

Experimental Determination of Activity of FeO, MnO and Cr₂O₃ in Slags

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Abstract

To appropriately design synthetic slags for secondary steel making treatments, activity of components is required.

Experimental determination of activity of FeO, MnO and Cr₂O₃ in synthetic slags containing CaO, Al₂O₃, and SiO₂ was carried out in selected range of slag composition specific for ladle refining of carbon and stainless steel.

Activity was determined by equilibrating the oxide of metal X (X=Fe, Mn, Cr) in slag, the metal X dissolved in solid platinum and a gas phase at fixed oxygen potential.

Results of activity measurements as a function of oxide concentration and slag composition are presented.

The results show a clear difference in the behaviour of the different oxides: FeO, MnO and Cr₂O₃.

In the range of composition studied it is found that the MnO activity increases nearly linearly with MnO concentration and is not significantly affected by base slag composition. FeO and Cr₂O₃ activities does not vary linearly with concentration and the dependence is different for different base slag composition and SiO₂ content affects activity of FeO and Cr₂O₃ in a different way for the different base slags

The relationships between oxide activity and slag composition provide the necessary data to design slag composition for different secondary steel making refining processes.

1. Introduction

For the production of clean steel the control of slag composition and properties is a basic prerequisite in all ladle refining practices. In particular slag components like FeO, MnO and Cr_2O_3 are the main responsible in determining the oxygen activity in metal, thus playing a crucial role in deoxidation and desulphurisation processes and in picking-up of inclusions. To improve slag engineering for refining operations thermodynamic data are necessary.

In the present work the main goal was to measure activity of reducible oxides in a set of slags, chosen in a range of composition of great interest for secondary steel making treatments. The influence of slag composition on oxide activity for a selected set of slags is determined; this information can be directly used to design appropriate synthetic slags or to develop models of ladle and tundish processes. Moreover the experimental data can be used to assess and improve the reliability of thermodynamic models of slag.

2. Systems investigated

A set of synthetic slags of base composition $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ (henceforth called master slags) containing different and low amounts of X_mO_n ($\text{X}=\text{Fe}$, Mn and Cr) was identified representing typical slags used in ladle treatments for carbon and stainless steels.

The composition of the master slags is reported in Table 1 and on ternary diagram in Figure 1 [1].

3. Experimental

3.1. Method, apparatus and procedures

Activity measurements were performed by an equilibration method; the equilibrium was realised between the reducible oxides FeO, MnO and Cr_2O_3 (pure or in slag phase) with the corresponding metal in solid platinum under fixed oxygen potential.

The experiments were performed in a Thermobalance apparatus by a procedure consisting of two steps.

Step 1

The relationship between activity and concentration of X in a X/Pt alloy is determined as follows.

Pure X_mO_n and platinum are equilibrated under a gas phase of fixed oxygen potential at fixed temperature.

The oxygen activity in the gas phase is fixed by means of a CO_2/H_2 mixture, of appropriate composition, which depends on the needed oxygen activity.

The temperature is fixed at 1600 °C.

The X activity in the X/Pt alloy is calculated from the corresponding equilibrium constant for the reaction:

X_mO_n (activity 1) \rightarrow mX (in X/Pt alloy; activity to be calculated) + $n/2 O_2$ (fixed activity)

The equilibrium constant of reaction K is expressed as:

$$K = (a_X)^m \cdot (P_{O_2})^{n/2} / a_{X_mO_n} \quad (1)$$

The X concentration in X/Pt alloy is determined by the mass loss of the sample, during the experiment, under the assumption that oxygen only is lost; this assumption is reasonable being in general the vapour pressure of X at 1600 °C negligible.

In this way, the relationship between concentration and activity of X in platinum are determinate for the chosen temperature.

Chemical analysis of both platinum crucible and material contained in it after the experiments confirmed that the mass loss is consistent with amount of metal dissolved in platinum and that no separate metal remains in the crucible.

In the present work, experimental determination of activity of X in platinum was performed only when data were not available in literature.

Step 2

In different experiments, slags of different X_mO_n contents are equilibrated with platinum at different oxygen activity in the gas phase (again fixed by a CO_2/H_2 mixture).

To obtain a slag containing X_mO_n one of the master slag shown in Table 1 is molten in platinum crucible together with pure X_mO_n and pure X . Depending on the oxygen potential in the gas atmosphere, some X_mO_n is reduced to X or *vice versa*. Metallic X is dissolved in platinum, while X_mO_n is dissolved in slag.

From the initial masses of slag, X and X_mO_n , and the mass variation during the experiment, the X content in X/Pt and X_mO_n concentration in slag are determined.

From the concentration of X , the corresponding activity of X is deduced by means of the relationship obtained in the first step.

Knowing activity of X and oxygen activity in the gas (defined by the gas composition and temperature), by means of the equilibrium constant, the activity of X_mO_n in slag is calculated.

Also in this case, chemical analysis of slag and platinum confirmed the concentration values obtained by the mass losses.

The experiment is performed under a gas stream of the mixture having the chosen oxygen potential.

The apparatus used is a Netzsch thermobalance (Netzsch STA 409), equipped with gas flow meters and sensor for gas phase oxygen potential.

The starting materials are pure oxides and metals, analytical grade, in platinum crucible.

The gas mixture (CO_2 and H_2) having the chosen oxygen potential is prepared by mixing the appropriate proportion of the components directly.

The gases react inside the furnace producing a mixture of CO , CO_2 , H_2 , and H_2O . The equilibrium gas/metal/oxide/platinum at the furnace temperature is reached if the gas is allowed to remain inside the furnace for the necessary time. The residence time depends on the gas flow rate. A set of trials, with different gas flow rates, permitted to define a flow rate of $0.5 \text{ cm}^3/\text{s}$ as the maximum value to be used for achieving the equilibrium.

To check the value of O_2 activity in the gas an electrochemical sensor was used, namely Yttria stabilized Zirconia solid electrolyte [2, 3].

On line monitoring of the O_2 activity in the gas in contact with the sample has been performed during the experiments is possible.

4. Results

4.1. Determination of FeO activity

FeO activity was measured in master slags with FeO concentration ranging up to about 5% by mass.

