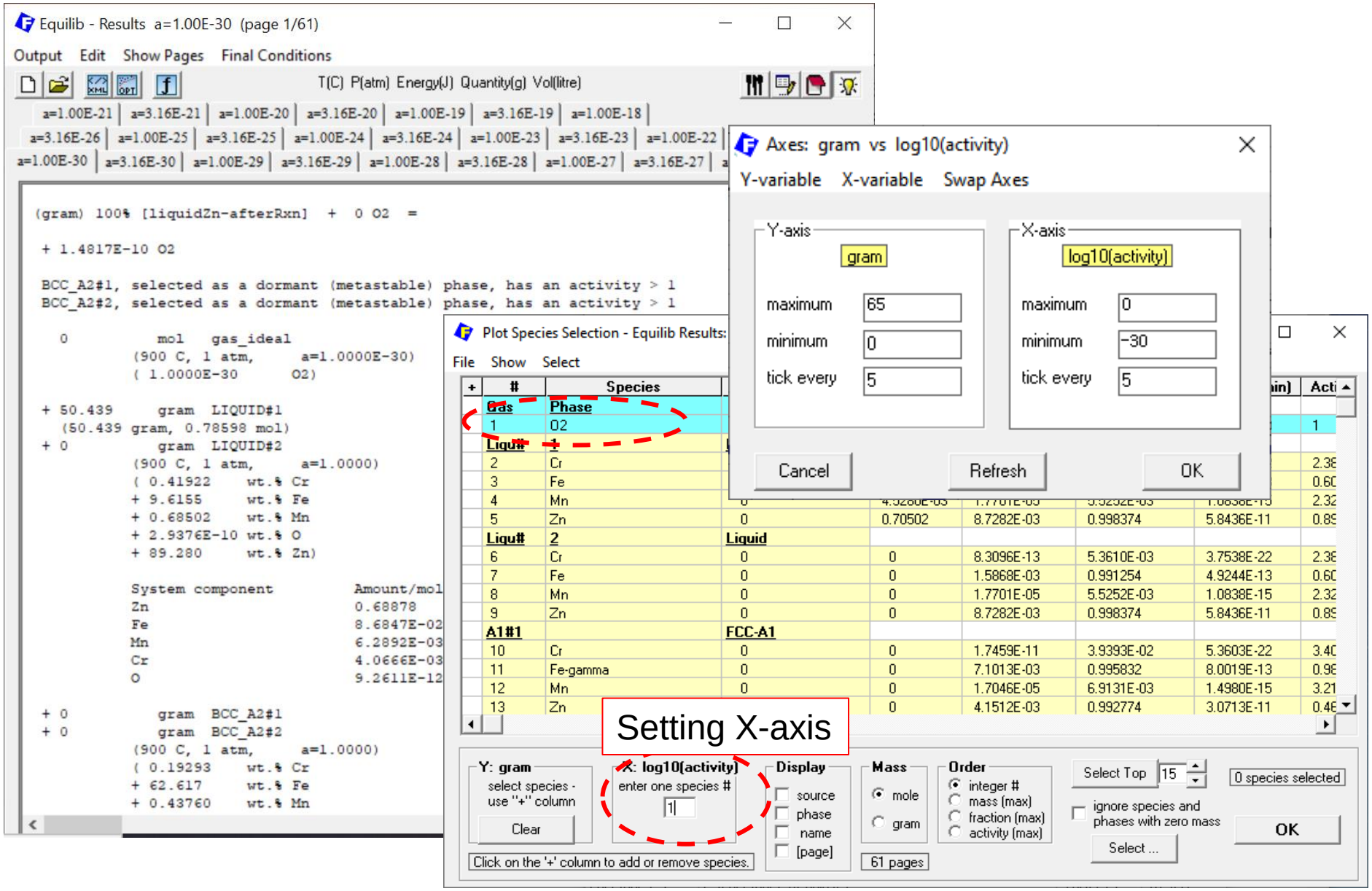


Oxidation of liquid Zn

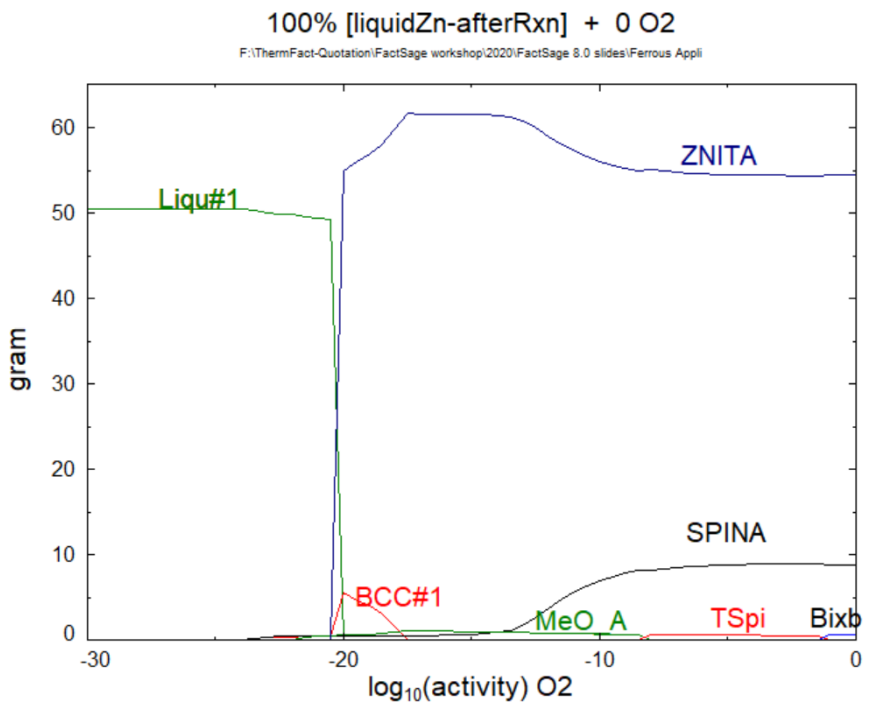
(1)-(2) Setting oxygen partial pressure: activity or log activity can be fixed

