Vanadium Partition Coefficient In Steel/Slag Melts FINAL REPORT

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MIME 572

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 = $\Upsilon_{V2O3} x_{V2O3}$
- $\log_{10}(\Upsilon_{V2O3}) = A/T + B$

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

Data

- 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

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

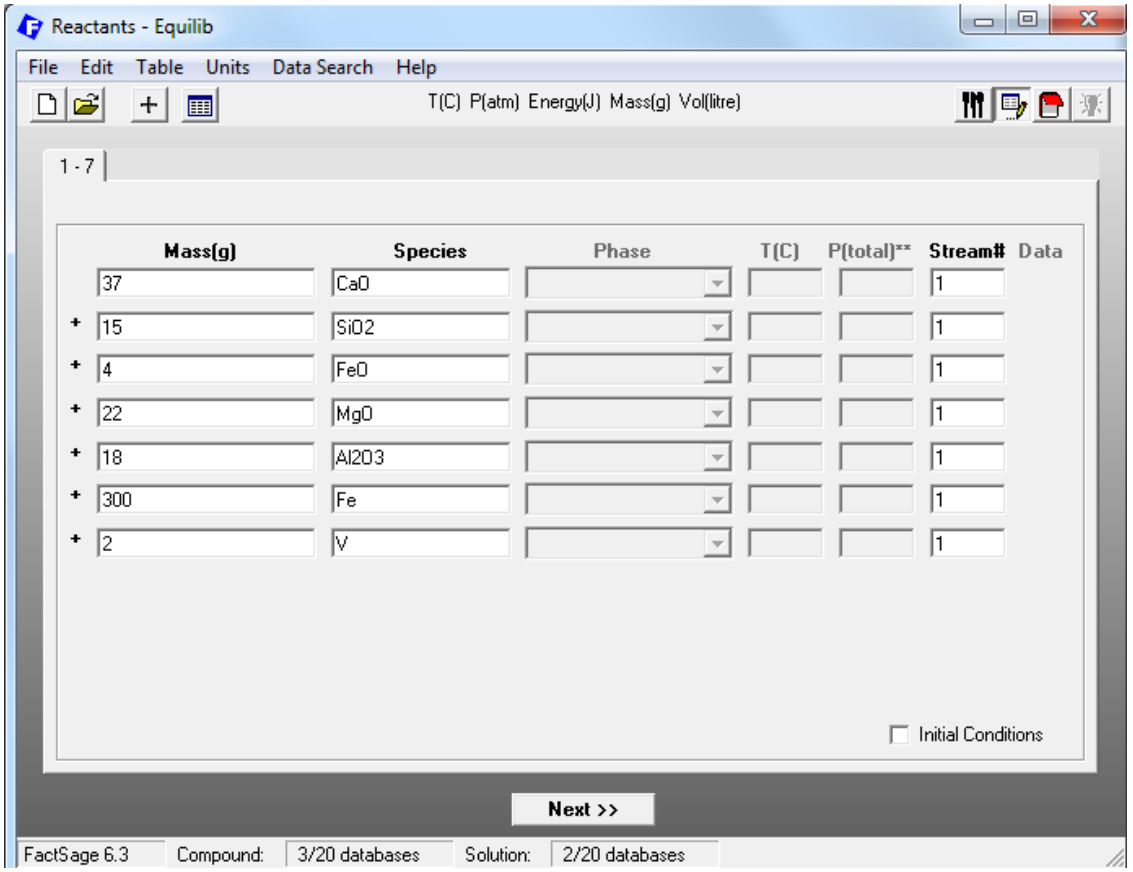
The amount of V in the slag was not considered. The same fixed amount of V was used for all equilibrium calculations and the subsequent calculation of Lv.

See Excel file for complete list of data

FactSage

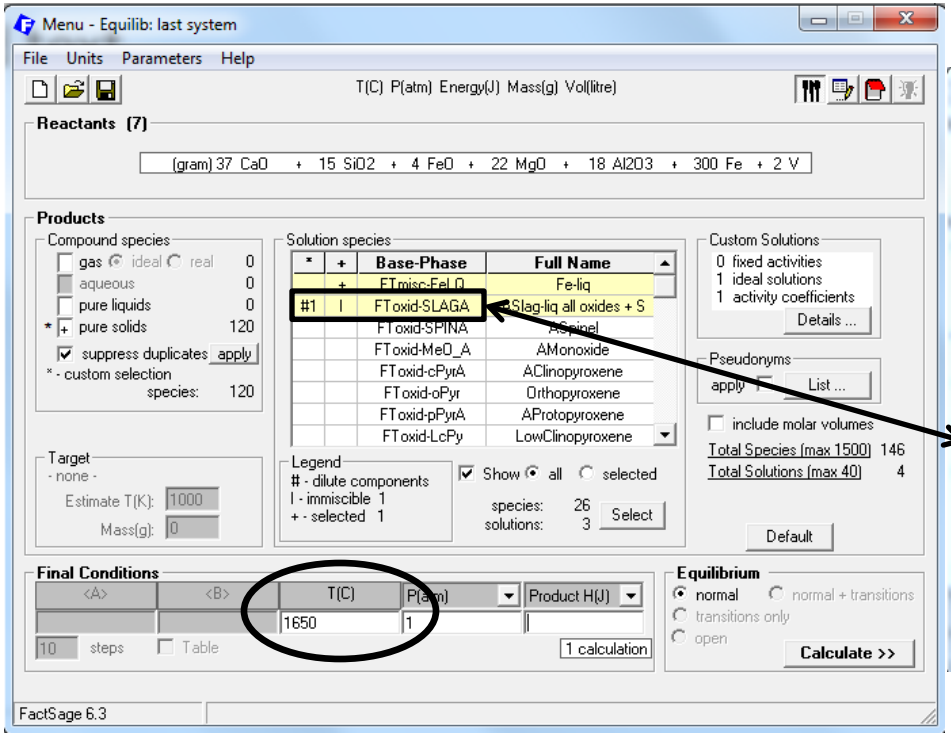
- Databases: FToxid, Ftmisc (FeLQ), FactPS
- Equilibrium
  - 100 g
    - x SiO_2
    - x CaO
    - x FeO
    - x Fe_2O_3
    - x MgO
  - 300 g Fe
  - 2 g V