The reason for choosing this low concentration range is twofold: the data are relevant for secondary metallurgy treatments using synthetic slags and are scarce in this range.

The results of FeO activity measurements are reported in Tables 2 and 3.

In Table 10 activity of FeO at about 1% by mass is reported, measured for all the eight master slags, showing the effect of master slag composition on FeO activity.

A synthetic representation of the results reported in Table 2 is shown in Figure 2, where the composition of the master slags is represented in a bar diagram.

The effect of different basicity indexes on FeO activity, for the whole set of master slags, is shown in Figure 3. In this figure (and in similarly in what follows) polynomial least square fitting of experimental data has been used to emphasise the trend.

In Table 3, FeO activity measured at different FeO concentration in master slag 3 is reported. Master slag 3 is representative of target slag to be used in carbon steel secondary refining.

Figure 4 shows in a diagram form the results of Table 3.

4.2. Determination of MnO activity

Table 4 and Figure 5 show the activity of MnO as a function of MnO concentration in the whole set of master slags.

4.3. Determination of Cr_2O_3 activity

The measured activities of Cr_2O_3 are shown in Tables 5 and Figure 6.

The influence of slag composition on Cr_2O_3 activity for concentration of 5%, 10%, and 15% is shown in Figure 7; the values at the exact concentration 5%, 10%, and 15% have been obtained interpolating the experimental values of Table 5.

The effect of different basicity indexes on FeO activity, for the whole set of master slags, is shown in Figures 8, 9 and 10.

4. Conclusion

Activity of FeO, MnO and Cr₂O₃, as function of concentration, have been measured in synthetic slags of base system CaO-Al₂O₃-SiO₂ in a selected range of composition, corresponding to typical slags used in ladle refining operations.

The results show a clear difference in the behaviour of the different oxides: FeO, MnO and Cr₂O₃.

In the range of composition studied it is found that:

- MnO activity increases nearly linearly with MnO concentration
- activity of MnO is not significantly affected by base slag composition
- FeO and Cr₂O₃ activities does not vary linearly with concentration and the dependence is different for different base slag composition and
- SiO₂ content affects activity of FeO and Cr₂O₃ in a different way for the different base slags

The relationships between oxide activity and slag composition provide the necessary data to design slag composition for different secondary steel making refining processes.

References

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2. B. Krafthefer et al.; "Life and performance of ZrO₂-Based Oxygen sensors"
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3. J. Fouletier, E. Siebert and A. Caneiro; "Accurate Monitoring of Low Oxygen Activity in Gses with Conventional Oxygen Gauges and Pumps"
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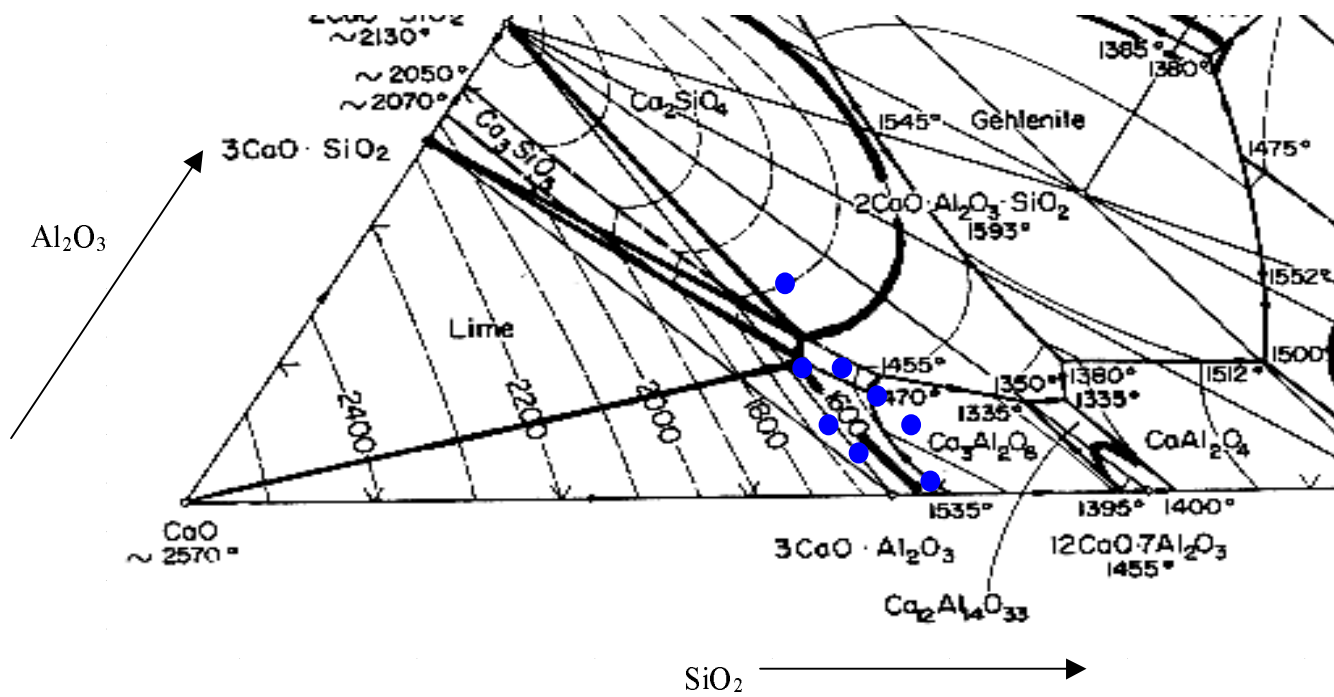
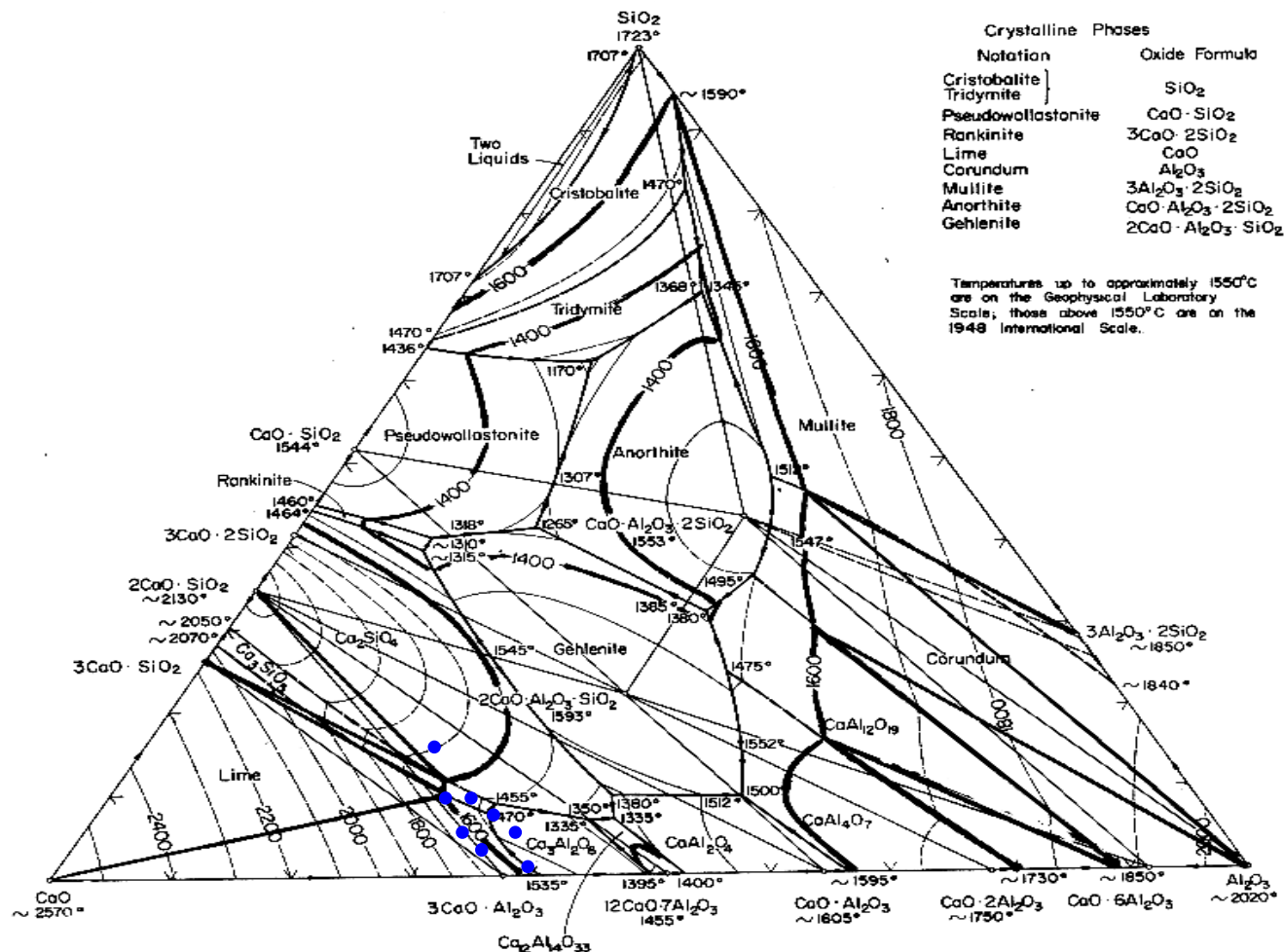