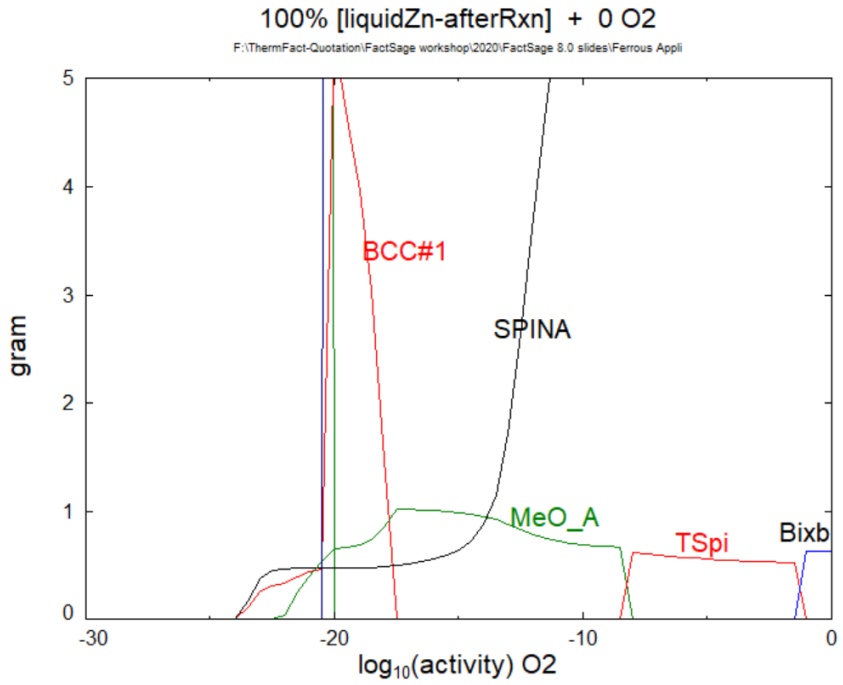


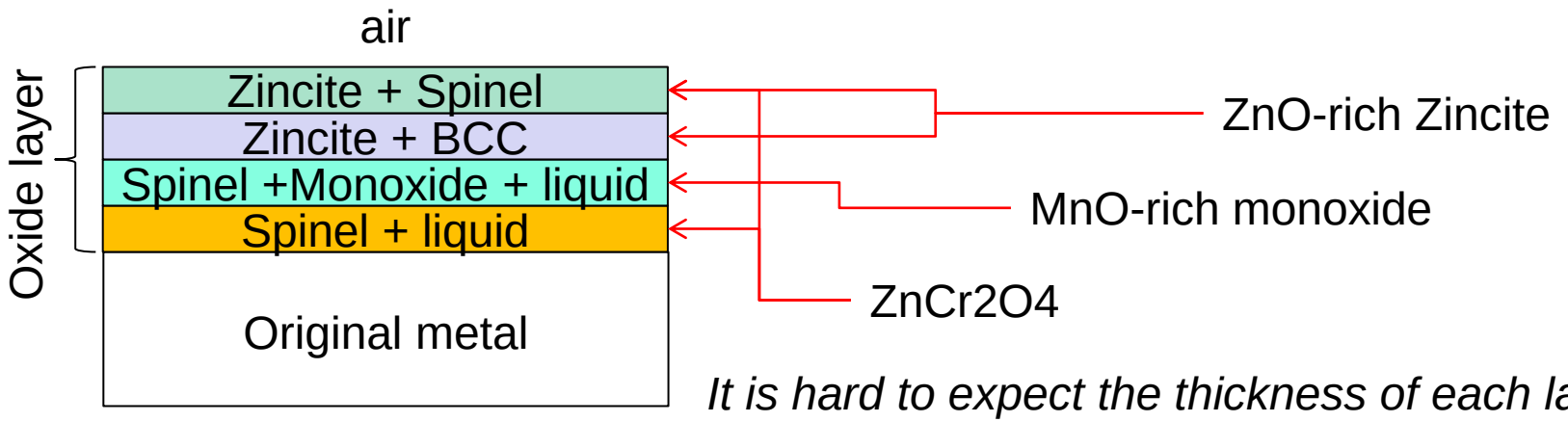
Oxidation of liquid Zn



Oxidation of liquid Zn

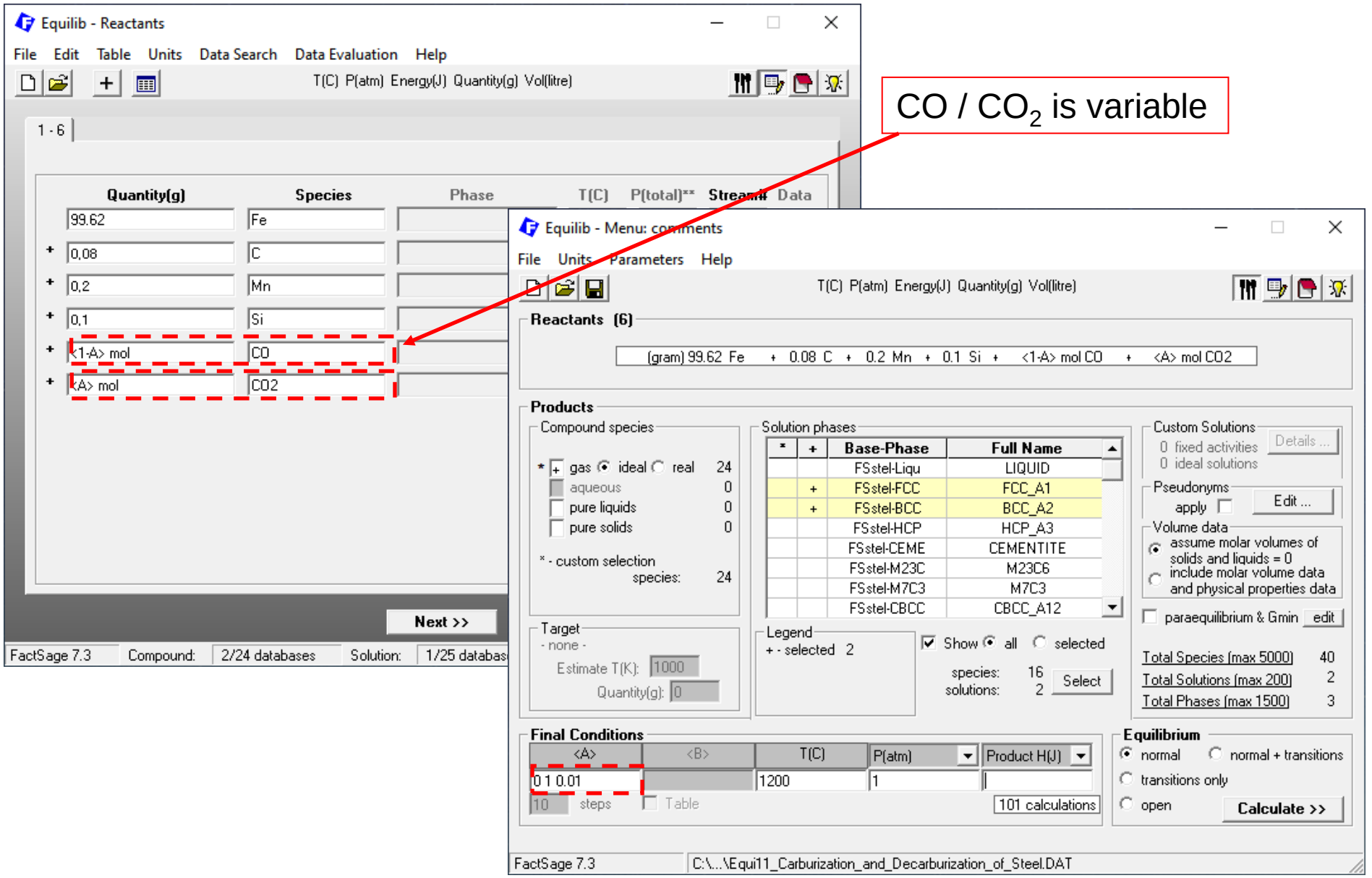