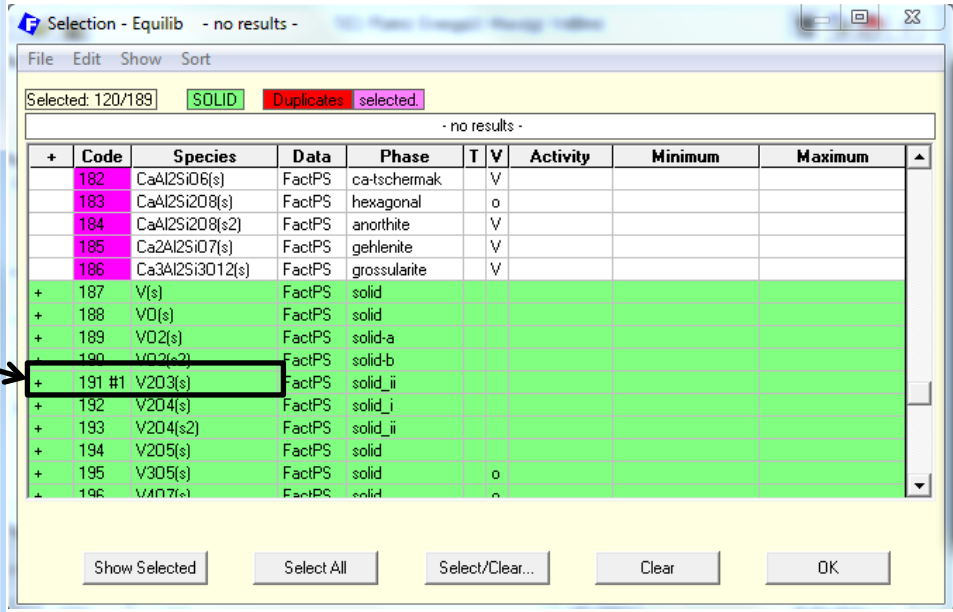
3:1 metal to slag ratio



FactSage

- Assume V in slag exists as V_2O_3

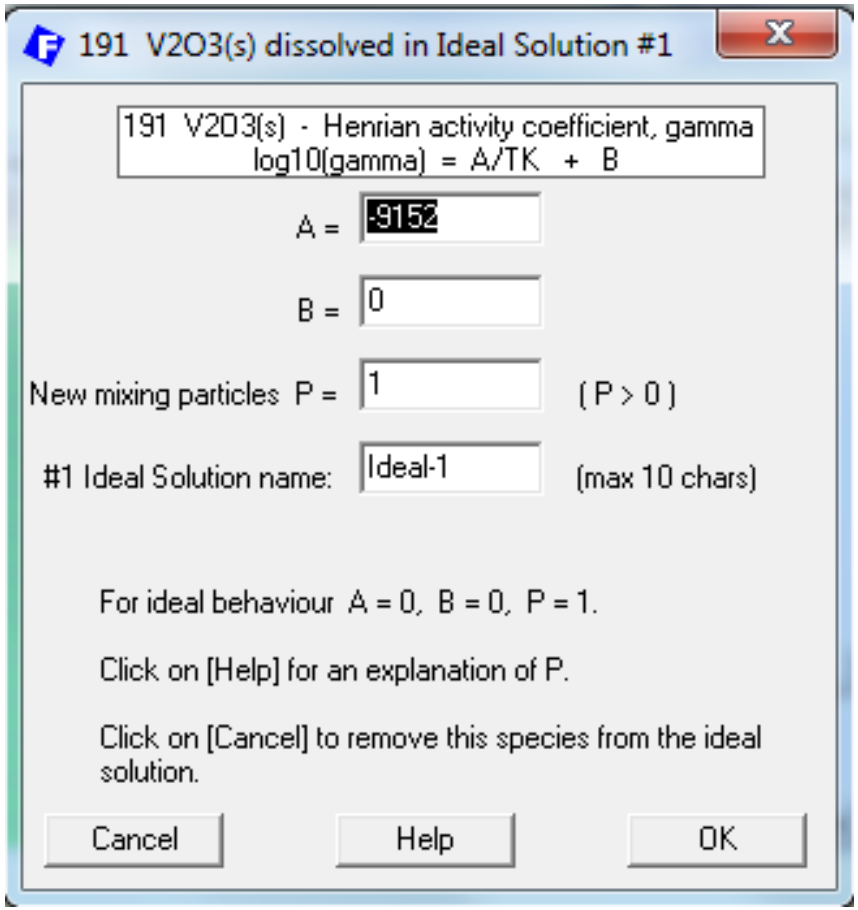


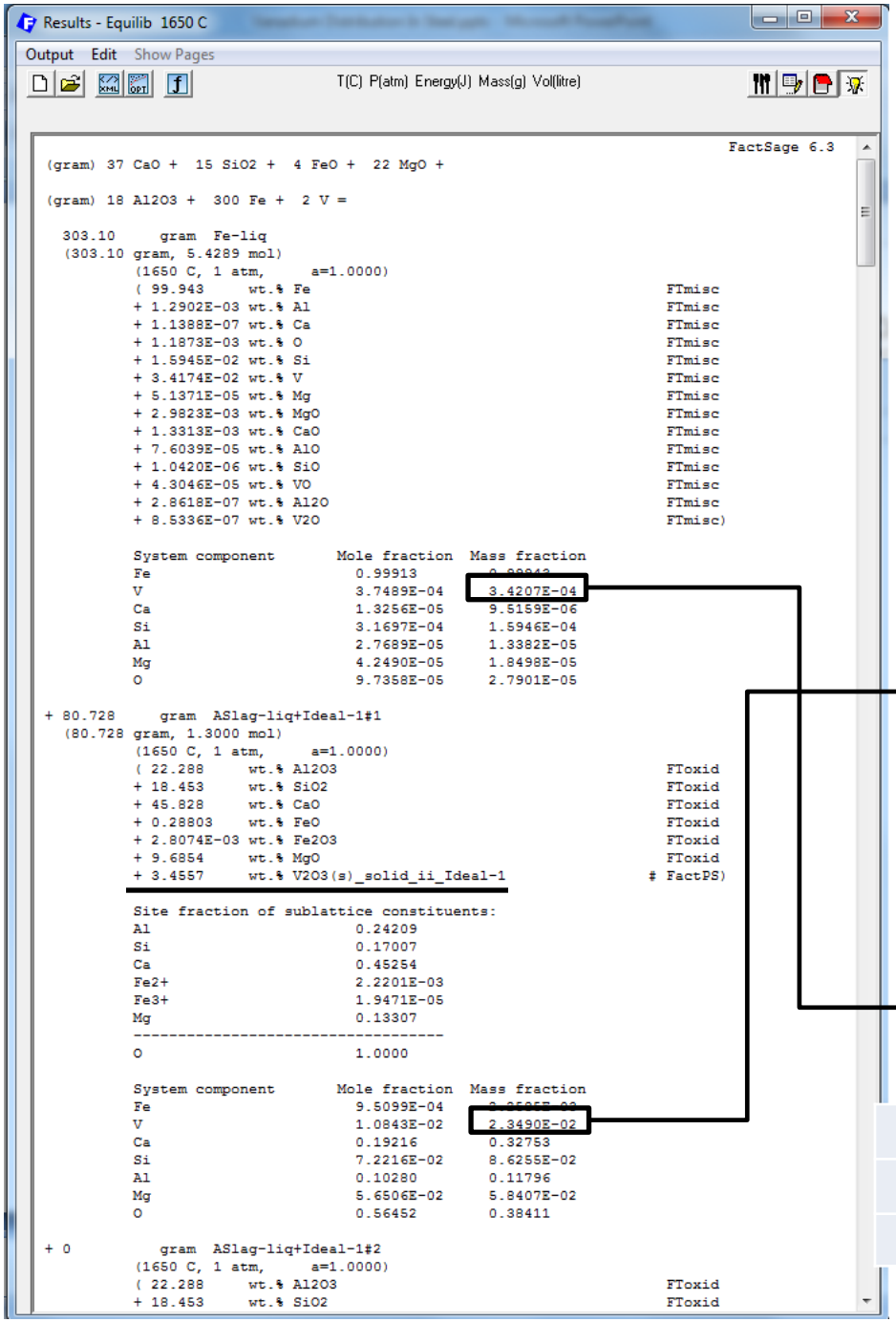


Solid V2O3 was considered because solid V2O3 is stable at these temperatures.

FactSage

- 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

$$L_v = \frac{(Wt\%\ V)}{[Wt\%\ V]} = 68.6$$

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

“A” Value to Activity Coefficient

	Slag (wt%)								
T (C)	(CaO)	(SiO2)	(FeO)	(Fe2O3)	(MgO)	(V)	Lv	A	ϒ
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

$\log_{10}(\Upsilon_{V2O3}) = A/T + B$

$\log_{10}(\Upsilon_{V2O3}) = -1025/1923$

$\Upsilon_{V2O3} = 10^{(-1025/1923)}$

$\Upsilon_{V2O3} = 0.293$

A more negative “A” value indicates a smaller activity coefficient.

See Excel file for complete list of data

Regression

- 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)

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

Regression Data

	Slag (wt%)					
T (K)	(CaO)	(SiO2)	(FeO + Fe2O3)	(MgO)	A	Lv
1923	27	28	23	19	-1025	410.1