Figure 1. Composition of master slags reported on ternary diagram CaO-Al₂O₃-SiO₂ [1].

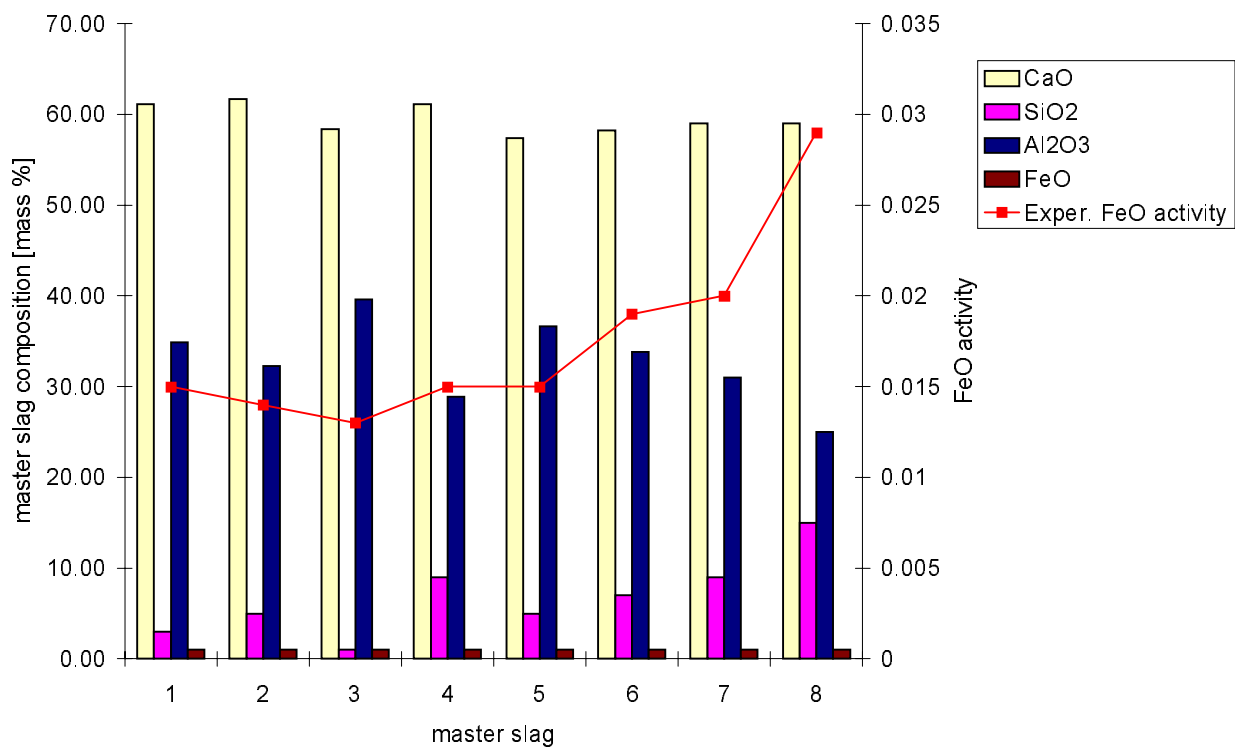


Figure 2. Experimental activity of FeO in synthetic slags at different compositions (FeO concentration is in all the slags near 1% in mass. Temperature 1600 °C; standard state pure 'FeO')

