Article

Optimization on Temperature Strategy of BOF Vanadium Extraction to Enhance Vanadium Yield with Minimum Carbon Loss

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Abstract: During the vanadium extraction process in basic oxygen furnace (BOF), unduly high temperature is unfavorable to achieve efficient vanadium yield with minimum carbon loss. A new temperature strategy was developed based on industrial experiments. The new strategy applies the selective oxidation temperature between carbon and vanadium (T_{sl}) and the equilibrium temperature of vanadium oxidation and reduction (T_{eq}) for the earlier and middle-late smelting, respectively. Industrial experiments showed 56.9 wt% of V was removed together with carbon loss for 5.6 wt% only in the earlier smelting. Additionally, 30 wt% of vanadium was removed together with carbon loss by 13.4 wt% in middle-late smelting. Applicability analyses confirmed T_{eq} as the high-limit temperature, vanadium removal remains low and carbon loss increased sharply when the molten bath temperature exceeded T_{eq} . With the optimized temperature strategy, vanadium removal increased from 69.2 wt% to 92.3 wt% with a promotion by 23 wt%.

Citation: Zhou, Z.-Y.; Tang, P. Optimization on Temperature Strategy of BOF Vanadium Extraction to Enhance Vanadium Yield with Minimum Carbon Loss. *Metals* **2021**, *11*, 906. <https://doi.org/10.3390/met11060906>

Academic Editor: Dariush Azizi

Received: 29 April 2021

Accepted: 28 May 2021

Published: 2 June 2021

Keywords: vanadium extraction process; vanadium yield; minimum carbon loss; temperature strategy

1. Introduction

Vanadium is a widely used rare metal in many areas such as steel-making, aerospace, and chemical industries [1,2]. It is usually found as a by-product in vanadium-titanium magnetite (VTM), and the most popular method of treating vanadium-bearing hot metal is oxygen blow smelting in converter to form vanadium-enriching slag and semi-steel [3]. Residual vanadium in semi-steel must remain low, mostly under 0.05 wt%. Meanwhile, to ensure subsequent steel-making, carbon content in semi-steel needs to above 3.4 wt% [4]. Therefore, vanadium extraction process demands ‘deep devanadium’ and ‘minimum carbon loss’ simultaneously.

The selective oxidation temperature between carbon and vanadium, T_{sl} , a thermodynamic temperature, used to be considered as a key to ensure smelting steps. It related to the transformation from preferential V removal to C [5,6]. Most studies tend to the selective oxidation theory, which required the molten bath temperature never went beyond T_{sl} [4]. However, the demand could not be reached in practice because of the molten bath temperature always exceeded T_{sl} in middle-late smelting. It ranged from 1340 to 1400 °C near the end, and was much higher than corresponding T_{sl} . D.X. Huang’s study employed the temperature control strategy based on T_{sl} . It showed that carbon loss must be accepted when the molten bath temperature exceeds T_{sl} for ‘deep devanadium’, and vanadium removal decreased when the molten bath temperature exceeded T_{sl} in the middle-late smelting. Thus, previous studies mostly focused on vanadium removal, the reduction of (V_2O_3) by C and carbon loss in molten iron was totally ignored [7]. Few studies have concentrated on ‘deep devanadium’ and ‘minimum carbon loss’ simultaneously. Further study on a reasonable temperature control strategy is very important to realize these two demands.

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In this paper, Industrial experiments were applied to determine the removal characteristics of C and V in various smelting period. Thermodynamic analyses were applied to settle the foundation of new temperature strategy for vanadium extraction. The applicability of new strategy was verified by analyses on final samples and production data.

2. Experimental Procedure

Industrial experiments have taken place, and six heats with similar parameters were performed as one to minimize the experimental errors. The original molten iron composition and temperature are listed in Table 1. The smelting parameters are given in Table 2. The measuring and sampling process is shown in Figure 1.

Table 1. Original compositions and temperatures of molten iron.