1923	19	22	40	16	-1200	751.4
1923	29	15	43	10	-2175	1087.6
1923	8	13	56	22	-1100	850.6
1923	25	7	57	8	-2750	1510.0
1923	17	3	70	7	-2300	1439.3
1923	1	4	77	16	-1300	1142.9
1923	1	15	53	29	-750	705.9
1923	19	28	31	20	-1000	522.1
1923	28	22	35	13	-1475	761.7
1923	37	14	38	8	-2925	1174.2
1923	21	13	52	11	-1550	937.9
1923	31	7	52	7	-3175	1495.1
1923	0	1	89	8	-1000	1006.2
1923	1	7	76	14	-925	900.7
1873	35	33	13	17	-425	251.1
1873	29	30	24	16	-825	593.2
1873	30	22	35	11	-1375	1126.2
1873	21	22	40	17	-1000	944.9

FeO and Fe2O3 were combined together for the regression and temperature was converted to Kelvin.

See Excel file for complete list of data

Regression

Option #1

	Coefficients
Intercept	1459.929
X Variable 1	-112.467
X Variable 2	119.4452
X Variable 3	-12.421
X Variable 4	-125.999

Regression Statistics	
Adjusted R Square	0.793258

Option #2

	Coefficients
Intercept	10100.63
X Variable 1	-7.13591
X Variable 2	-51.6744
X Variable 3	132.7536
X Variable 4	31.25214
X Variable 5	-37.3305

Regression Statistics	
Adjusted R Square	0.88311

Option #2 has a better fit.

