

Supplementary Materials

Table S1. Standard chemical potentials of pure components, for $T = 800$ K [62,63].

Component	μ_i^0 [J/mol]
Fe _(s)	-29964
Fe ₃ O _{4(s)}	-1287418
Fe ₂ O _{3(s)}	-929580
FeCl _{2(s)}	-459241
FeCl _{2(g)}	-397550
H ₂ O _(g)	-402982
HCl _(g)	-250261
H _{2(g)}	-112937
O _{2(g)}	-172901
Cl _{2(g)}	-188680
NaCl _(s)	-484053
NaCl _(g)	-375822
Na ₂ O _(s)	-500326
NaFeO _{2(s)}	-794281

Table S2. The Deacon reaction (HCl–O₂–H₂O–Cl₂)_(g).

$2\text{HCl}_{(g)} + \frac{1}{2}\text{O}_{2(g)} = \text{H}_2\text{O}_{(g)} + \text{Cl}_{2(g)}$			
ΔG_T^0 [J/mol], $T = 800$ K	K	$\lg K$	
-4689	2.0239	0.3062	$\lg P_{\text{O}_2} = 2(\lg P_{\text{Cl}_2} + \lg P_{\text{H}_2\text{O}} - 2\lg P_{\text{HCl}} - \lg K)$

Table S3. The range of persistence of the Fe_(s)–Fe₃O_{4(s)} system.

$3\text{Fe}_{(s)} + 2\text{O}_{2(g)} = \text{Fe}_3\text{O}_{4(s)}$			
ΔG_T^0 [J/mol], $T = 800$ K	K	$\lg K$	$a_{\text{Fe}_{(s)}} = 1, a_{\text{Fe}_3\text{O}_{4(s)}} = 1$
-851,724	$4.11 \cdot 10^{55}$	55.6138	$\lg P_{\text{O}_2} = -\frac{1}{2}\lg K$
			$\lg P_{\text{O}_2} = -27.8069$

Table S4. The range of persistence of the Fe₃O_{4(s)}–Fe₂O_{3(s)} system.

$2\text{Fe}_3\text{O}_{4(s)} + \frac{1}{2}\text{O}_{2(g)} = 3\text{Fe}_2\text{O}_{3(s)}$			
ΔG_T^0 [J/mol], $T = 800$ K	K	$\lg K$	$a_{\text{Fe}_3\text{O}_{4(s)}} = 1, a_{\text{Fe}_2\text{O}_{3(s)}} = 1$
-127,453	$20.9 \cdot 10^7$	8.3221	$\lg P_{\text{O}_2} = -2\lg K$
			$\lg P_{\text{O}_2} = -16.6444$

Table S5. The range of persistence of the Fe_(s)–FeCl_{2(s)} system.

Fe _(s) + Cl _{2(g)} = FeCl _{2(s)}			
ΔG_T^0 [J/mol], $T = 800$ K	K	lgK	$a_{Fe(s)} = 1, a_{FeCl_{2(s)}} = 1$ $lgP_{Cl_2} = -lgK$ $lgP_{Cl_2} = -15.7129$
−240,641	$5.13 \cdot 10^{15}$	15.7129	

Table S6. The range of persistence of the FeCl_{2(s)}–Fe₃O_{4(s)} system.

3FeCl _{2(s)} + 2O _{2(g)} = Fe ₃ O _{4(s)} + 3Cl _{2(g)}			
ΔG_T^0 [J/mol], $T = 800$ K	K	lgK	$a_{FeCl_{2(s)}} = 1, a_{Fe_3O_{4(s)}} = 1$ $lgP_{Cl_2} = 2.828 + \frac{2}{3} lgP_{O_2}$
−129,933	$3.05 \cdot 10^8$	8.4841	

Table S7. The range of persistence of the FeCl_{2(s)}–Fe₂O_{3(s)} system.

2FeCl _{2(s)} + $\frac{3}{2}$ O _{2(g)} = Fe ₂ O _{3(s)} + 2Cl _{2(g)}			
ΔG_T^0 [J/mol], $T = 800$ K	K	lgK	$a_{FeCl_{2(s)}} = 1, a_{Fe_2O_{3(s)}} = 1$ $lgP_{Cl_2} = 4.215 + \frac{3}{4} lgP_{O_2}$
−129,106	$2.69 \cdot 10^8$	8.4301	

Table S8. Hydrogen production at Fe_(s)/Fe₃O_{4(s)} interface, in Fe_(s)–HCl_(g) reaction, $lgP_{H_2} = f(lgP_{HCl})$.