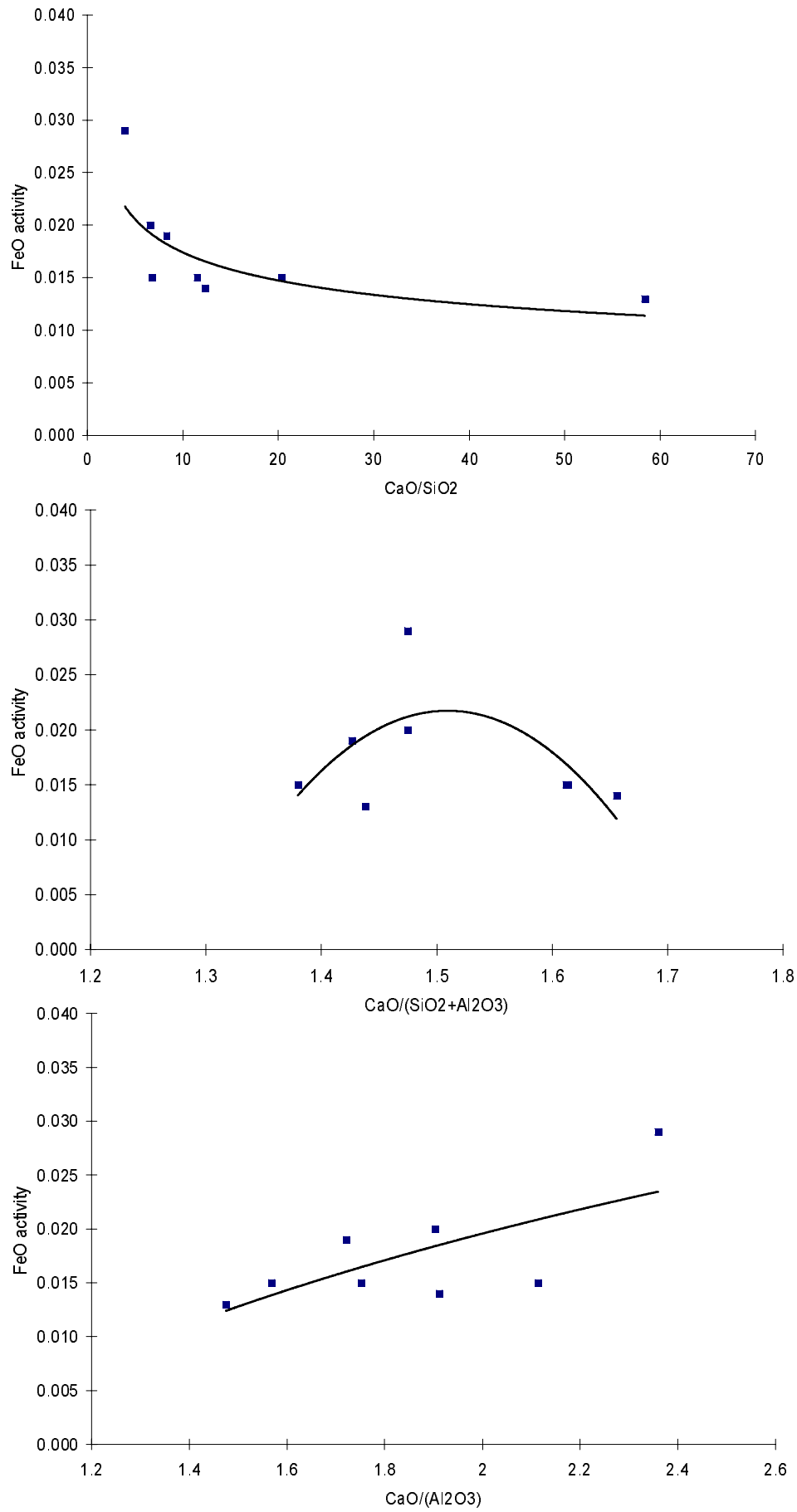


figure 3. FeO activity as a function of CaO/SiO_2 , $\text{CaO}/(\text{SiO}_2 + \text{Al}_2\text{O}_3)$, and $\text{CaO}/\text{Al}_2\text{O}_3$ ratios. Temperature 1600 °C; standard state pure 'FeO'

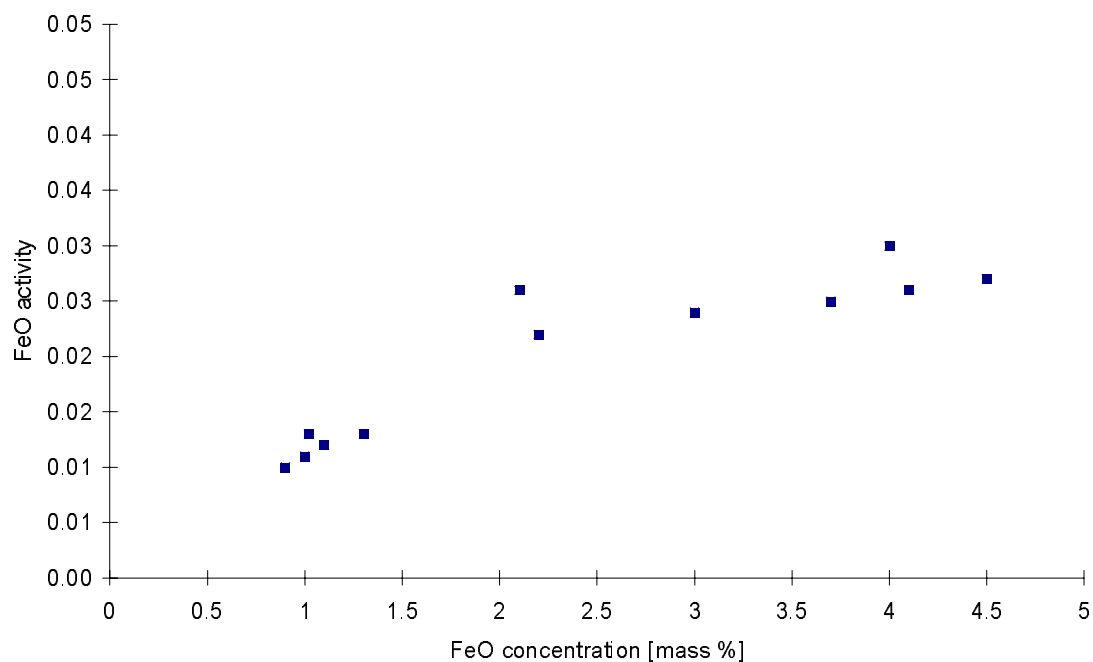


Figure 4. FeO activity as a function of FeO concentration (master slag number 3). Temperature 1600 °C; standard state pure 'FeO'.