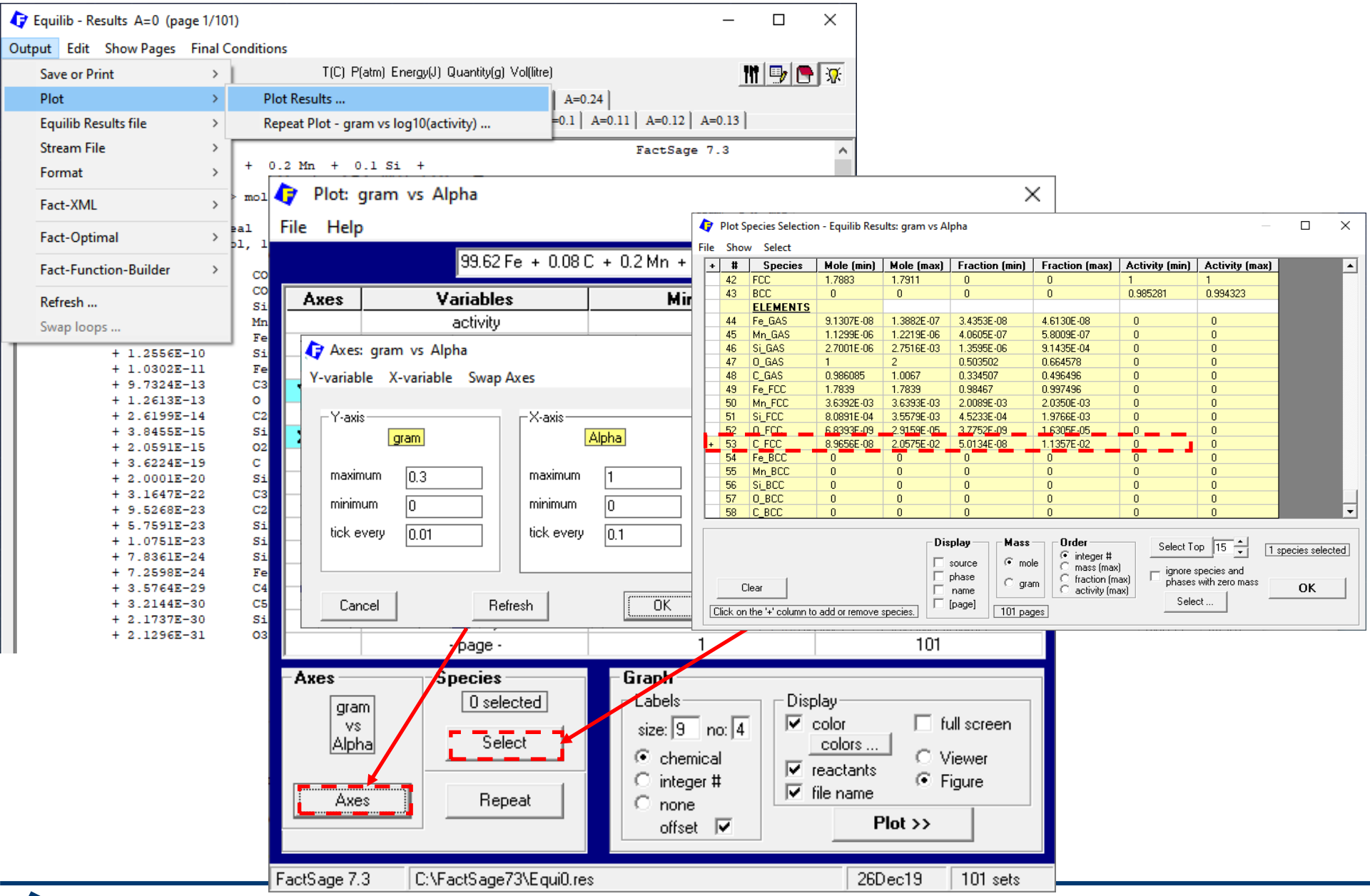


It is hard to expect the thickness of each layer

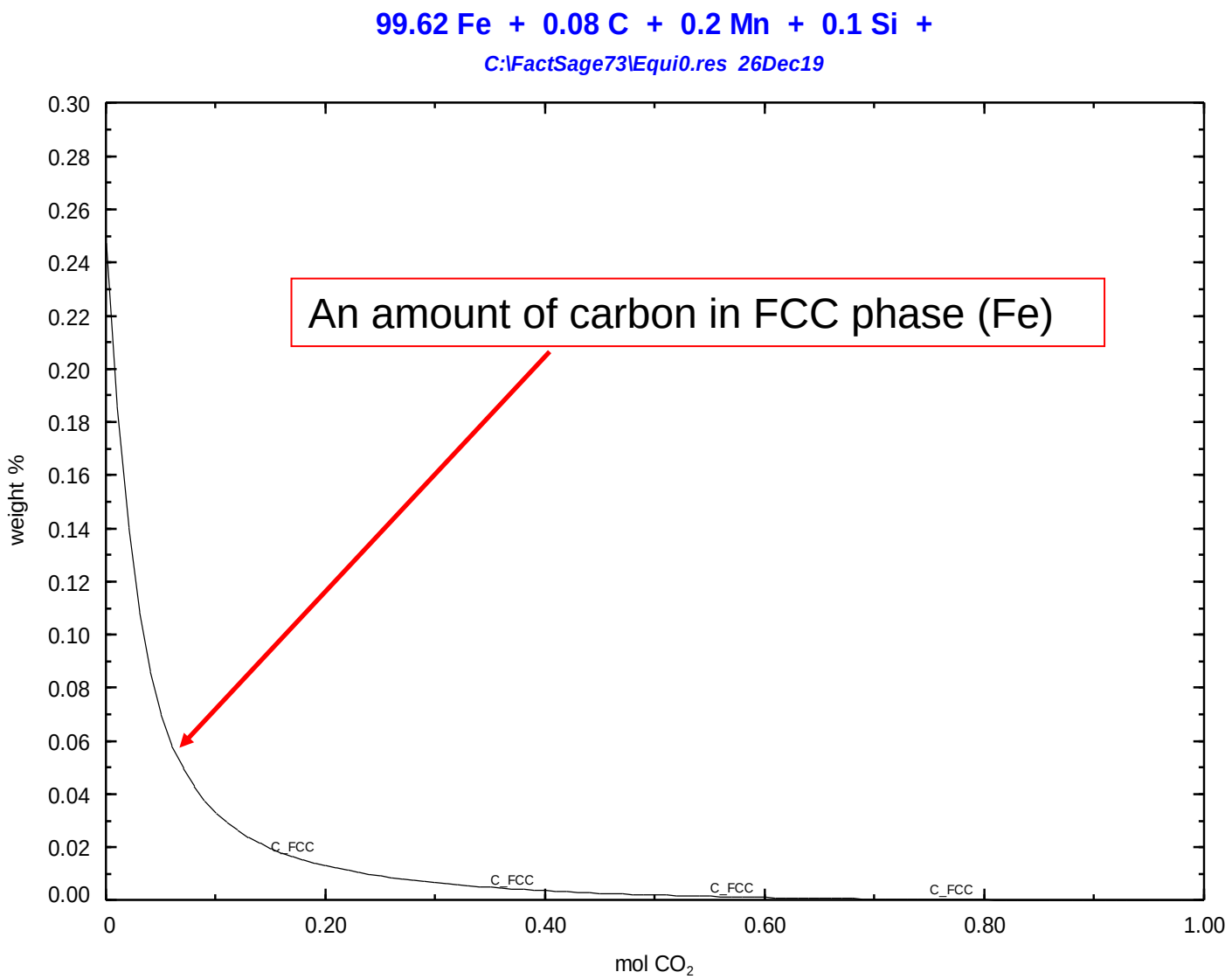
Carburization and Decarburization of Steel