Fe _(s) + 2HCl _(g) = FeCl _{2(s)} + H _{2(g)}			
ΔG_T^0 [J/mol], $T = 800$ K	K	lgK	$a_{FeCl_{2(s)}} = 1, a_{Fe(s)} = 1$ $lgP_{H_2} = lgK + 2lgP_{HCl}$ $lgP_{H_2} = 2.722 + 2lgP_{HCl}$ $lgP_{H_2} = -9.278 + 2lgP_{HCl}$ [ppm]
−41,692	527	2.722	

Table S9. Hydrogen partial pressure at Fe_(s)/Fe₃O_{4(s)} interface, in Fe_(s)–HCl_(g) reaction, $lgP_{H_2} = f(lgP_{HCl})$.

P_{HCl} [ppm]	P_{HCl} [atm]	lgP_{HCl} [atm]	lgP_{H_2} [atm]	P_{H_2} [ppm]
500	0.0005	−3.3010	−3.8800	132
1000	0.0010	−3.0000	−3.2780	527
1500	0.0015	−2.8239	−2.9258	1186
2000	0.0020	−2.6990	−2.6759	2109
2500	0.0025	−2.6021	−2.4821	3295
3000	0.0030	−2.5229	−2.3238	4745

Table S10. Hydrogen pressure in iron oxidation, $\lg P_{H_2} = f(\lg P_{H_2O})$.

$3\text{Fe}_{(s)} + 4\text{H}_2\text{O}_{(g)} = \text{Fe}_3\text{O}_{4(s)} + 4\text{H}_{2(g)}$			
ΔG_T^0 [J/mol], $T = 800$ K	K	$\lg K$	$a_{\text{Fe}_3\text{O}_{4(s)}} = 1, \quad a_{\text{Fe}_{(s)}} = 1$ $\lg P_{H_2} = 0.25 \lg K + \lg P_{H_2O}$ $\lg P_{H_2} = 0.6096 + \lg P_{H_2O}$
−37,346	274	2.4386	

Table S11. Hydrogen pressure in magnetite oxidation, $\lg P_{H_2} = f(\lg P_{H_2O})$.

$3\text{Fe}_2\text{O}_{3(s)} + \text{H}_{2(g)} = 2\text{Fe}_3\text{O}_{4(s)} + \text{H}_2\text{O}_{(g)}$			
ΔG_T^0 [J/mol], $T = 800$ K	K	$\lg K$	$a_{\text{Fe}_3\text{O}_{4(s)}} = 1, \quad a_{\text{Fe}_2\text{O}_{3(s)}} = 1$ $\lg P_{H_2} = \lg P_{H_2O} - \lg K$ $\lg P_{H_2} = \lg P_{H_2O} - 4.9708$
−76,126	93,487	4.9708	

Table S12. The dissociation of water vapour.

$\text{H}_2\text{O}_{(g)} = \text{H}_{2(g)} + \frac{1}{2}\text{O}_{2(g)}$			
ΔG_T^0 [J/mol], $T = 800$ K	K	$\lg K$	$\lg P_{O_2} = 2(\lg K + \lg P_{H_2O} - \lg P_{H_2})$ $\lg P_{H_2} = -9.278 + 2\lg P_{HCl}[\text{ppm}]$ (Table S8) $\lg P_{O_2} = 2(-4.0134 + \lg P_{H_2O} - 2\lg P_{HCl}[\text{ppm}])$ $\lg P_{O_2} = -27.8069 \quad ; \quad \text{Fe} \rightarrow \text{Fe}_3\text{O}_{4(s)}$ $\lg P_{H_2O} = -9.89 + 2\lg P_{HCl}[\text{ppm}]$
203,594	$5.1 \cdot 10^{-14}$	−13.2914	

Table S13. The carbon content in the boiler steel.

Boiler steels:	$C = 0.08 - 0.2\%$
16M03(16)	$C = 0.16 - 0.22\%$
$C = 0.2\%$	$x_C = 0.0092; \quad x_{Fe} = 0.9908$
Assumption:	$C = \text{Fe}_3\text{C}$

Table S14. Thermodynamic properties of the Fe–C system, $\ln \gamma_{\text{Fe}_3\text{C}} = f(T, x_{Fe})$, $a_{[C]} = f(T, x_{\text{Fe}_3\text{C}})$, $T = 800$ K [66].