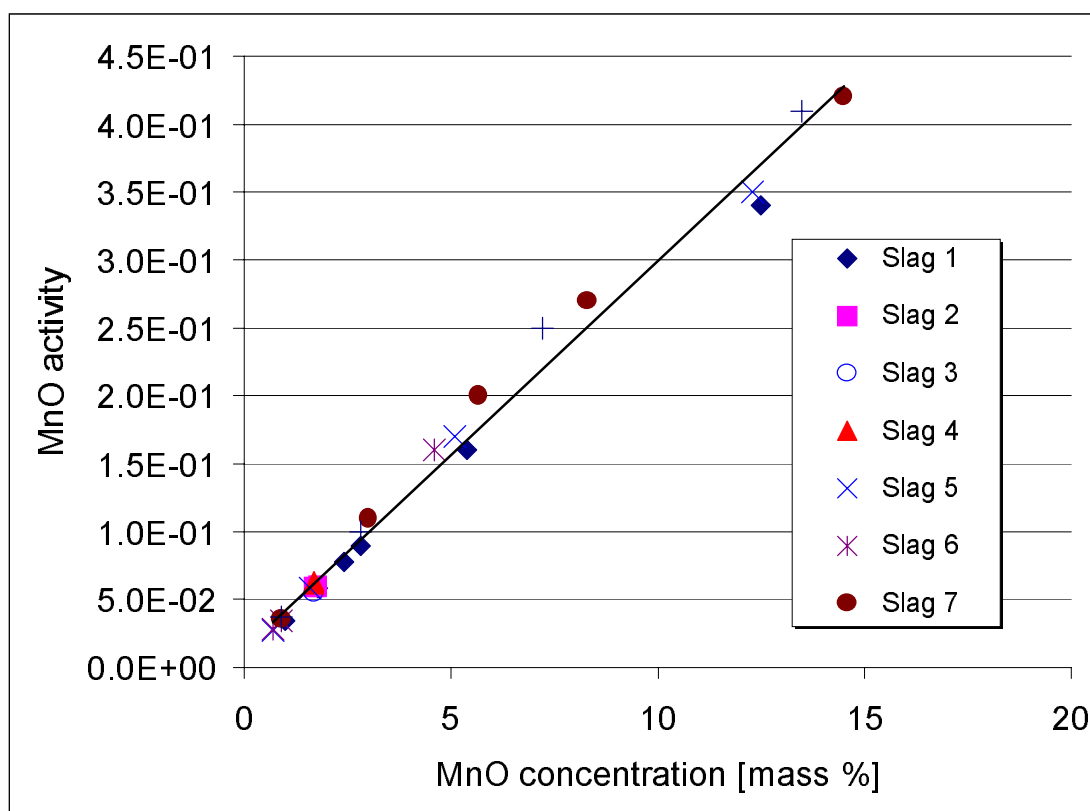


Figure 5. MnO activity as a function of MnO concentration measured along the whole set of master slags. Temperature: 1600 °C; MnO standard state: pure 'MnO'.

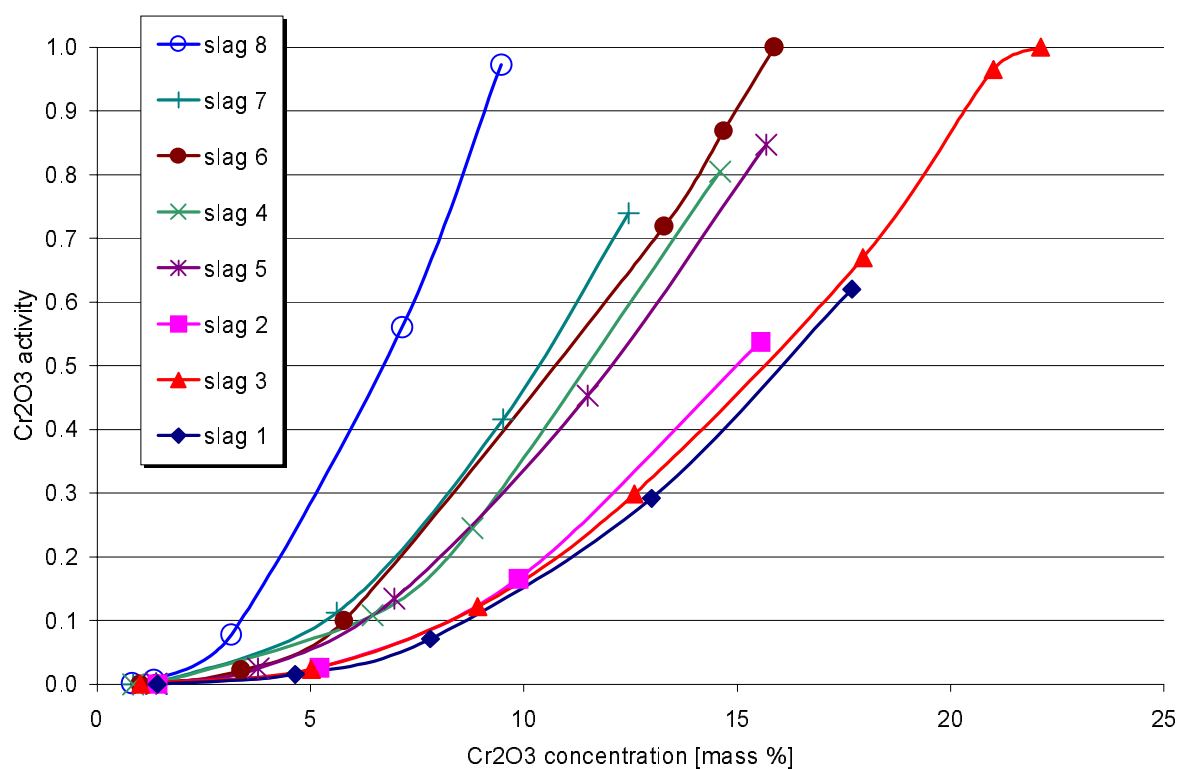


Figure 6. Cr_2O_3 activity as a function of Cr_2O_3 concentration measured in the whole set of master slags. Temperature: 1600 °C; Cr_2O_3 standard state: pure ' Cr_2O_3 '