Temperature/°C	Composition (wt%)				
	C	V	Si	Mn	Ti
1294 ± 6	4.35 ± 0.05	0.39 ± 0.03	0.11 ± 0.02	0.22 ± 0.02	0.12 ± 0.02

Table 2. Parameters during vanadium extraction smelting.

Furnace Capacity/t	Lance Height/m	Top Flow Rate (Nm ³ /h)	Bottom Flow Rate (Nm ³ /h)	Number of Nozzle	Ma	Blowing Time/s	Coolant (Kg/t)
210	1.6~1.9	24,000	1000	4	1.99	~360	41.6 ± 0.6

Figure 1. Schematic of sampling and temperature measuring operations.

Coolants were added into molten bath for three times at 60 s, 120 s and 180 s to ensure the molten bath temperature below T_{sl} in the earlier smelting [8]. Sampling and temperature measuring were carried out from 210 s with an interval about 25 ± 5 s. The total smelting lasted around 360 s based on production experience. X-Ray Fluorescence analyses (XRF-1800, Rh-target, 60 KV, 140 mA) were applied to determine the compositions of metal and slag.

3. Results

The thermodynamic temperature T_{sl} for each sample was calculated by equaling ΔG of reaction (1) to reaction (2), as Equation (3).

$$T_{sl} = \frac{250,170}{153.09 + 19.147 \lg \frac{\gamma_{V_2O_3}^{1/3} \cdot x_{V_2O_3}^{1/3} \cdot (\%C) \cdot f_C}{(\%V)^{2/3} \cdot f_V^{2/3} \cdot P_{CO}}} \quad (3)$$

where $x_{V_2O_3}$ was the mole fraction of V_2O_3 in slag and $\gamma_{V_2O_3}$ was the activity coefficient. f_C and f_V were the activity coefficients of carbon and vanadium which referred to Equations (4) and (5). (%C) and (%V) were the mass fractions of carbon and vanadium, respectively. P_{CO} was the partial pressure of CO in the converter.

However, about 55–65% (V_2O_3) in the vanadium slag precipitated by vanadium spinels ($FeO \cdot V_2O_3$) during smelting [9]. Therefore, the current study employed the value from D.X. Huang based on industrial production data, 10^{-5} [4].

$$\lg f_C = \Sigma e_C^i(\%) = e_C^C(\%C) + e_C^V(\%V) + e_C^{Si}(\%Si) + e_C^{Mn}(\%Mn) + e_C^{Ti}(\%Ti) + \dots \quad (4)$$

$$\lg f_V = \Sigma e_V^j(\%) = e_V^V(\%V) + e_V^C(\%C) + e_V^{Mn}(\%Mn) + e_V^{Si}(\%Si) + e_V^{Ti}(\%Ti) + \dots \quad (5)$$

where e_C^i was the interaction coefficient to carbon, and e_V^j was the interaction coefficients to vanadium.

The molten bath temperatures, compositions of metal and slag measured in industrial experiments were listed in Tables 3 and 4. Removal ratios of C and V and T_{sl} for each sample were shown in Table 5.

Table 3. The molten bath temperatures and molten iron compositions (wt%) in various time during industrial experiments.

NO.	Time/s	C	V	Si	Mn	Ti	$T_{bt}/(^{\circ}C)$
0	0	4.31	0.39	0.11	0.22	0.12	1294
1#-1	210	4.07	0.168	0.044	0.096	0.011	1318
1#-2	240	4.0	0.137	0.030	0.060	0.008	1320
1#-3	252	3.82	0.115	0.019	0.054	0.006	1337
1#-4	282	3.60	0.087	0.018	0.046	0.006	1342
1#-5	282	3.66	0.094	0.022	0.049	0.004	1348
1#-6	306	3.59	0.078	0.010	0.034	0.003	1349
2#-1 *	366	3.54	0.051	0.006	0.026	0.001	1376
2#-2 *	366	3.45	0.042	0.009	0.023	0.001	1382
2#-3 *	366	3.51	0.06	0.010	0.030	0.002	1378
2#-4 *	372	3.61	0.053	0.007	0.027	0.001	1394
2#-5 *	378	3.45	0.054	0.005	0.026	0.001	1382
2#-6 *	390	3.49	0.06	0.006	0.024	0.001	1379

* Final samples.