$\ln \gamma_{\text{Fe}_3\text{C}} = \left(\frac{3350}{T} + 0.04 \right) \cdot x_{Fe}$		$\ln \gamma_{\text{Fe}_3\text{C}} = 4.1886 \rightarrow \lg \gamma_{\text{Fe}_3\text{C}} = 1.8191$ $\lg x_{\text{Fe}_3\text{C}} = -2.03621$ $\lg a_{\text{Fe}_3\text{C}} = \lg \gamma_{\text{Fe}_3\text{C}} + \lg x_{\text{Fe}_3\text{C}}$ $\lg a_{\text{Fe}_3\text{C}} = -0.217112 \rightarrow a_{[\text{Fe}_3\text{C}]} = 0.60658$
$\text{Fe}_3\text{C}_{(s)} = 3\text{Fe}_{(s)} + \text{C}_{(s)}$	$\lg K = \left(\frac{557}{T} - 0.536 \right)$	$\lg K = 0.16025 \rightarrow K = 1.4463$ $a_{[C]} = K \cdot a_{[\text{Fe}_3\text{C}]}$ $a_{[C]} = \mathbf{0.8773} \quad ; \quad \lg a_{[C]} = -0.05685$

Table S15. Oxidation of carbon in steel, at Fe_(s)/Fe₃O_{4(s)} phase interface, $P_{CO_2} = f(P_{O_2}, a_{[C]})$.

$C_{(s)} + O_{2(g)} = CO_{2(g)}$			
ΔG_T^0 [J/mol], $T = 800$ K	K	lgK	$lgP_{CO_2} = lgK + lgP_{O_2} + lga_{[C]}$ for $Fe_{(s)} - Fe_3O_{4(s)}$
−395,525	$6.7 \cdot 10^{25}$	25.8262	$lgP_{O_2} = -27.8069$ (Table S3)
			$lga_{[C]} = -0.05685$ (Table S14)
			$lgP_{CO_2} = -2.03755 \rightarrow P_{CO_2} = 9.172 \cdot 10^{-3}$ [atm]

Table S16. Boudouard reaction at Fe_(s)/Fe₃O_{4(s)} phase interface.

$C_{(s)} + CO_{2(g)} = 2CO_{(g)}$			
ΔG_T^0 [J/mol], $T = 800$ K	K	lgK	$lgP_{CO} = \frac{1}{2}(lgK + lgP_{CO_2} + lga_{[C]})$
30,537	0.01014	−1.994	$lgP_{CO_2} = -2.03755$ (Table S15)
			$lga_{[C]} = -0.05685$ (Table S14)
			$lgP_{CO} = -2.0442 \rightarrow P_{CO} = 9.032 \cdot 10^{-3}$ [atm]

Table S17. Influence of H_{2(g)}, CO_(g), H₂O_(g) gas phase on the activity of carbon in steel at Fe_(s)/Fe₃O_{4(s)} interface, $lga_{[C]} = f(lgP_{H_2O}, lgP_{HCl})$.

$H_{2(g)} + CO_{(g)} = H_2O_{(g)} + C_{(s)}$			
ΔG_T^0 [J/mol], $T = 800$ K	K	lgK	$lga_{[C]} = lgK + lgP_{H_2} + lgP_{CO} - lgP_{H_2O}$
−21,062	23.7301	1.3753	$lgP_{CO} = -2.0442$ (Table S16)
			$lgP_{H_2} = -9.278 + 2lgP_{HCl}$ [ppm] Table S8
			$lga_{[C]} = -9.9468 - lgP_{H_2O} + 2lgP_{HCl}$ [ppm]

Table S18. Carbon activity and carbon surface saturation coefficient of Fe_(s)–Fe₃C_(s) alloy as a function of steam pressure and various HCl_(g) partial pressures, $a_{[C]} = f(lgP_{H_2O})$, for $P_{HCl} = 500 - 3000$ ppm.