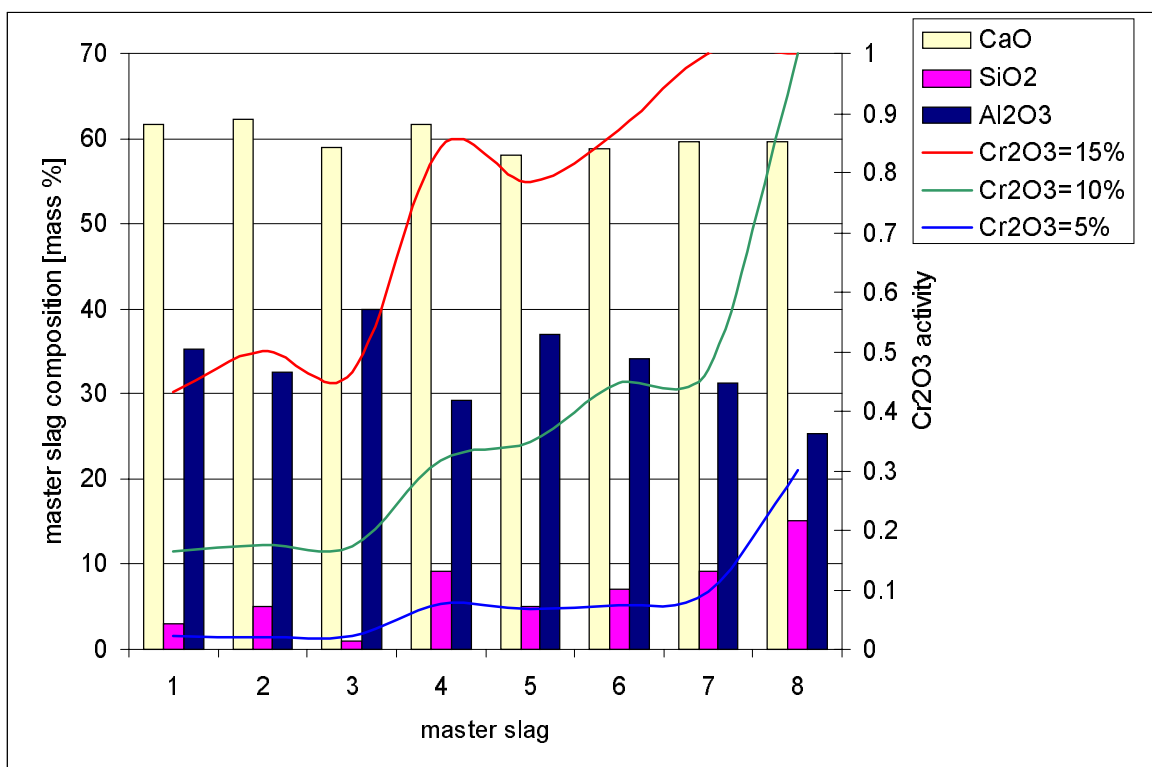


Figure 7. Cr_2O_3 activity measured in synthetic slags at different Cr_2O_3 concentration reported together with the concentration of master slags (see Table 1) from which the slags are obtained. Temperature: 1600 °C; Cr_2O_3 standard state: pure ' Cr_2O_3 '.

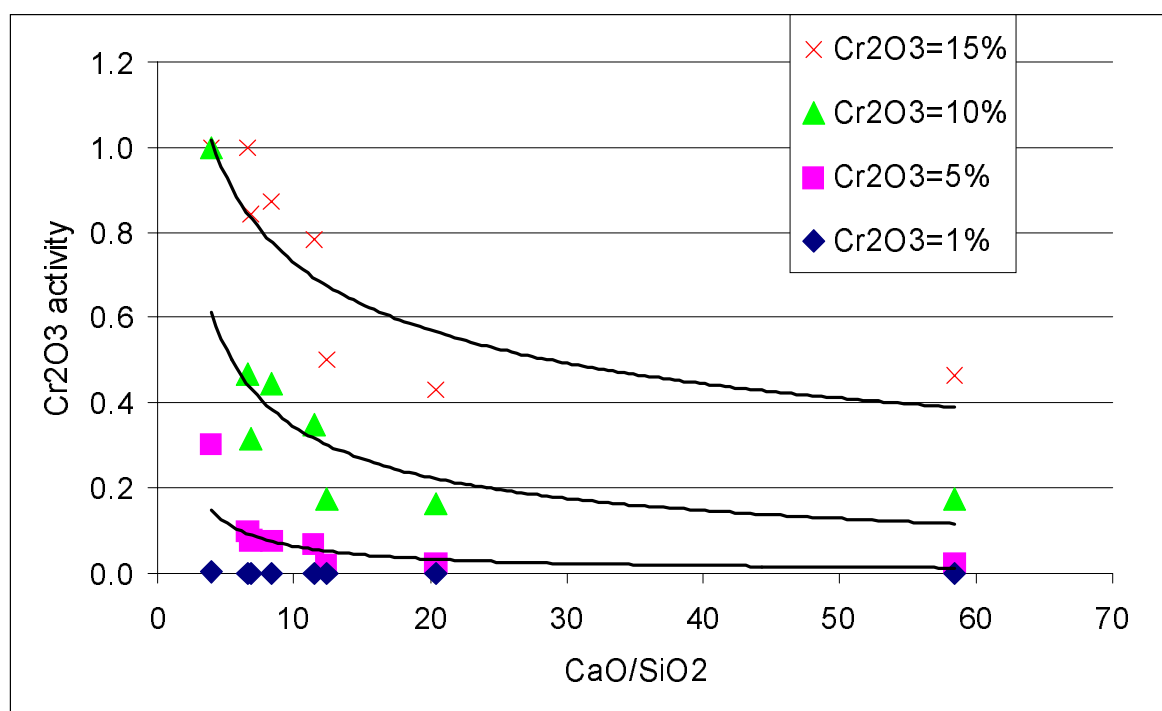


Figure 8. Cr_2O_3 activity as a function of CaO/SiO_2 mass ratio in slags at different Cr_2O_3 concentration. Temperature: 1600 °C; Cr_2O_3 standard state: pure ' Cr_2O_3 '.