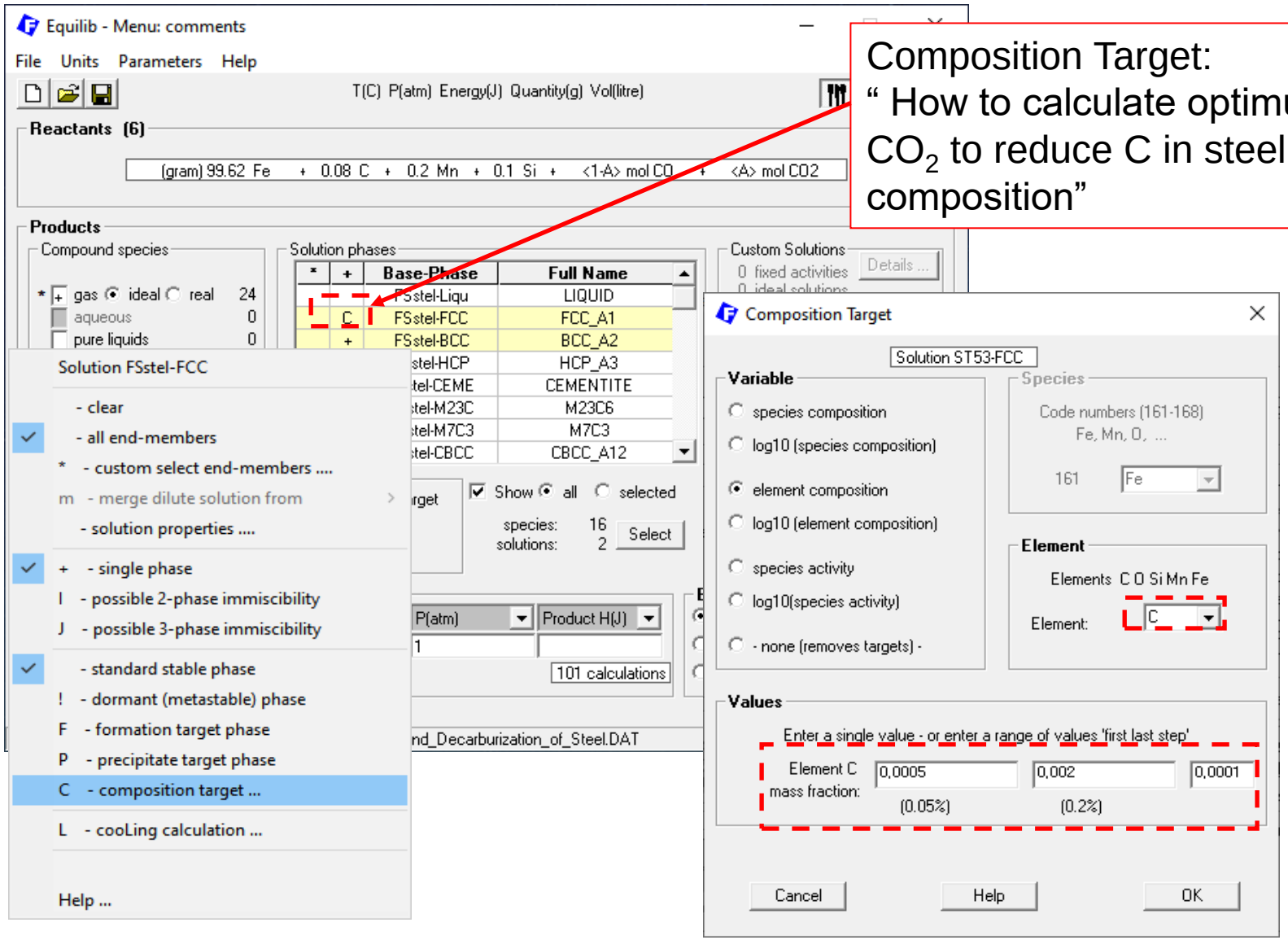
Carburization and Decarburization of Steel



Carburization and Decarburization of Steel



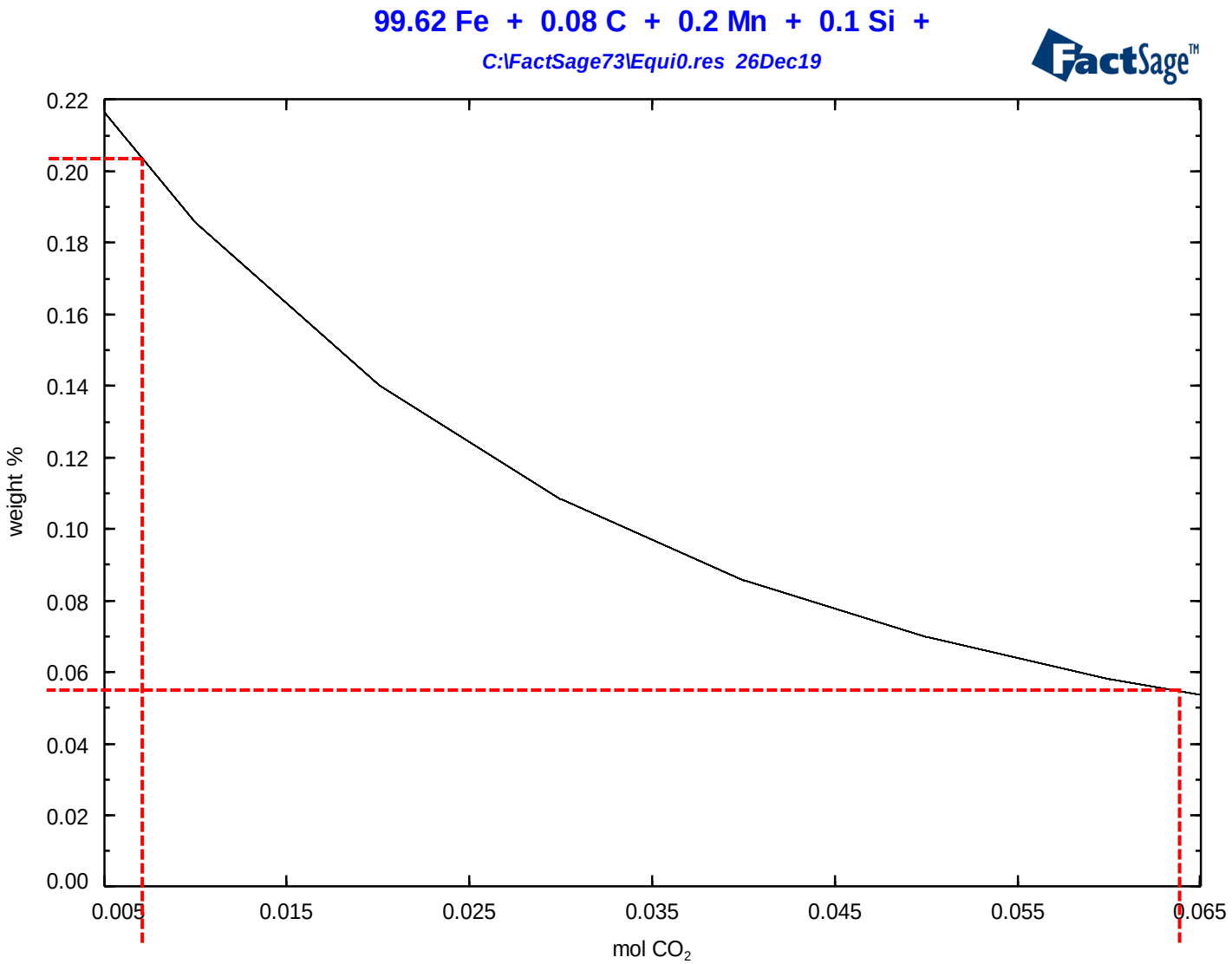
Carburization and Decarburization: Composition target



Composition Target:

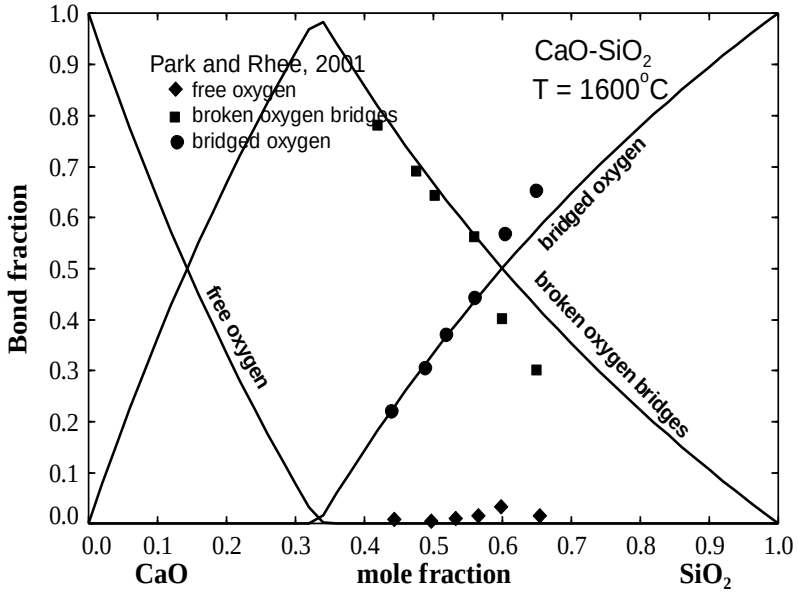
" How to calculate optimum amount of CO_2 to reduce C in steel to a targeted composition"

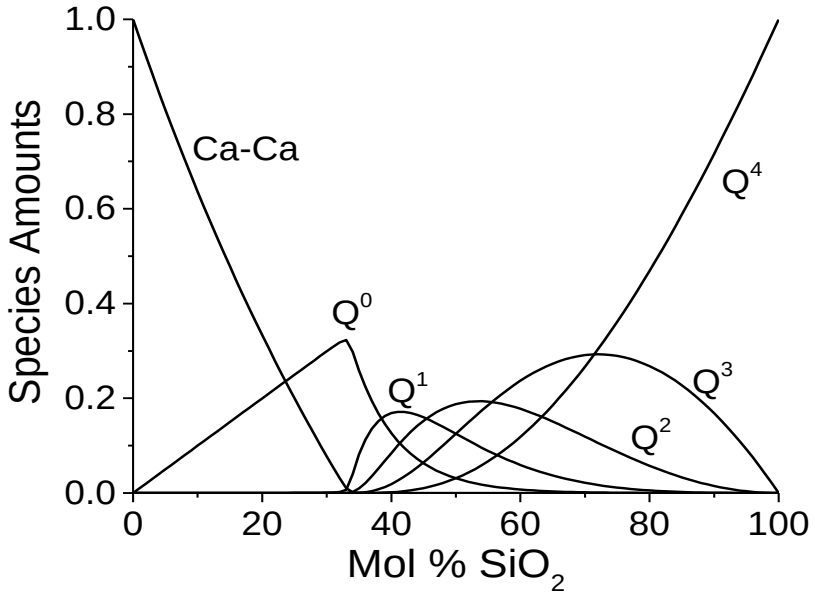
Carburization and Decarburization: Composition target