Table 4. Slag compositions (wt%) in various time during industrial experiments.

NO.	Time/s	V_2O_3	FeO	SiO_2	MnO	TiO_2	CaO	MgO
0	0	1.6	90.0	2	2	2	1.5	1.5
1#-1	210	8.2	70.6	4.4	4.4	5.8	1.6	1.4
1#-2	240	10.3	65.5	5.6	5.9	7.8	1.9	1.6
1#-3	252	10.7	62.5	5.9	6.7	8.6	1.9	1.5
1#-4	282	11.1	56.5	7.2	8	9.6	1.7	1.5
1#-5	282	11.5	54.4	8.4	8	9.2	2.0	1.7
1#-6	306	14.0	48.6	9.2	8.5	10.0	1.8	1.9
2#-1 *	366	16.2	32.4	10.2	9.8	10.5	2.0	2.0
2#-2 *	366	17.3	34.5	10.4	10.2	11.2	2.4	1.8
2#-3 *	366	16.5	33.4	9.8	10.4	10.0	1.8	2.2
2#-4 *	372	15.7	35.4	10.2	10.2	11.4	2.0	1.8
2#-5 *	378	16.5	30.9	10.6	11.0	10.8	2.2	2.4
2#-6 *	390	16.5	32.6	10.2	10.6	10.6	2.4	2.0

* Final samples.

Table 5. Removal ratios, T_{sl} and T_{eq} in various time during industrial experiments.

NO.	Time/s	V	V Removal Ratio/wt%	C	C Removal Ratio/wt%	$T_{bt}/(^{\circ}\text{C})$	$T_{sl}/(^{\circ}\text{C})$	$T_{eq}/(^{\circ}\text{C})$
0	0	0.39	-	4.31	0.0	1294	1382	1782
1#-1	210	0.168	56.9	4.07	5.6	1318	1295	1595
1#-2	240	0.137	64.9	4.0	7.2	1320	1285	1566
1#-3	252	0.115	70.5	3.82	11.4	1337	1292	1568
1#-4	282	0.087	77.7	3.60	16.5	1342	1294	1547
1#-5	282	0.094	75.9	3.66	15.1	1348	1294	1542
1#-6	306	0.078	80.0	3.59	16.7	1349	1281	1504
2#-1 *	366	0.051	86.9	3.54	17.9	1376	1260	1407
2#-2 *	366	0.042	89.2	3.45	20.0	1382	1257	1402
2#-3 *	366	0.06	84.6	3.51	18.6	1378	1272	1408
2#-4 *	372	0.053	86.4	3.61	16.2	1394	1257	1415
2#-5 *	378	0.054	86.2	3.45	20.0	1382	1271	1389
2#-6 *	390	0.06	84.6	3.49	19.0	1379	1273	1412

* Final samples.

4. Discussions

4.1. V and C Removal in Various Temperatures

Variations on molten bath temperatures, T_{sl} , V, C and V_2O_3 contents, were shown in Figure 2. The molten bath temperature increased due to the oxidation of dissolved elements. It turned out more rapidly without coolant addition in the middle-late smelting. T_{sl} decreased during vanadium extraction with the decrease in V content and increase in (V_2O_3) in slag, as shown in Figure 2b. The molten bath temperature was controlled below T_{sl} in the earlier smelting and became higher than T_{sl} 23 °C at 210 s.

Figure 2. Variations on V, C, (V_2O_3), the molten bath temperature and T_{sl} . (a) variation on T_{bt} and T_{sl} , (b) variation on V, C, and (V_2O_3).