See Excel file for complete list of data

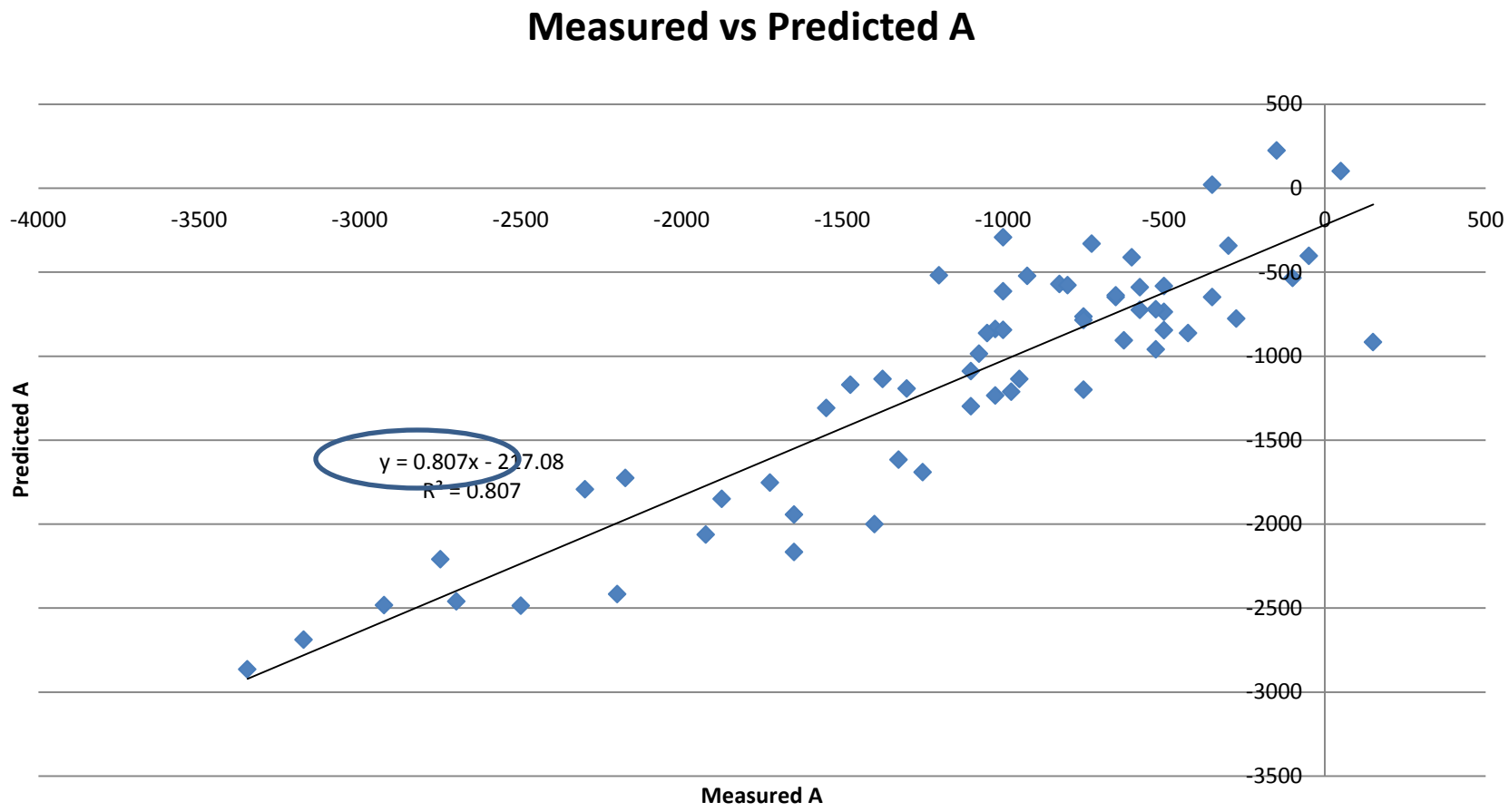
Predicted Lv – Regression #1

	Slag (wt%)								
T (C)	(CaO)	(SiO2)	FeO	Fe2O3	(MgO)	A	Lv	Predicted A	Predicted Lv
1650	27	28	21	2	19	-1025	410	-839	369
1650	19	22	36	4	16	-1200	751	-520	
1650	29	15	36	6	10	-2175	1088	-1726	836
1650	8	13	52	4	22	-1100	851	-1299	
1650	25	7	47	11	8	-2750	1510	-2209	1102
1650	17	3	58	12	7	-2300	1439	-1793	
1650	1	4	71	6	16	-1300	1143	-1193	1073
1650	1	15	50	3	29	-750	706	-1201	
1650	19	28	29	2	20	-1000	522	-292	342
1650	28	22	30	4	13	-1475	762	-1172	
1650	37	14	31	8	8	-2925	1174	-2484	905
1650	21	13	46	6	11	-1550	938	-1310	
1650	31	7	40	13	7	-3175	1495	-2689	1121
1650	0	1	82	6	8	-1000	1006	-614	
1650	1	7	71	5	14	-925	901	-523	707
1600	35	33	12	2	17	-425	251	-863	
1600	29	30	22	2	16	-825	593	-572	504
1600	30	22	31	4	11	-1375	1126	-1136	
1600	21	22	36	4	17	-1000	945	-844	854
1600	31	14	39	8	8	-1875	1332	-1850	

The “A” values predicted by the model were used in FactSage to calculate the corresponding predicted Lv (for half the data points for simplicity)

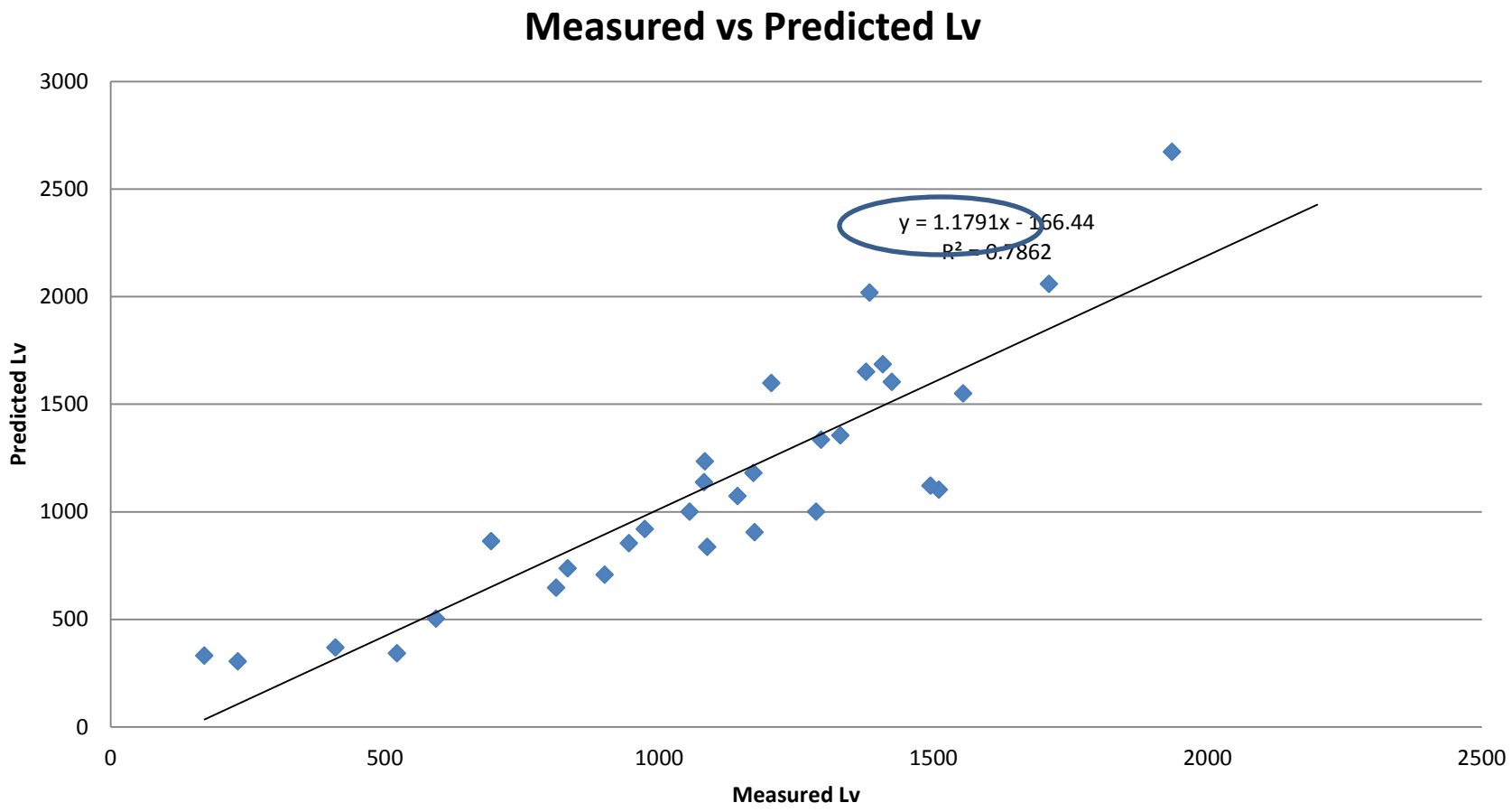
See Excel file for complete list of data