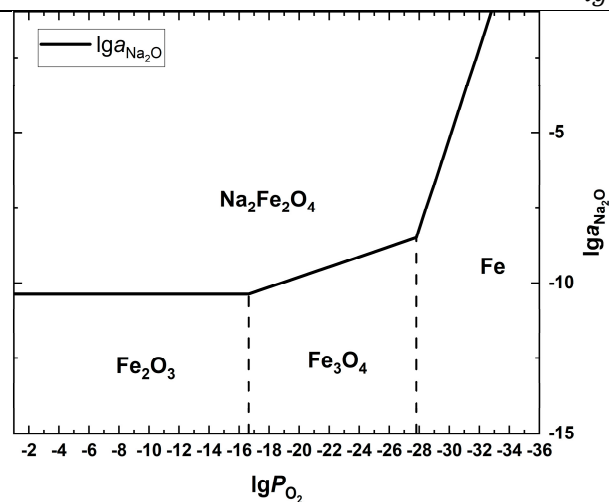
lgP_{H_2O}	$a_{[C]}; \bar{a}_{[C]} \gg 1$					
	500 ppm HCl _(g)	1000 ppm HCl _(g)	1500 ppm HCl _(g)	2000 ppm HCl _(g)	2500 ppm HCl _(g)	3000 ppm HCl _(g)
−1	$2.8 \cdot 10^{-4}$	$1.13 \cdot 10^{-3}$	0.0025	0.0045	0.0071	0.0102
−2	$2.8 \cdot 10^{-3}$	0.0113	0.0254	0.0452	0.0706	0.1017
−3	0.0283	0.113	0.2543	0.4522	0.7065	1.02
−4	0.2826	1.13	2.54	4.52	7.06	10.17
−5	2.8	11.3	25.4	45.2	70.6	101.7
−6	28	113	254	452	706	1017

Table S19. Pressure of saturated chloride sodium vapour above solid NaCl.

$\text{NaCl}_{(g)} = \text{NaCl}_{(s)}$
$\mu_{\text{NaCl}(s)} = \mu_{\text{NaCl}(g)}$
$\mu_{\text{NaCl}(s)}^0 = \mu_{\text{NaCl}(g)}^0 + RT \ln P_{\text{NaCl}}^0$
$RT \ln P_{\text{NaCl}}^0 = \mu_{\text{NaCl}(s)}^0 - \mu_{\text{NaCl}(g)}^0$
$\ln P_{\text{NaCl}}^0 = -16.2724 \quad \lg P_{\text{NaCl}}^0 = -7.067$
$P_{\text{NaCl}}^0 = 0.0857 \text{ [ppm]} \quad \text{saturation state}$

Table S20. Phase equilibrium of a Fe–O–Na₂O system, $\lg a_{\text{Na}_2\text{O}} = f(\lg P_{\text{O}_2})$, $T = 800 \text{ K}$.

(j)	Reaction	$\lg K_j$	$a_{2\text{NaFeO}_{2(s)}} = 1, \quad a_{\text{Fe}_2\text{O}_{3(s)}} = 1$
1	$\text{Na}_2\text{O}_{(s)} - \text{Fe}_2\text{O}_{3(s)}$ $\text{Na}_2\text{O}_{(s)} + \text{Fe}_2\text{O}_{3(s)} = 2\text{NaFeO}_{2(s)}$	10.359	$\lg a_{\text{Na}_2\text{O}} = -\lg K_1$ $\lg a_{\text{Na}_2\text{O}} = -10.359$ $-16.6444 \leq \lg P_{\text{O}_2}$
2	$\text{Na}_2\text{O}_{(s)} - \text{Fe}_3\text{O}_{4(s)}$ $2\text{Fe}_3\text{O}_{4(s)} + 1/2\text{O}_{2(g)} = 3\text{Fe}_2\text{O}_{3(s)}$	8.3221	$a_{\text{Fe}_3\text{O}_{4(s)}} = 1, \quad a_{\text{Fe}_2\text{O}_{3(s)}} = 1$ $\lg a_{\text{Na}_2\text{O}} = -\lg K_1 - \frac{1}{3}\lg K_2 - \frac{1}{6}\lg P_{\text{O}_2}$ $\lg a_{\text{Na}_2\text{O}} = -13.133 - \frac{1}{6}\lg P_{\text{O}_2}$ $-27.8069 \leq \lg P_{\text{O}_2} \leq -16.6444$
3	$\text{Na}_2\text{O}_{(s)} - \text{Fe}_{(s)}$ $3\text{Fe}_{(s)} + 2\text{O}_{2(g)} = \text{Fe}_3\text{O}_{4(s)}$	55.6138	$a_{\text{Fe}_{(s)}} = 1, \quad a_{\text{Fe}_3\text{O}_{4(s)}} = 1$ $\lg a_{\text{Na}_2\text{O}} = -\lg K_1 - \frac{1}{3}\lg K_2 - \frac{2}{3}\lg K_3 - \frac{3}{2}\lg P_{\text{O}_2}$ $\lg a_{\text{Na}_2\text{O}} = -50.2089 - \frac{3}{2}\lg P_{\text{O}_2}$ $\lg P_{\text{O}_2} \leq -27.8069$

**Table S21.** $\lg P_{\text{NaCl}} = f(\lg a_{\text{Na}_2\text{O}}, \lg P_{\text{H}_2\text{O}}, \lg P_{\text{HCl}})$ in thermodynamic interpretation of $2\text{NaFeO}_{2(s)}$ production.