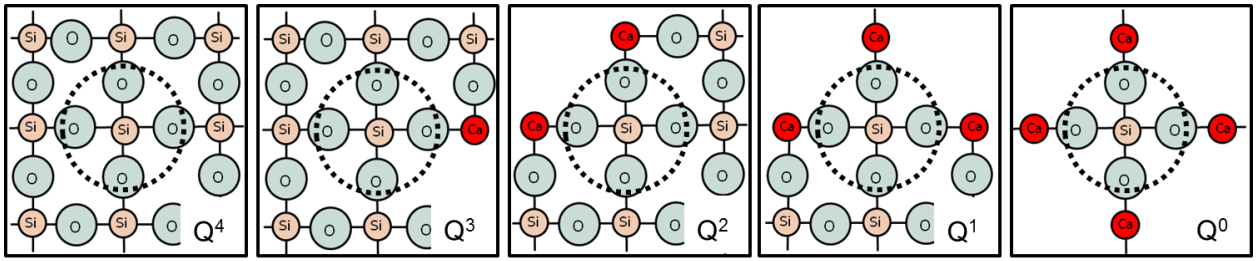


Structure of silicate slag

Modified Quasichemical Model: $O^{2-} + O^0 = 2O^-$

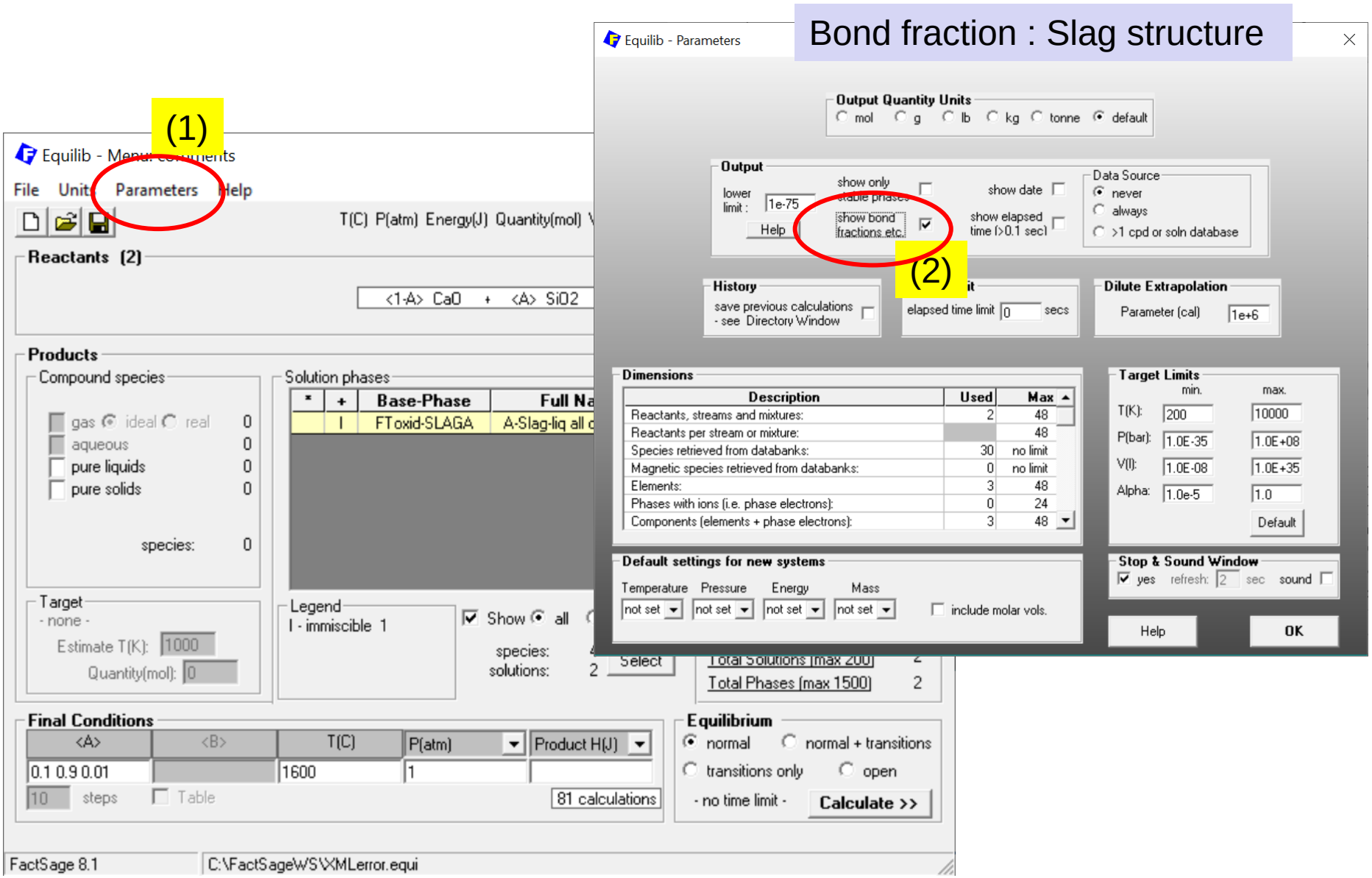






See the following paper for the calculation of Q species from bond fraction:
ERIC THIBODEAU, AIMEN E. GHERIBI, and IN-HO JUNG: METALLURGICAL AND MATERIALS TRANSACTIONS B vol. 47B, 2016, p. 1147

Structure of molten slag



Structure of molten slag

Equilib - Results A=0.1 (page 11/101)

Output Edit Show Pages Final Conditions

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

A=0.13 | A=0.14 | A=0.15 | A=0.16 | A=0.17 | A=0.18 | A=0.19 | A=0.2 | A=0.21 | A=0.22 | A=0.23 | A=0.24

A=0 | A=0.01 | A=0.02 | A=0.03 | A=0.04 | A=0.05 | A=0.06 | A=0.07 | A=0.08 | A=0.09 | - A=0.1 - | A=0.11 | A=0.12

```
                                                                FactSage 8.1
<1-A> CaO  +  <A> SiO2  =

  1.0000     mol   Slag-liq#1
  (56.478 gram, 1.0000 mol)
+ 0          mol   Slag-liq#2
          (1600 C, 1 atm,     a=1.0000)
          ( 0.10000          SiO2
          + 0.90000          CaO)

          Site fraction of sublattice constituents:
          Si                          0.10000
          Ca                          0.90000
          ------------------------------------
          O                           1.0000

          Mole fraction of quadruplets:
          Si-Si-O-O                             1.3397E-05
          Ca-Ca-O-O                             0.63638
          Si-Ca-O-O                             0.36361
          Total amount/mol                      0

          System component          Amount/mol    Amount/gram   Mole fraction  Mass fractio
          Ca                        0.90000         36.070        0.42857       0.63866
          Si                        0.10000         2.8085        4.7619E-02    4.9728E-02
          O                         1.1000          17.599        0.52381       0.31161

where "A" on the reactant side is 0.10000

Cut-off limit for phase activities = 1.00E-75

*********************************************************************
```

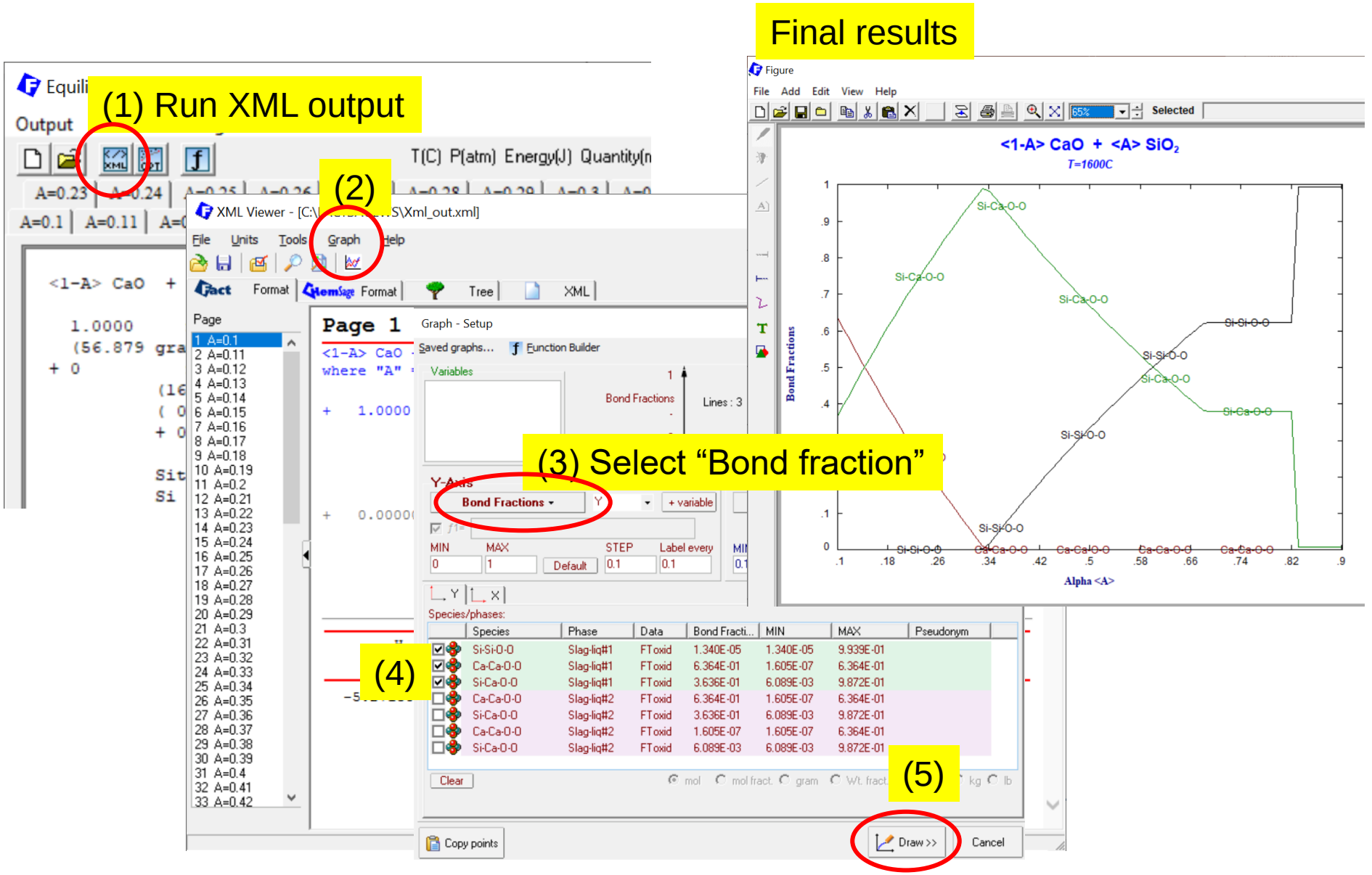
Bond fraction : Slag structure

Si-Si-O-O : O^0 (bridged oxygen)

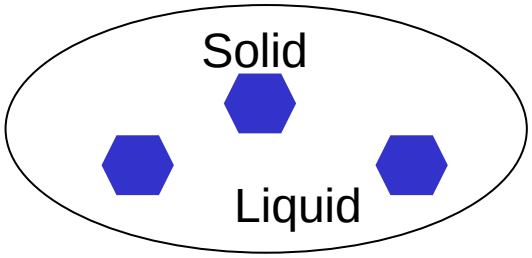
Ca-Ca-O-O: O^{2-} (free oxygen)

Si-Ca-O-O: O^- (broken oxygen)

Structure of molten slag



Viscosity Calculation: S+L mixtures (Einstein-Roscoe Eq.)