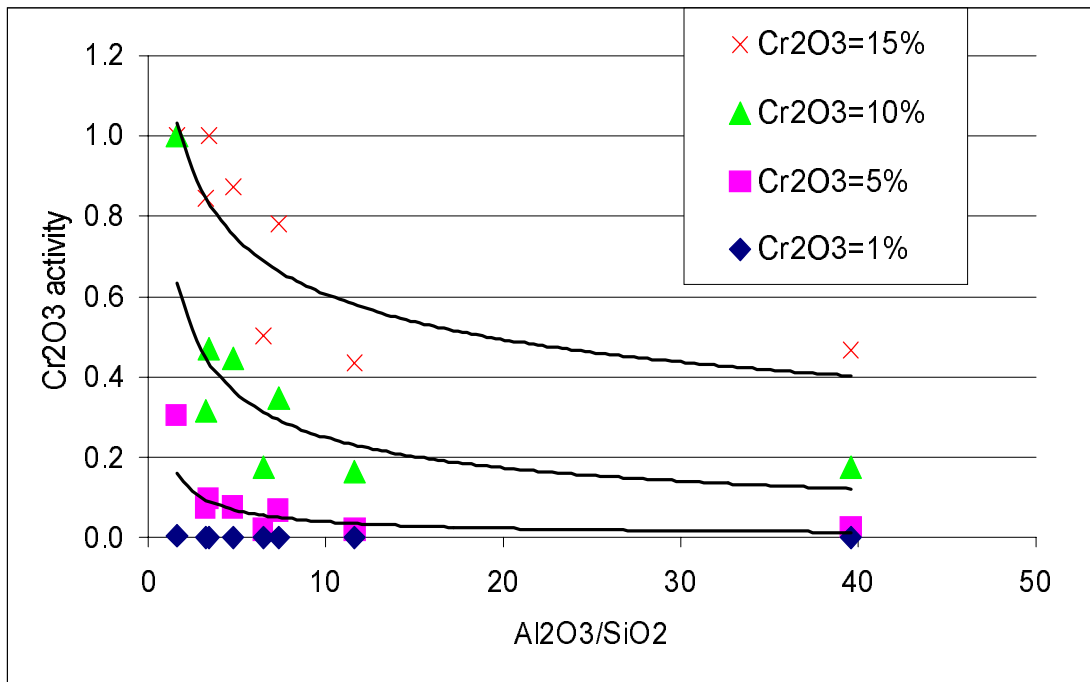


Figure 9. Cr_2O_3 activity as a function of $\text{Al}_2\text{O}_3/\text{SiO}_2$ mass ratio in slags at different Cr_2O_3 concentration. Temperature: 1600 °C; Cr_2O_3 standard state: pure ' Cr_2O_3 '.

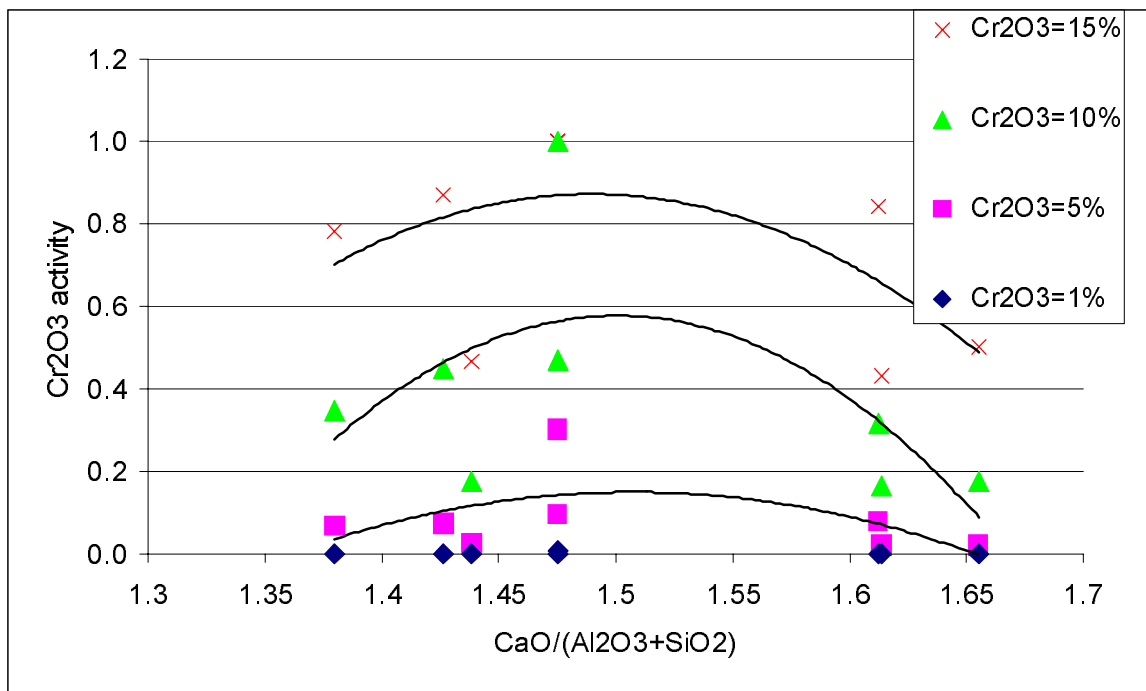


Figure 10. Cr_2O_3 activity as a function of $\text{CaO}/(\text{Al}_2\text{O}_3 + \text{SiO}_2)$ mass ratio in slags at different Cr_2O_3 concentration. Temperature: 1600 °C; Cr_2O_3 standard state: pure ' Cr_2O_3 '.