Measured vs Predicted A – Regression #1



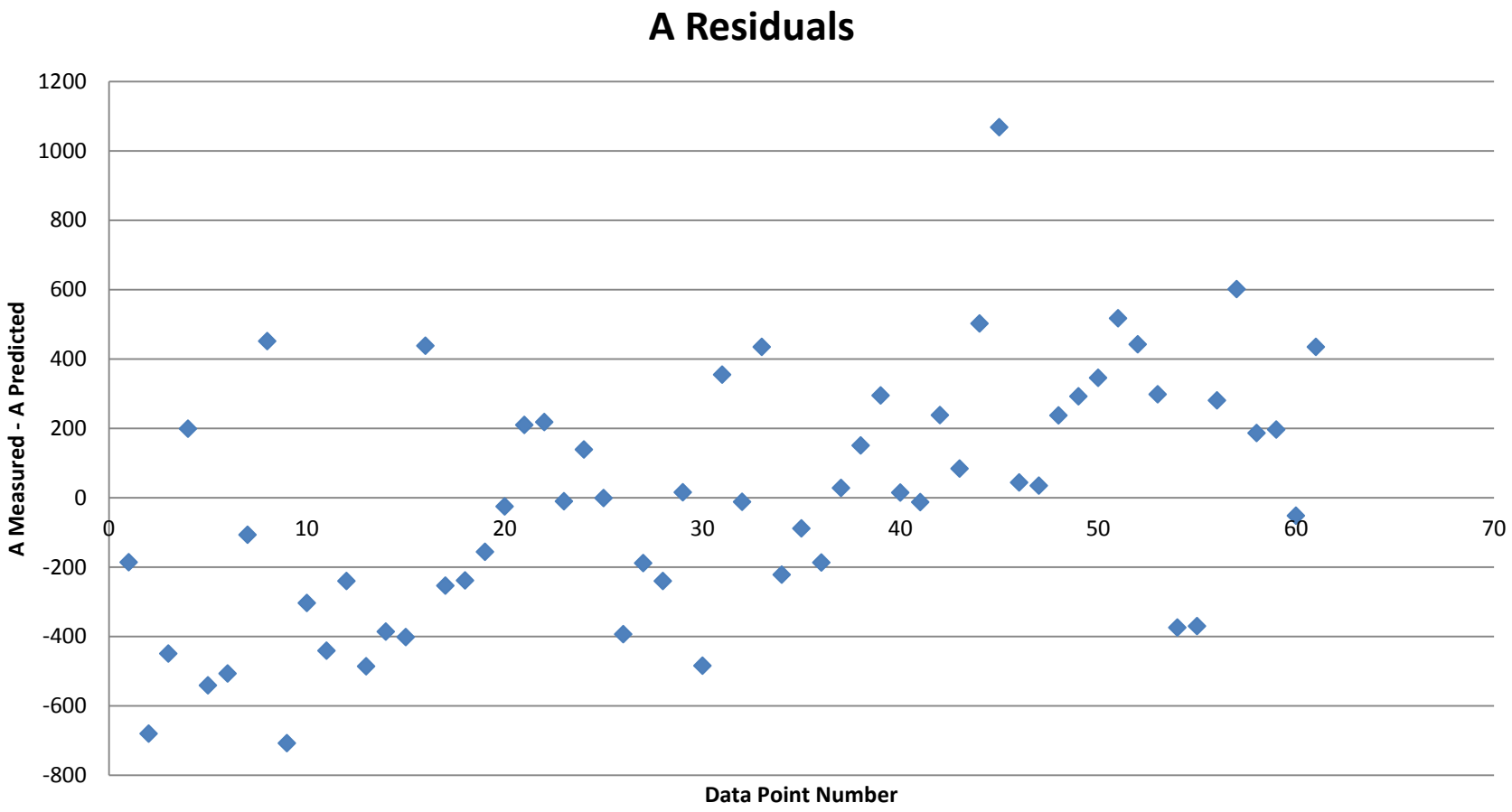
A slope of 1 would indicate that the measured and predicted “A” values are the same. In this case, the model slightly underestimates the measured “A” value.

Measured vs Predicted Lv – Regression #1



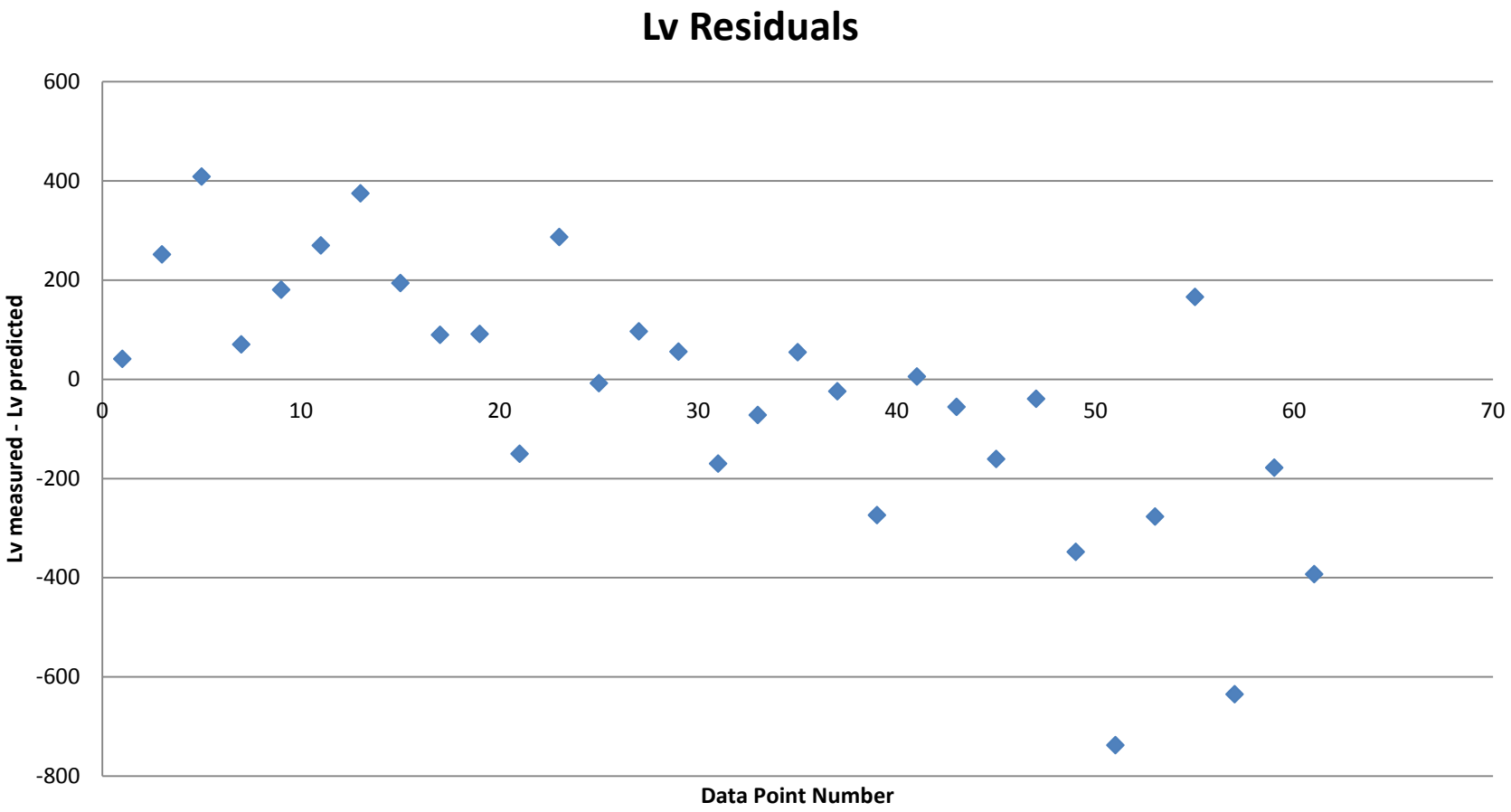
A slope of 1 would indicate that the measured and predicted Lv values are the same. In this case, the model slightly overestimates the measured Lv value.