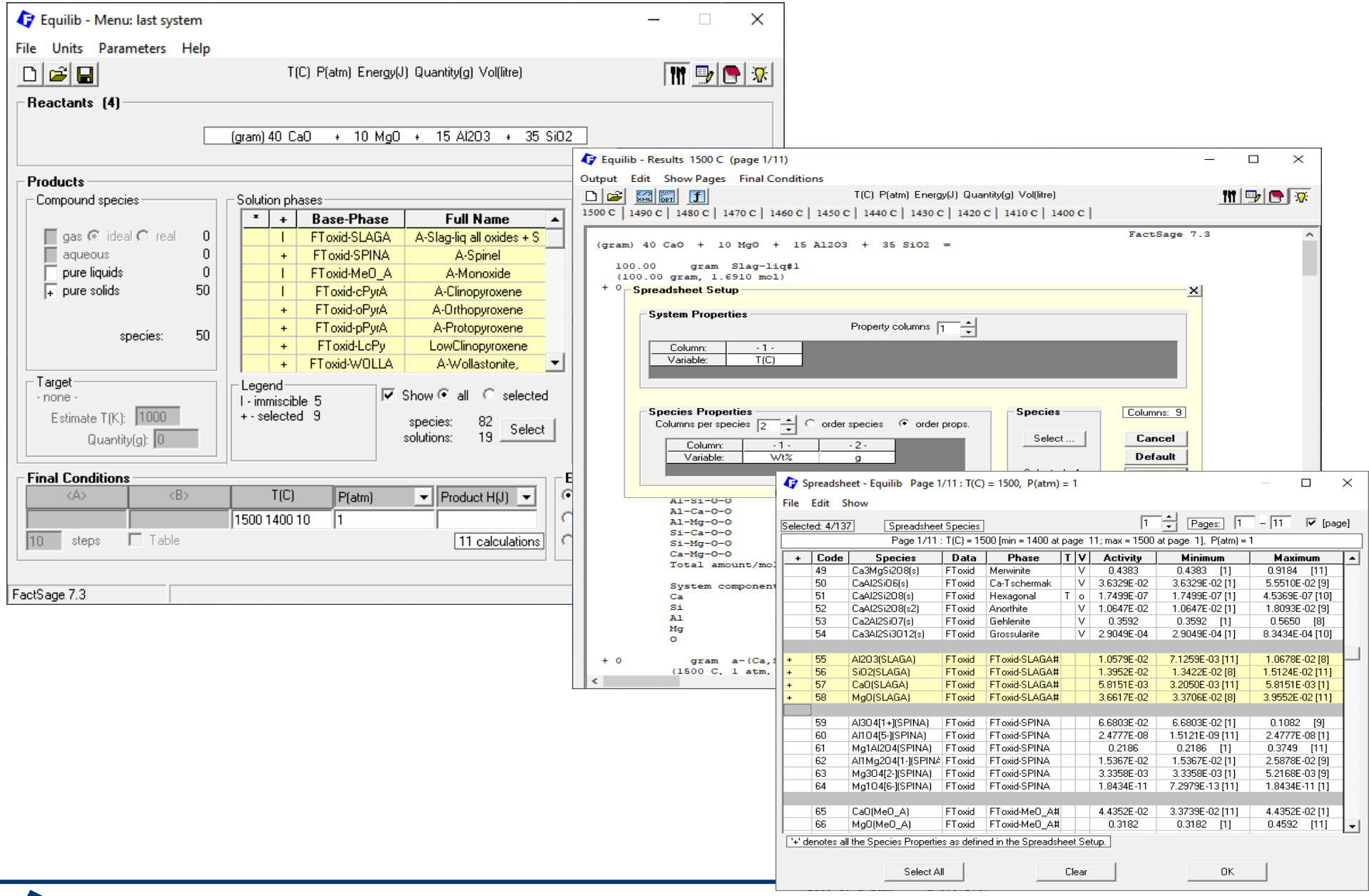
Viscosity of liquid slag can be calculated from "Viscosity" module from slag composition calculated from "Equilib" (Step-2)

Einstein-Roscoe Equation (one of the most well-accepted equation of viscosity for solid+liquid mixture)

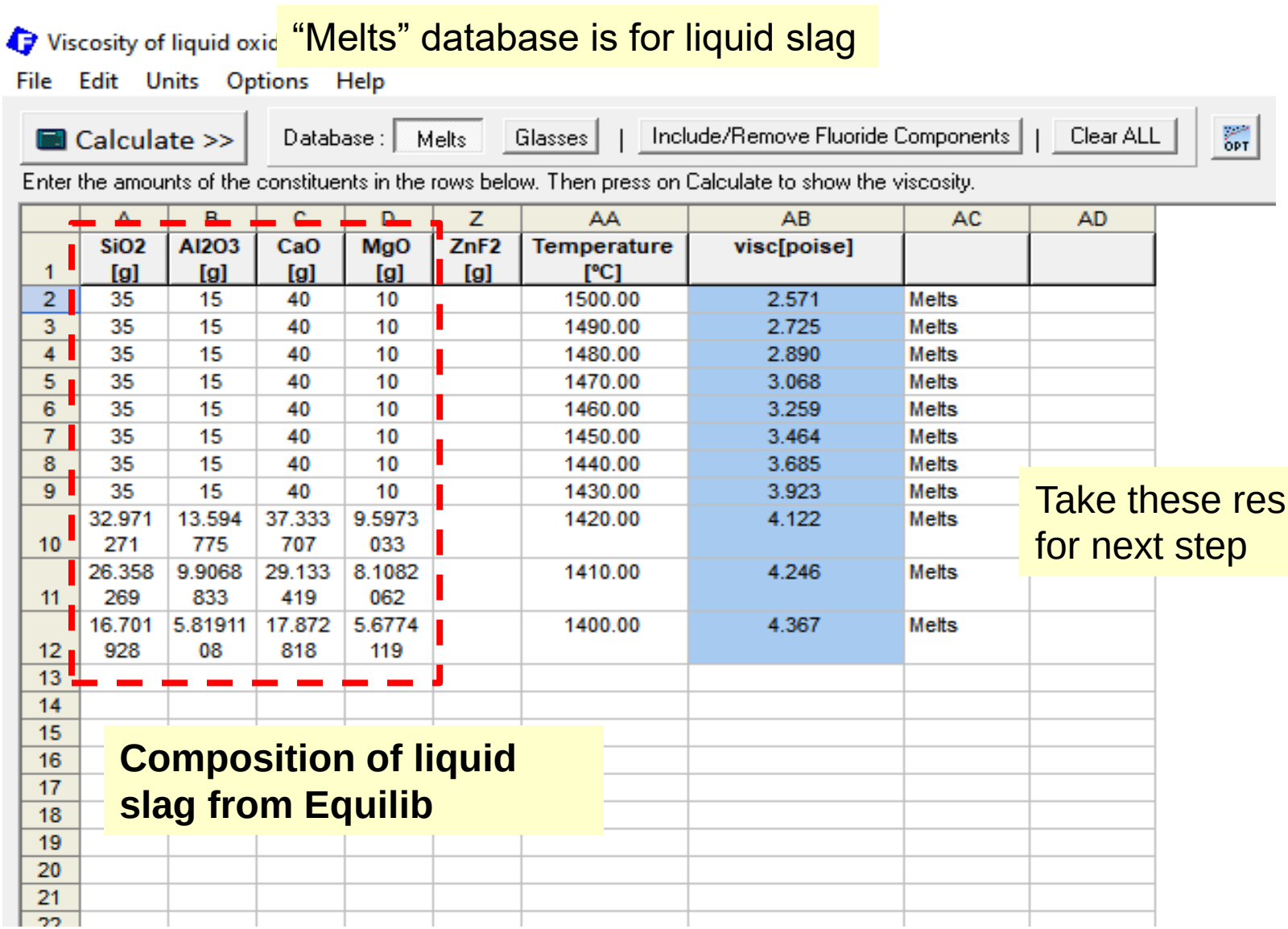
$$\text{Viscosity}_{\text{(solid+liquid mixture)}} \approx \text{Viscosity}_{\text{(liquid)}} \cdot (1 - \text{solid fraction})^{-2.5}$$

Original Einstein-Roscoe equation use 'volume fraction of solid' instead of 'solid fraction' and correction term for morphology, but all these values are not very well-known for general solids, we can simply use the solid fraction (wt fraction) for this equation as approximation.
This value can be calculated using "Equilib" module at given system composition and temperature (Step-1).