Table 1. Composition of synthetic master slags

Slag N.	1	2	3	4	5	6	7	8
Component	%	%	%	%	%	%	%	%
CaO	62	62	59	62	58	59	60	60
SiO ₂	3	5	1	9	5	7	9	15
Al ₂ O ₃	35	33	40	29	37	34	31	25

Table 2. FeO activity in slags of master slags 1-8 of Table 1. Temperature 1600 °C; standard state pure 'FeO'.

Master Slag N.	FeO conc. (mass %)	FeO activity	FeO conc. (mass %)	FeO activity
1	1.04	0.015		
2	1.04	0.014		
3	1.02	0.013	see Table 3	
4	1.00	0.015	3.66	0.063
5	1.00	0.015	2.24	0.122
6	0.98	0.019	3.70	0.067
7	1.10	0.020		
8	1.07	0.029		

Table 3. Experimental activity of FeO at different concentrations in master slag 3. Temperature 1600 °C; standard state pure 'FeO'.

FeO concentration (mass %)	FeO activity
0.9	0.010
1.0	0.011
1.0	0.013
1.1	0.012
1.3	0.013
2.1	0.026
2.2	0.022
3.0	0.024
3.7	0.025
4.0	0.030
4.1	0.026
4.5	0.027

Table 4. MnO activity in master slags. Temperature: 1600 °C; MnO standard state: pure MnO.

Master slag	MnO concentration (mass %)	MnO activity
1	1.0	$3.4 \cdot 10^{-2}$
1	2.4	$7.8 \cdot 10^{-2}$
1	5.4	$1.6 \cdot 10^{-1}$
1	12.5	$3.4 \cdot 10^{-1}$
1	1.8	$5.8 \cdot 10^{-2}$
1	2.8	$9.0 \cdot 10^{-2}$
2	1.8	$6.0 \cdot 10^{-2}$
2	1.8	$5.9 \cdot 10^{-2}$
2	1.7	$5.9 \cdot 10^{-2}$
3	1.7	$5.4 \cdot 10^{-2}$
4	1.7	$6.1 \cdot 10^{-2}$
4	1.7	$6.2 \cdot 10^{-2}$
4	1.7	$6.3 \cdot 10^{-2}$
5	0.7	$2.7 \cdot 10^{-2}$
5	1.6	$5.8 \cdot 10^{-2}$
5	5.1	$1.7 \cdot 10^{-1}$
5	12.3	$3.5 \cdot 10^{-1}$
6	0.7	$2.8 \cdot 10^{-2}$
6	0.9	$3.4 \cdot 10^{-2}$
6	4.6	$1.6 \cdot 10^{-1}$
7	0.9	$3.5 \cdot 10^{-2}$
7	3.0	$1.1 \cdot 10^{-1}$
7	5.7	$2.0 \cdot 10^{-1}$
7	8.3	$2.7 \cdot 10^{-1}$
7	14.5	$4.2 \cdot 10^{-1}$
8	0.9	$3.7 \cdot 10^{-2}$
8	2.8	$1.0 \cdot 10^{-1}$
8	7.2	$2.5 \cdot 10^{-1}$
8	13.5	$4.1 \cdot 10^{-1}$

Table 5. Cr₂O₃ activity in master slags. Temperature: 1600 °C; Cr₂O₃ standard state: pure 'Cr₂O₃'.

Master slag	Cr ₂ O ₃ concentration (mass %)	Cr ₂ O ₃ activity
1	1.41	$4.69 \cdot 10^{-4}$
1	4.64	$1.56 \cdot 10^{-2}$
1	7.81	$7.11 \cdot 10^{-2}$
1	12.99	$2.92 \cdot 10^{-1}$
1	17.68	$6.20 \cdot 10^{-1}$
2	1.41	$5.81 \cdot 10^{-4}$
2	5.21	$2.65 \cdot 10^{-2}$
2	9.87	$1.66 \cdot 10^{-1}$
2	15.54	$5.38 \cdot 10^{-1}$
3	1.01	$1.99 \cdot 10^{-4}$
3	5.02	$2.39 \cdot 10^{-2}$
3	8.92	$1.22 \cdot 10^{-1}$
3	12.59	$2.99 \cdot 10^{-1}$
3	17.95	$6.70 \cdot 10^{-1}$
3	21.00	$9.65 \cdot 10^{-1}$
3	22.11	1.0
4	0.85	$3.07 \cdot 10^{-4}$
4	1.39	$1.33 \cdot 10^{-3}$
4	6.46	$1.08 \cdot 10^{-1}$
4	8.79	$2.46 \cdot 10^{-1}$
4	14.60	$8.05 \cdot 10^{-1}$
5	1.38	$1.27 \cdot 10^{-3}$
5	3.78	$2.50 \cdot 10^{-2}$
5	6.96	$1.34 \cdot 10^{-1}$
5	11.49	$4.53 \cdot 10^{-1}$
5	15.67	$8.47 \cdot 10^{-1}$
6	1.00	$5.88 \cdot 10^{-4}$
6	1.38	$1.60 \cdot 10^{-3}$
6	3.37	$2.23 \cdot 10^{-2}$
6	5.78	$9.94 \cdot 10^{-2}$
6	13.29	$7.19 \cdot 10^{-1}$
6	14.68	$8.69 \cdot 10^{-1}$
6	15.87	1.0
7	0.84	$4.53 \cdot 10^{-4}$
7	1.38	$2.02 \cdot 10^{-3}$
7	5.62	$1.12 \cdot 10^{-1}$
7	9.51	$4.15 \cdot 10^{-1}$
7	12.45	$7.40 \cdot 10^{-1}$
8	0.81	$1.62 \cdot 10^{-3}$
8	1.33	$7.15 \cdot 10^{-3}$
8	3.15	$7.84 \cdot 10^{-2}$
8	7.15	$5.60 \cdot 10^{-1}$
8	9.47	$9.72 \cdot 10^{-1}$