The removal ratio of V and C at 210 s were 56.9 wt% and 5.6 wt%. The removal ratios of the final point were 86.3 wt% and 19 wt% (average), as shown in Table 5. As the molten bath temperature exceeded T_{sl} in the middle-late smelting (after 210 s), vanadium oxidation has lost thermodynamic advantage to carbon. Vanadium removal showed a weak tendency compared with the earlier smelting. Therefore, only about 30 wt% V was removed in middle-late smelting. However, carbon removal showed an opposite feature and has no longer been suppressed by vanadium removal. Therefore, about 13.4 wt% C was removed in middle-late smelting, and it was 2.4 times more than the earlier smelting (5.6 wt%), as shown in Table 5. Thus it can be seen, vanadium removal efficiency decreased when the molten bath temperature exceeded T_{sl} in the middle-late smelting. However, carbon

removal seemed to climb up rapidly. It was certain to desire a reasonable principle for final temperature control to assure ‘enhance vanadium removal’ with ‘minimum carbon loss’.

4.2. Thermodynamic Analyses of Vanadium Extraction

The present study considered that carbon and vanadium oxidation in the molten bath were mainly indirect [10]. Oxygen was transferred by ferrous oxide (FeO). Carbon monoxide (CO) was considered as the oxidative product of C as it was saturated in molten iron (≥ 3.4 wt%). In addition, vanadium trioxide (V_2O_3) would be reduced by C, as displayed in Equation (6). The standard Gibbs free energies (ΔG^θ) of reaction (1), (2) and (6) with various temperatures were showed as follows Figure 3.

Figure 3. Relationship between ΔG^θ and temperature.

The molten bath temperature exceeded T_{sl} rapidly without coolant addition in the middle-late smelting, as shown in Figure 2a. The removal of C is prior to V in this period, and (V_2O_3) in the slag also was reduced by C, as shown in Figure 3. However, ΔG of reaction (2) was still less than (6), which meant the thermodynamic driving force of vanadium removal was greater than the reduction. V removal and reduction of (V_2O_3) exist simultaneously.

As the molten bath temperature increasing continuously, there was a temperature-made ΔG of reaction (2) equal to (6). It stood for the thermodynamic equilibrium of vanadium removal and reduction, as shown in Figure 3 [11,12]. In this study, this temperature was described as ‘The equilibrium temperature of vanadium oxidation and reduction, T_{eq} ’. A coupled reaction represented V removal was deduced by equalizing ΔG of reaction (2) and (6), as displayed in Equation (7). T_{eq} was calculated by the following Equation (8). T_{eq} for each sample was listed in Table 5, and variation on the molten bath temperature and T_{eq} was shown in Figure 4.

$$T_{eq} = \frac{401,551}{215.42 + 19.147 \lg \frac{\gamma_{V_2O_3}^{2/3} \cdot x_{V_2O_3}^{2/3} \cdot [\%C] \cdot f_C}{[\%V]^{4/3} \cdot f_V^{4/3} \cdot a_{FeO} \cdot P_{CO}}} \quad (8)$$

Figure 4. Variations on the molten bath temperature and T_{eq} .

Thus, a new temperature strategy for ‘enhance vanadium yield’ with ‘minimum carbon loss’ can be proposed. In the earlier smelting, the molten bath temperature must be controlled below T_{sl} by coolant addition. In middle-late smelting, the molten bath temperature exceeding T_{sl} , T_{eq} was considered as the high-limit temperature. Potential for vanadium removal could be fully exploited and excessive carbon loss was avoided.