Viscosity Calculations “Step-1”: Composition of liquid slag



Viscosity Calculations “Step-2”: Viscosity of liquid slag



	A	B	C	D	Z	AA	AB	AC	AD
1	SiO2 [g]	Al2O3 [g]	CaO [g]	MgO [g]	ZnF2 [g]	Temperature [°C]	visc[poise]		
2	35	15	40	10		1500.00	2.571	Melts	
3	35	15	40	10		1490.00	2.725	Melts	
4	35	15	40	10		1480.00	2.890	Melts	
5	35	15	40	10		1470.00	3.068	Melts	
6	35	15	40	10		1460.00	3.259	Melts	
7	35	15	40	10		1450.00	3.464	Melts	
8	35	15	40	10		1440.00	3.685	Melts	
9	35	15	40	10		1430.00	3.923	Melts	
10	32.971271	13.594775	37.333707	9.5973033		1420.00	4.122	Melts	
11	26.358269	9.9068833	29.133419	8.1082062		1410.00	4.246	Melts	
12	16.701928	5.8191108	17.872818	5.6774119		1400.00	4.367	Melts	
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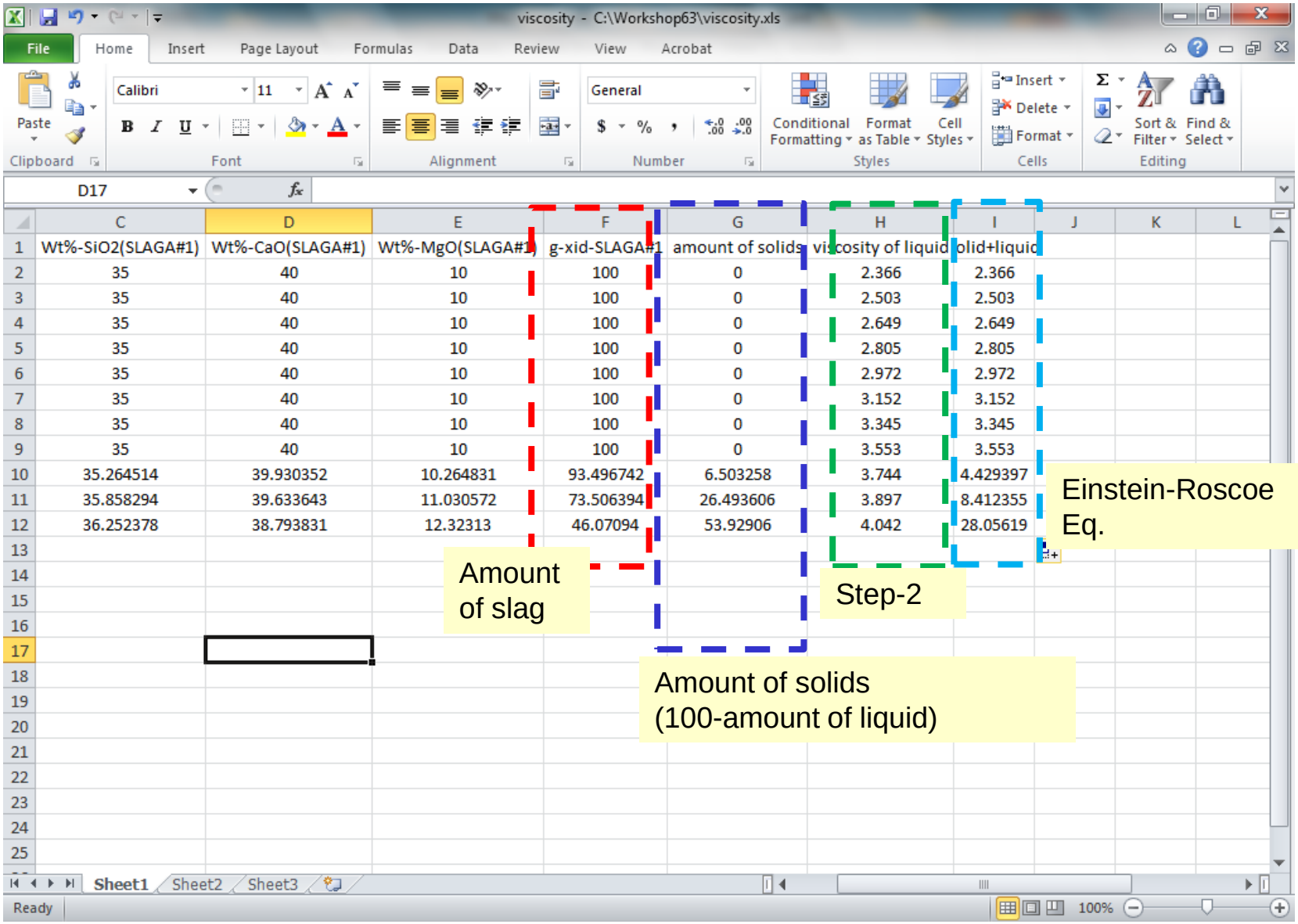
Viscosity Calculations “Step-3”: Liquid + Solid mixture



	C	D	E	F	G	H	I	J	K	L
1	Wt%-SiO2(SLAGA#1)	Wt%-CaO(SLAGA#1)	Wt%-MgO(SLAGA#1)	g-xid-SLAGA#1	amount of solids	viscosity of liquid	olid+liquid			
2	35	40	10	100	0	2.366	2.366			
3	35	40	10	100	0	2.503	2.503			
4	35	40	10	100	0	2.649	2.649			
5	35	40	10	100	0	2.805	2.805			
6	35	40	10	100	0	2.972	2.972			
7	35	40	10	100	0	3.152	3.152			
8	35	40	10	100	0	3.345	3.345			
9	35	40	10	100	0	3.553	3.553			
10	35.264514	39.930352	10.264831	93.496742	6.503258	3.744	4.429397			
11	35.858294	39.633643	11.030572	73.506394	26.493606	3.897	8.412355			
12	36.252378	38.793831	12.32313	46.07094	53.92906	4.042	28.05619			
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Amount of slag

Amount of solids (100-amount of liquid)

Step-2

Einstein-Roscoe Eq.

Thanks to
FactSage Steelmaking Consortium Members

posco

TATA STEEL

voestalpine

NUCOR

HYUNDAI STEEL

NIPPON STEEL

DOOSAN
Doosan Heavy Industries & Construction

SeAH Besteel

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SCHOTT
glass made of ideas

RHI MAGNESITA

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