$2\text{NaCl}_{(g)} + \text{H}_2\text{O}_{(g)} = \text{Na}_2\text{O}_{(s)} + 2\text{HCl}_{(g)}$			
$\Delta G_T^0 \text{ [J/mol]}, T = 800 \text{ K}$	K	$\lg K$	$\lg a_{\text{Na}_2\text{O}} = \lg K + \lg P_{\text{H}_2\text{O}} + 2\lg P_{\text{NaCl}} - 2\lg P_{\text{HCl}}$

153,778	$9.1 \cdot 10^{-11}$	-10.041	$lgP_{NaCl} = \frac{1}{2}(lga_{Na_2O} - lgK - lgP_{H_2O} + 2lgP_{HCl})$
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Table S22. $lga_{Na_2O} = f(P_{H_2O}, P_{NaCl}, P_{HCl})$ in thermodynamic interpretation of $2NaFeO_{2(s)}$ production, for $P_{NaCl} = 100$ ppm ($lgP_{NaCl} = -4$).

lgP_{H_2O}	lga_{Na_2O}		
	$P_{HCl} = 1000$ ppm	$P_{HCl} = 2000$ ppm	$P_{HCl} = 3000$ ppm
1.682 / 48 atm/	-10.359	-	-
2.284 / 192 atm/	-	-10.359	-
2.636 / 432 atm/	-	-	-10.359
-1	-13.041	-13.643	-13.995
-3	-15.041	-15.643	-15.995
-6	-18.041	-18.643	-18.995

Table S23. $lgP_{NaCl} = f(P_{H_2O})$ in thermodynamic interpretation of $2NaFeO_{2(s)}$ production, for $P_{HCl} = 1000$ ppm and $lga_{Na_2O} = -10.359$.

lgP_{H_2O}	lgP_{NaCl}	P_{NaCl} [ppm]
1.682	-4	100
-1	-2.659	2192
-3	-1.659	21,928
-6	-0.159	693,425

Table S24. Standard chemical potential $\mu_{i(s,l)}^0 = f(T)$ temperature function of $i(s,l) = FeCl_2, NaCl$ [63].

i	$\mu_{i(s,l)}^0 = a + bT + cT \ln T$ [J/mol]			$\mu_{i(T=800\text{ K})}^0$ [J/mol]
	a	b	c	
$FeCl_{2(s)}$	-367,000	438.3	-82.82575	-459,286
$FeCl_{2(l)}$	-341,800	544.3	-102.15442	-452,650
$NaCl_{(s)}$	-428,700	310.1	-56.75335	-484,119
$NaCl_{(l)}$	-410,300	367.1	-67.375498	-476,923

Table S25. The coordinates of the liquidus curve $FeCl_2$ - $NaCl$ (pseudo-eutectic range) [94].

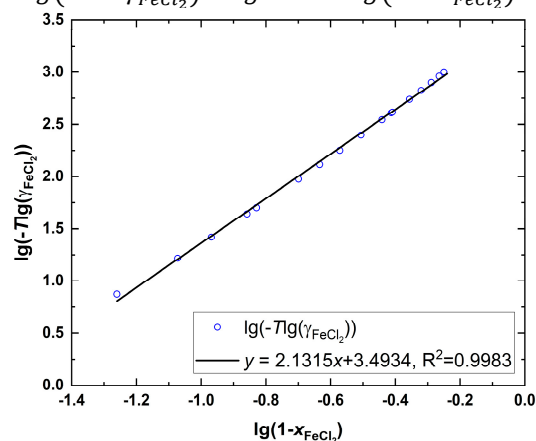
T [K]	x_{FeCl_2}	T [K]	x_{FeCl_2}
939	0.94509	845	0.68808
932	0.91540	816	0.63791
926	0.89245	800	0.61299
917	0.86139	798	0.60999
914	0.85177	762	0.55981
896	0.80002	731	0.52147
883	0.76755	699	0.48576
867	0.73171	648	0.43762

Table S26. Gibbs-Duhem equation of two components liquid solution $\ln \gamma_i = f(T, x_i)$, $i = 1, 2$ [66].