4.3. Applicability Analyses of T_{eq} for the Final Temperature

4.3.1. Final Samples

The theoretical residual vanadium in molten iron at the final point was calculated based on Equations (9) and (10) which deduced from Equations (3) and (8), respectively. Six final samples were treated as repetitive measurements in one heat. The Mean Absolute Difference (MAD) between theoretical vanadium contents and measurements were applied to evaluate the applicability of T_{sl} and T_{eq} on temperature strategy, as shown in Figure 5.

$$(\%V)_{sl} = \left[\frac{\gamma_{V_2O_3}^{1/3} \cdot x_{V_2O_3}^{1/3} \cdot (\%C) \cdot f_C}{10^{(250,170/T - 153.09)/19.147} \cdot f_V^{2/3} \cdot P_{CO}} \right]^{3/2} \quad (9)$$

$$(\%V)_{eq} = \left[\frac{\gamma_{V_2O_3}^{2/3} \cdot x_{V_2O_3}^{2/3} \cdot (\%C) \cdot f_C}{10^{(401,551/T - 219.422)/19.147} \cdot f_V^{4/3} \cdot a_{FeO} \cdot P_{CO}} \right]^{3/4} \quad (10)$$

Figure 5. Theoretical vanadium contents and measuring values at the final.

Theoretical vanadium contents was a bit lower than measurements because of the idealized status. The MAD between measurements and theoretical vanadium content calculated based on T_{sl} (Equation (10)) was 0.313 wt% (average). The theoretical values were much higher than measurements, which meant mistakes in calculation foundation. The MAD based on T_{eq} (Equation (10)) was 0.026 wt% (average) and theoretical values were a little lower than measurements. It showed a better fitting with measurements. Thus, it can be seen, T_{eq} should be considered as the thermodynamic basis for describing behaviors in middle-late smelting of vanadium extraction rather than T_{sl} .

4.3.2. Production Data

The temperature strategy was applied in Pansteel. The residual vanadium, molten bath temperature and T_{eq} at the final were also discussed based on production data. The residual vanadium, the temperature differences (ΔT , between T_{eq} and the molten bath temperature) in the final point were shown in Figure 6.

Figure 6. Relationship between the residual vanadium and ΔT at the final.

The temperature differences in most heats were far above zero, which showed the poor understanding on temperature control. The residual vanadium decreased with the decrease in ΔT . It did not decrease further when ΔT approached zero, as shown in Figure 6. The thermodynamic driving force of vanadium removal was bigger than reduction when $\Delta T > 0$, there was still potential on vanadium removal. Therefore, residual vanadium contents decreased with the decrease in ΔT . Vanadium removal and reduction showed fluctuant equilibrium status when the molten pool temperature exceeded T_{eq} (i.e., $\Delta T < 0$).

With the decrease in ΔT , the potential for vanadium removal in middle-late smelting has been fully developed. The vanadium removal ratio has increased from 69.2 wt% to 92.3 wt% with a promotion by 23 wt%. However, the serious carbon loss must be avoided when the molten bath temperature exceeded T_{eq} . T_{eq} must be considered as a maximum temperature limit of the final stage in vanadium extraction.

5. Conclusions

- (1) A temperature strategy of vanadium extraction process has been developed to consider the effects of T_{sl} in the earlier smelting and T_{eq} for the high-limit temperature to ensure 'enhance vanadium removal' with 'minimum carbon loss'.
- (2) The vanadium removal rate was highly efficient accompanied by slight carbon removal when the molten bath temperature was lower than T_{sl} . The removal rate of vanadium decreased and carbon removal increased when the molten bath temperature exceeded T_{sl} .

- (3) Vanadium removal efficiency remained poor while significant carbon loss was expected when the melt temperature went over T_{eq} , and T_{eq} must be considered as the high-limit temperature in vanadium extraction.
- (4) With the optimized temperature strategy, vanadium removal increased from 69.2 wt% to 92.3 wt% with a promotion by 23 wt% by production data.

Author Contributions: Conceptualization, Z.-Y.Z. and P.T.; methodology, Z.-Y.Z. and P.T.; validation, Z.-Y.Z.; formal analysis, Z.-Y.Z. and P.T.; investigation, Z.-Y.Z. and P.T.; resources, P.T.; data curation, Z.-Y.Z.; writing—original draft preparation, Z.-Y.Z.; writing—review and editing, Z.-Y.Z. and P.T.; visualization, Z.-Y.Z.; supervision, P.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflict of interest.

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