Residuals Plot – Regression #1



This plot shows that the residuals of “A” are centered around 0 and randomly distributed.

Residuals Plot – Regression #1



This plot shows that the residuals of Lv are centered around 0, although there seems to be a decreasing trend towards lower temperatures (higher data point numbers)

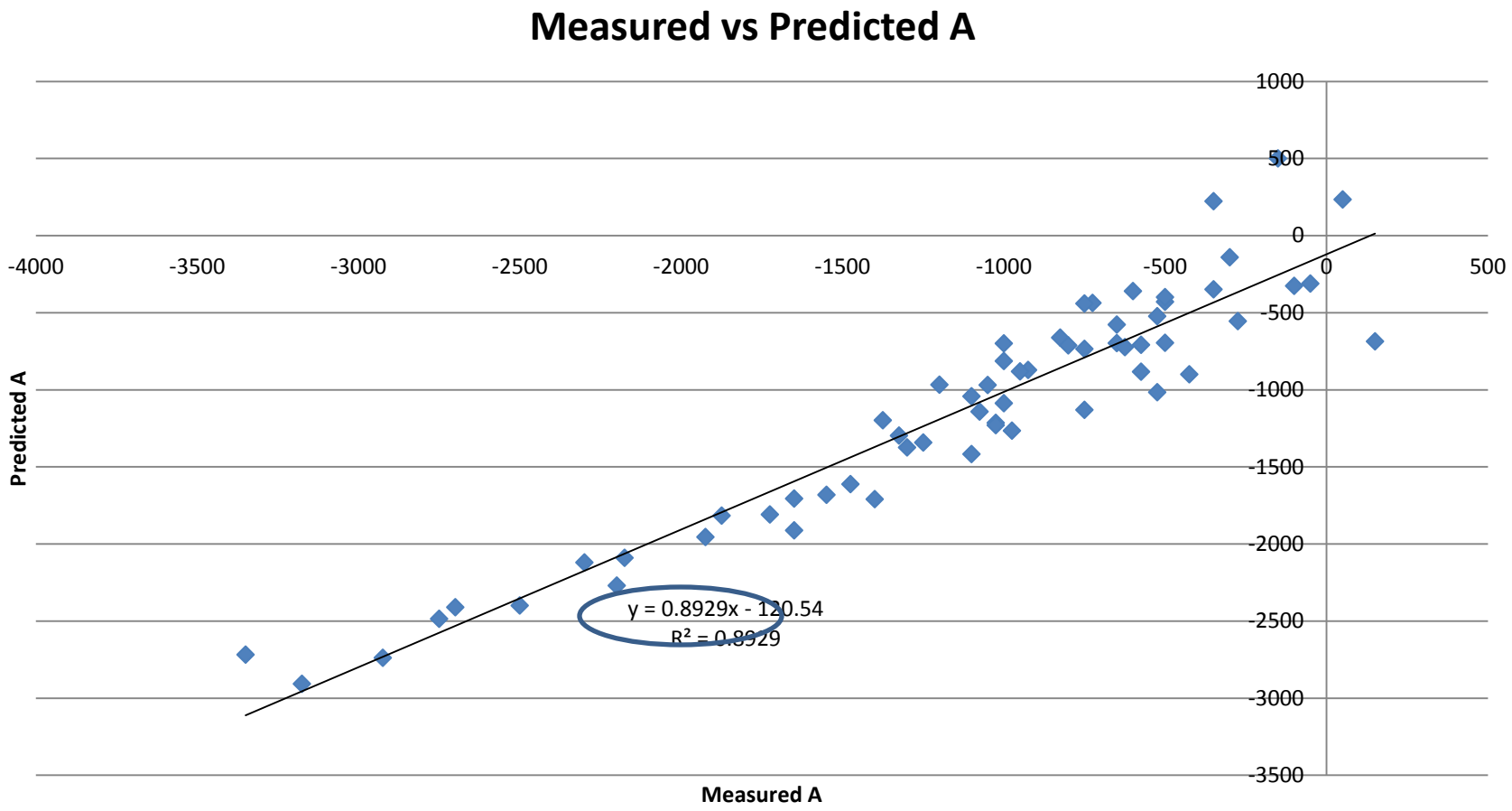
Predicted Lv – Regression #2

	Slag (wt%)								
T (C)	(CaO)	(SiO2)	FeO	Fe2O3	(MgO)	A	Lv	Predicted A	Predicted Lv
1650	27	28	21	2	19	-1025	410	-1216	462
1650	19	22	36	4	16	-1200	751	-968	
1650	29	15	36	6	10	-2175	1088	-2091	1039
1650	8	13	52	4	22	-1100	851	-1417	
1650	25	7	47	11	8	-2750	1510	-2486	1296
1650	17	3	58	12	7	-2300	1439	-2120	
1650	1	4	71	6	16	-1300	1143	-1374	1195
1650	1	15	50	3	29	-750	706	-1132	
1650	19	28	29	2	20	-1000	522	-699	435
1650	28	22	30	4	13	-1475	762	-1612	
1650	37	14	31	8	8	-2925	1174	-2739	1050
1650	21	13	46	6	11	-1550	938	-1683	
1650	31	7	40	13	7	-3175	1495	-2909	1275
1650	0	1	82	6	8	-1000	1006	-1089	
1650	1	7	71	5	14	-925	901	-873	869
1600	35	33	12	2	17	-425	251	-900	
1600	29	30	22	2	16	-825	593	-662	534
1600	30	22	31	4	11	-1375	1126	-1198	
1600	21	22	36	4	17	-1000	945	-814	840
1600	31	14	39	8	8	-1875	1332	-1818	