$$\sum_{i=1}^n x_i d \ln \gamma_i = 0 \quad \rightarrow i = (1, 2) \rightarrow \begin{cases} \ln \gamma_1 = \omega(T) x_2^m \\ \ln \gamma_2 = \omega(T) \left[x_2^m - \frac{m}{m-1} x_2^{m-1} + \frac{1}{m-1} \right] \\ \omega(T) = \frac{\alpha}{T} \end{cases}$$

Table S27. Calculation procedure of $\ln \gamma_{FeCl_2} = f(T, x_{FeCl_2})$, activity a_{FeCl_2} and x_{FeCl_2} , for hypoeutectic composition.

$$\begin{aligned} \mu_{FeCl_2(s)} &= \mu_{FeCl_2(l)} \\ \mu_{(s)}^0 - \mu_{(l)}^0 &= RT \ln a_{FeCl_2(l)} \\ RT \ln a_{FeCl_2} &= A + BT + CT \ln T \\ \ln a_{FeCl_2} &= \frac{A+BT+CT \ln T}{RT}; \quad R = 8.314 \left[\frac{J}{mol \cdot K} \right] \\ A &= a_s - a_l; \quad B = b_s - b_l; \quad C = c_s - c_l \\ A &= -25200; \quad B = -106; \quad C = 19.32867 \\ \ln a_{FeCl_2}(800 \text{ K}) &= -0.997756 \\ \ln a_{FeCl_2} &= f(T); \quad x_{FeCl_2} = f(T) \text{ (liq. Table S25)} \\ \ln a_{FeCl_2} &= \ln x_{FeCl_2} + \ln \gamma_{FeCl_2} \\ \ln \gamma_{FeCl_2} &= \ln a_{FeCl_2} - \ln x_{FeCl_2} \\ \ln \gamma_{FeCl_2} &= \frac{\alpha}{T} (1 - x_{FeCl_2})^m \\ T \ln \gamma_{FeCl_2} &= \alpha (1 - x_{FeCl_2})^m \\ \lg(-T \ln \gamma_{FeCl_2}) &= \lg \alpha + m \lg(1 - x_{FeCl_2}) \end{aligned}$$



$$\begin{aligned} \alpha &= -3121, \quad m = 2.1314 \\ \ln \gamma_{FeCl_2} &= -\frac{3121}{T} (1 - x_{FeCl_2})^{2.1314} \\ T = 800 \text{ K}, x_{FeCl_2} &\text{ (liq.) - hypoeutectic composition} \\ -0.997756 &= \ln x_{FeCl_2} - 3.90125 (1 - x_{FeCl_2})^{2.1314} \\ x_{FeCl_2} &= \mathbf{0.614657}; \quad x'_{FeCl_2} = 0.61299 \text{ [94]} \end{aligned}$$

Table S28. Calculation procedure of $\ln\gamma_{FeCl_2} = f(T, x_{FeCl_2})$, activity a''_{FeCl_2} and x''_{FeCl_2} , for hypereutectic composition.

$$\ln\gamma_{NaCl} = -\frac{\alpha}{T} \left[(1 - x_{FeCl_2})^m - \frac{m}{m-1} (1 - x_{FeCl_2})^{m-1} + \frac{1}{m-1} \right]$$

for $\alpha = -3121$, $m = 2.1314$

$$\ln\gamma_{NaCl} = -\frac{3121}{T} \left[(1 - x_{FeCl_2})^{2.1314} - 1.883861(1 - x_{FeCl_2})^{1.1314} + 0.883861 \right]$$

$$\mu_{NaCl(s)} = \mu_{NaCl(l)}$$

$$\mu_{(s)}^0 - \mu_{(l)}^0 = RT \ln a_{NaCl(l)}$$

$$RT \ln a_{NaCl} = A + BT + CT \ln T$$

$$\ln a_{NaCl} = \frac{A+BT+CT \ln T}{RT}; R = 8.314 \left[\frac{J}{mol \cdot K} \right]$$

$$A = a_s - a_l; B = b_s - b_l; C = c_s - c_l$$

$$A = -18400; B = -57; C = 10.62215$$

$$\ln a_{NaCl}(800 \text{ K}) = -1.081919$$

$T = 800 \text{ K}, x''_{FeCl_2(l)} - \text{hypereutectic composition}$

$$\ln a_{NaCl} = \ln x_{NaCl} + \ln \gamma_{NaCl}$$

$$-1.081919 = \ln(1 - x''_{FeCl_2})$$

$$-3.90125 \left[(1 - x''_{FeCl_2})^{2.1314} - 1.883861(1 - x''_{FeCl_2})^{1.1314} + 0.883861 \right]$$

$$x''_{FeCl_2} = \mathbf{0.3858}; \quad x'_{FeCl_2} = 0.3561 [94]$$

Table S29. Iron chloride activity for various concentration ($x'_{FeCl_2} - x''_{FeCl_2}$) of FeCl₂–NaCl liquid solution, for $T = 800 \text{ K}$.

x'_{FeCl_2}	$lg a'_{FeCl_2}$	a'_{FeCl_2}	x''_{FeCl_2}	$lg a''_{FeCl_2}$	a''_{FeCl_2}
0.6147	−0.4333	0.3687	0.3858	−1.0131	0.097

Table S30. Hydrogen partial pressure above FeCl₂–NaCl liquid solution, at metal–oxide interface, $lg P_{H_2} = f(lg P_{HCl}, lg a_{FeCl_2(l)})$.

$Fe_{(s)} + 2HCl_{(g)} = FeCl_{2(l)} [FeCl_2-NaCl]_{(l)} + H_{2(g)}$		
$\Delta G_T^0 [J/mol]$	K	$lg K$
−35,056	194.5	2.289
$a_{FeCl_2(s)} = 1, a_{Fe(s)} = 1$		
$lg P_{H_2} = lg K + 2lg P_{HCl} - lg a_{FeCl_2(l)}$		
$lg P_{H_2} = 2.289 + 2lg P_{HCl} - lg a_{FeCl_2(l)}$		

Table S31. Hydrogen partial pressure above FeCl₂–NaCl liquid solution, at metal–oxide interface, $lg P_{H_2} = f(lg P_{HCl}, lg a_{FeCl_2(l)})$, for various concentration of HCl(g).

x_{FeCl_2}	$lg P_{H_2}$
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	$lga_{FeCl_2(l)}$	1000 ppm $lgP_{HCl} = -3$	2000 ppm $lgP_{HCl} = -2.699$	3000 ppm $lgP_{HCl} = -2.523$
$x'_{FeCl_2} = 0.6147$	-0.4333	-3.278	-2.676	-2.324
$x''_{FeCl_2} = 0.3858$	-1.0131	-2.698	-2.096	-1.744

Table S32. Pressure of iron chloride saturated vapour P_{FeCl_2} above $FeCl_2$ –NaCl liquid solution, $lgP_{FeCl_2} = f(a_{FeCl_2(l)})$, for $T = 800$ K.

$FeCl_{2(l)} = FeCl_{2(g)}$
$\mu_{FeCl_2(l)} = \mu_{FeCl_2(g)}$
$\mu_{(l)}^0 + RTlna_{FeCl_2(l)} = \mu_{(g)}^0 + RTlnP_{FeCl_2}$
$RTlnP_{FeCl_2} = \mu_{(l)}^0 - \mu_{(g)}^0 + RTlna_{FeCl_2(l)}$
$lgP_{FeCl_2} = -3.5949 + lga_{FeCl_2(l)}$

Table S33. Pressure of iron chloride saturated vapour P_{FeCl_2} above $FeCl_2$ –NaCl liquid solution, $lgP_{FeCl_2} = f(a_{FeCl_2(l)})$, for $T = 800$ K.

x_{FeCl_2}	$lga_{FeCl_2(l)}$	lgP_{FeCl_2}	P_{FeCl_2} [ppm]
$x'_{FeCl_2} = 0.6147$	-0.4333	-4.0282	93.7
$x''_{FeCl_2} = 0.3858$	-1.0131	-4.608	24.7

Table S34. Parametric Equation Formalism [58–61].

$x_i = x_i^0 + \tau \cos \alpha_i \quad i = 1, \dots, s$
s is a number of reagents,
x_i, x_i^0 are equilibrium and inlet molar fraction of gas component i ,
α_i is direction angle,
τ is a line parameter, $\tau \in R$.
$\cos \alpha_i = \frac{v_i - x_i^0 \sum_{i=1}^s v_i}{\sqrt{\sum_{i=1}^s (v_i - x_i^0 \sum_{i=1}^s v_i)^2}} \quad i = 1, \dots, s$
v_i is stoichiometric coefficient of reactant i .
$x_i = x_i^0 + \tau \frac{v_i - x_i^0 \sum_{i=1}^s v_i}{\sqrt{\sum_{i=1}^s (v_i - x_i^0 \sum_{i=1}^s v_i)^2}} \quad i = 1, \dots, s$
v_i adopts positive values for the products of the reaction and negative values for the subtracts,
$\left(\sum_{i=1}^s v_i \neq 0 \right) \Rightarrow x_i = x_i^0 + \tau (\bar{x}_i - x_i^0) \quad ; \quad \bar{x}_i = \frac{v_i}{\sum_{i=1}^s v_i} \quad i = 1, \dots, s$
$\left(\sum_{i=1}^s v_i = 0 \right) \Rightarrow x_i = x_i^0 + \tau \frac{v_i}{\sqrt{\sum_{i=1}^s (v_i)^2}} \quad i = 1, \dots, s$

Table S35. Fe–O phase diagram fragment, in a range of $FeCl_{2(l)}$ – $Fe_2O_{3(s)}$ equilibrium.