The “A” values predicted by the model were used in FactSage to calculate the corresponding predicted Lv (for half the data points for simplicity)

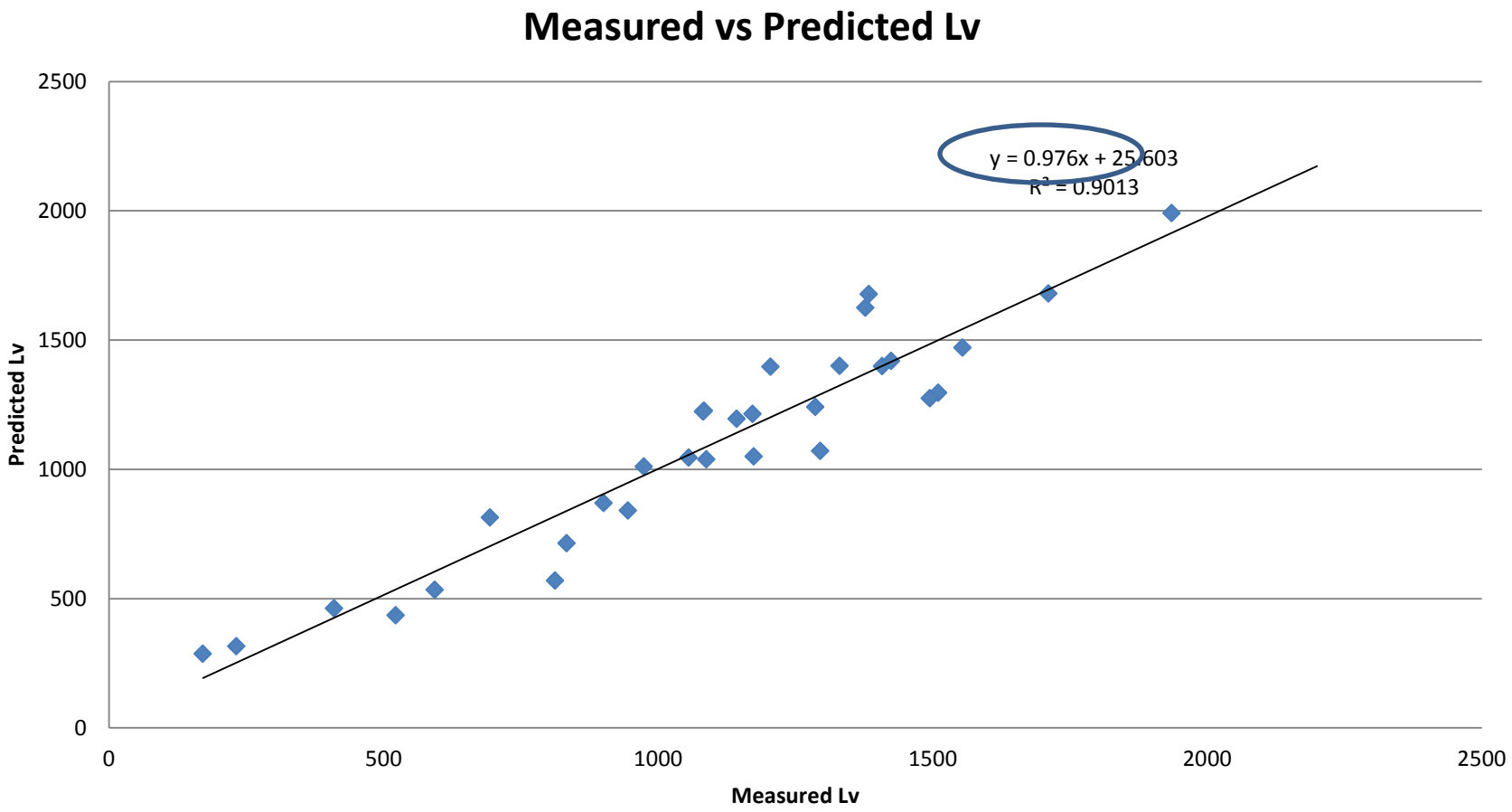
See Excel file for complete list of data

Measured vs Predicted A – Regression #2



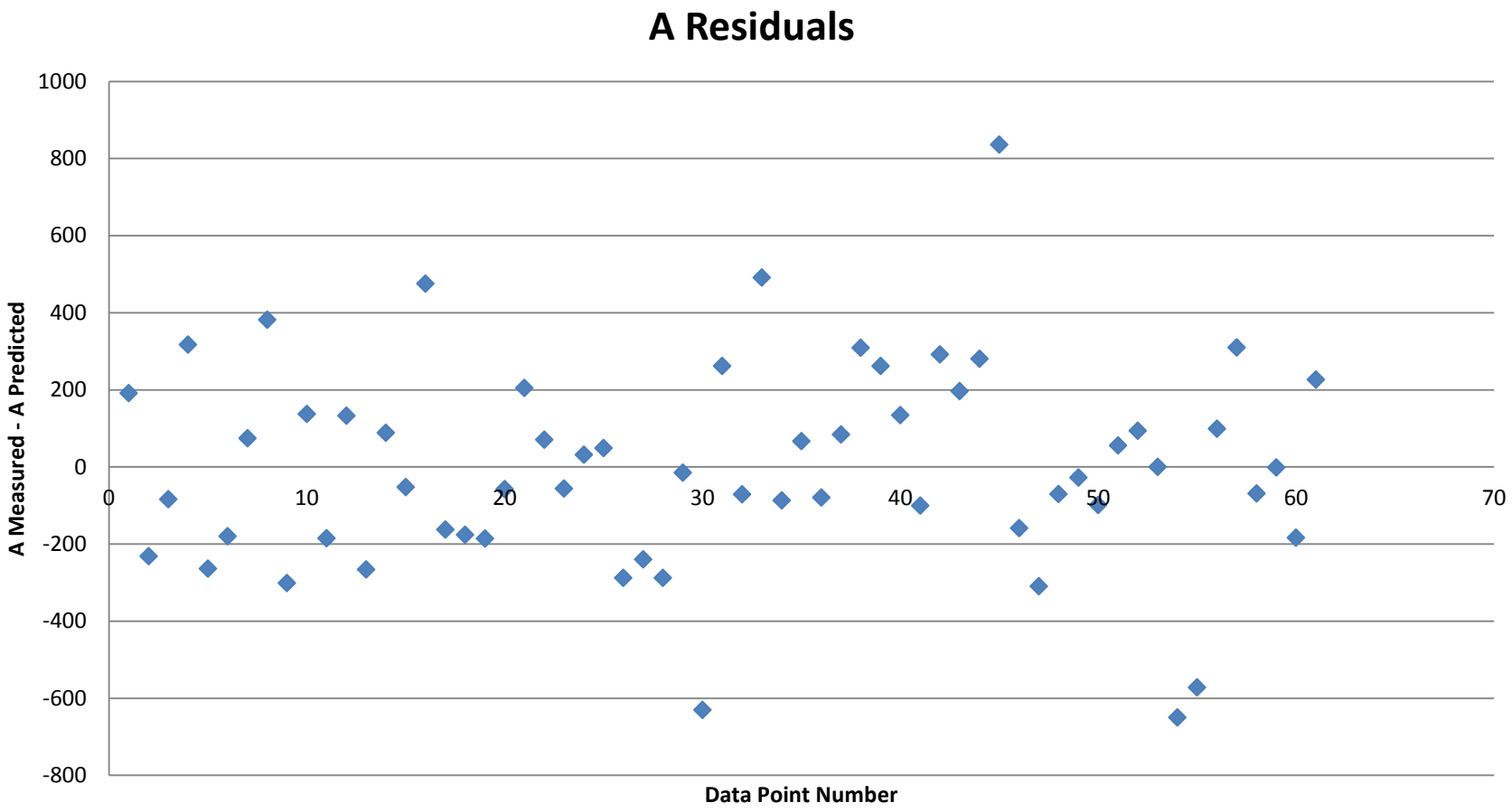
A slope of 1 would indicate that the measured and predicted “A” values are the same. In this case, the model slightly underestimates the measured “A” value, but it is closer to 1 than regression #1

Measured vs Predicted Lv – Regression #2



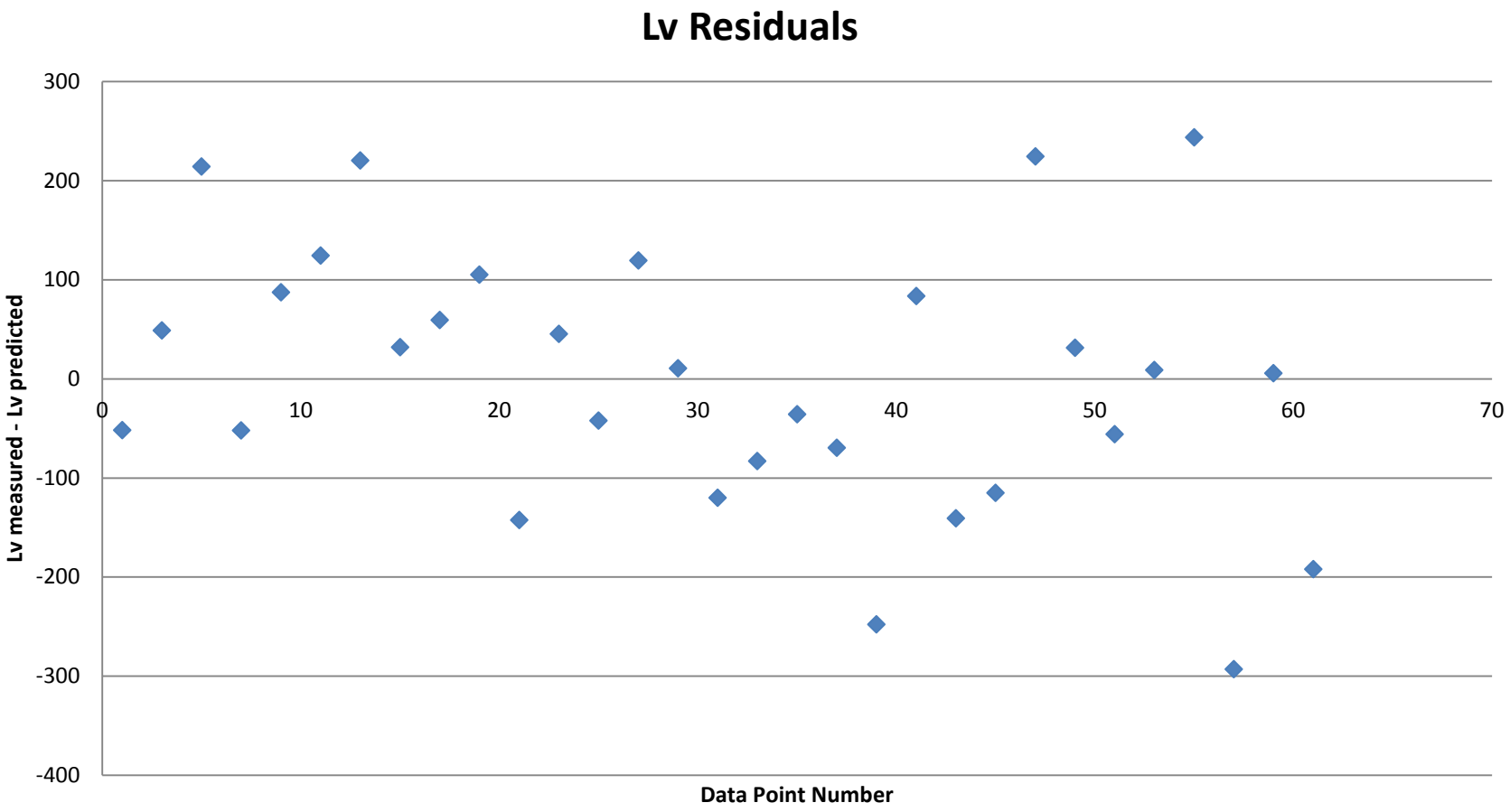
A slope of 1 would indicate that the measured and predicted Lv values are the same. In this case, the model slightly underestimates the measured Lv value, but it is much closer to 1 than regression #1

Residuals Plot – Regression #2



This plot shows that the residuals of “A” are smaller than regression #1 , centered around 0 and are randomly distributed.

Residuals Plot – Regression #2



This plot shows that the residuals of Lv are smaller than regression #1, are centered around 0 and randomly distributed, instead of a decreasing trend like in regression #1.

Final Results

- 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!