$FeCl_{2(l)} - Fe_2O_{3(s)}$	$\Delta G_{T=800\text{ K}}^0$ [J/mol]	lgK
$2FeCl_{2(l)} + 1.5 O_2 = Fe_2O_{3(s)} + 2Cl_2$	-142,378	9.2967

Table S36. Phase system of Fe–O in the range of $\text{FeCl}_{2(l)}\text{--Fe}_2\text{O}_{3(s)}$ equilibrium, $\lg P_{\text{Cl}_2} = f(\lg P_{\text{O}_2}, \lg a_{\text{FeCl}_{2(c)}})$.

$\lg a_{\text{FeCl}_{2(l)}}$	$\lg P_{\text{Cl}_2} = 4.64835 + 0.75 \lg P_{\text{O}_2} + \lg a_{\text{FeCl}_{2(l)}}$	Range of $\lg P_{\text{O}_2}$
$x'_{\text{FeCl}_2}; -0.4333$	$4.2150 + 0.75 \lg P_{\text{O}_2}$	[−16.6444 – −1]
$x''_{\text{FeCl}_2}; -1.0131$	$3.6352 + 0.75 \lg P_{\text{O}_2}$	

Table S37. The range of persistence of the $\text{Fe}_{(s)}\text{--FeCl}_{2(l)}$ system.

$\text{Fe}_{(s)} + \text{Cl}_{2(g)} = \text{FeCl}_{2(l)}$			
ΔG_T^0 [J/mol], $T = 800$ K	K	$\lg K$	$a_{\text{Fe}_{(s)}} = 1$ $\lg K = \lg a_{\text{FeCl}_{2(l)}} - \lg P_{\text{Cl}_2}$
−234,006	$1.9 \cdot 10^{15}$	15.2796	

Table S38. Equilibrium of $\text{HCl}\text{--Cl}\text{--H}$ system.

$2\text{HCl}_{(g)} = \text{H}_{2(g)} + \text{Cl}_{2(g)}$			
ΔG_T^0 [J/mol], $T = 800$ K	$\lg K$	$\lg K = \lg H_2 + \lg P_{\text{Cl}_2} - 2 \lg \text{HCl}$	
198,905	−12.9876		

Table S39. Oxidation of iron chloride in the "active oxidation" model.

Reaction	$\Delta G_{T=800\text{ K}}^0$ [J/mol]	$\lg K$
$2\text{HCl}_{(g)} + 0.5 \text{O}_{2(g)} = \text{H}_2\text{O}_{(g)} + \text{Cl}_{2(g)}$	−4689	0.3062
$3\text{FeCl}_{2(g)} + 2\text{O}_{2(g)} = \text{Fe}_3\text{O}_{4(s)} + 3\text{Cl}_{2(g)}$	−315,006	20.5686
$2\text{FeCl}_{2(g)} + 1.5 \text{O}_{2(g)} = \text{Fe}_2\text{O}_{3(s)} + 2\text{Cl}_{2(g)}$	−252,488	16.4864

Table S40. Oxidation of iron chloride in the "active oxidation" model, $\lg P_{\text{FeCl}_2} = f(\lg P_{\text{O}_2})$.

System	$\lg P_{\text{FeCl}_2}$	Range of $\lg P_{\text{O}_2}$
$\text{FeCl}_{2(g)} - \text{Fe}_3\text{O}_{4(s)}$	$-6.55 - \lg P_{\text{H}_2\text{O}} + 2\lg P_{\text{HCl}} - \frac{1}{6}\lg P_{\text{O}_2}$	[−27.8069 – −16.6444]
$\text{FeCl}_{2(g)} - \text{Fe}_2\text{O}_{3(s)}$	$-7.937 - \lg P_{\text{H}_2\text{O}} + 2\lg P_{\text{HCl}} - \frac{1}{4}\lg P_{\text{O}_2}$	[−16.6444 – −1]