A Novel Green Technique to Recovery Valued Nonferrous-metal Compounds from Molten Slags

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Abstract: Based on several case studies in precipitating behavior of valued nonferrous-metal compounds (VNMC) in molten slags a green technology to recovery VNMC from molten slags was proposed, in which three steps are involved: (1) The selective enriching the dispersed VNMC into the designed mineral phase in molten slag; (2) The selective coarsening the designed mineral phase to critical grain size in molten slag; (3) The selective separating the grown mineral phase in solidified slag from tailing by dressing or hydrometallurgy processes. The features of the technique are clean, low-cost and a great capacity to deal with a large quantity of slags. The utilization of recovered VNMC such as titanium, boron, vanadium compounds was summarized as examples of technique's application. It was confirmed by experiments that the precipitating behavior of the designed mineral phases like perovskite ($CaTiO_3$), suanite ($2MgO\cdot B_2O_3$) and sincosite ($CaO\cdot V_2O_5\cdot P_2O_5$) in molten slags is obviously affected by operation factors such as temperature, chemical composition, heat-treatment, additives and so on. The precipitating kinetics and mechanism of VNMC from molten slags during solidification processes were also investigated.

Key words: Molten slag, selective enriching, perovskite, suanite, sincosite

1. Introduction

China is rich in mineral resources, but around 80% of those are complex mineral ores accompanied with valued nonferrous-metal compounds (VNMC), as shown in Table 1. Usually, when the ores are treated in a smelting furnace such as blast furnace, reverberatory, blowing furnace and so on, volue nonferrous metal oxides are mostly concentrated into molten slags and separated from liquid metals. So metallurgical slags become an importan man-made resources (Table 2), in which VNMC occur on various mineral phases with fine grain size.[1-2]

The dispersion and fine grain of VNMC in the slag make it very difficult to recovery VNMC from the slag efficiently by metallurgical or mineral processes conventionally, that results in the slag waste and environment pollution seriously.[3]

Table 1 Typical chemical composition of various complex mineral ores (wt.%)

Complex ore	T Fe	CaO	SiO_2	Al_2O_3	MgO	TiO_2	V_2O_5	REOx	Nb_2O_5	B_2O_3
V-Ti-Magnetite	31.3	7.0	22.4	9.0	6.6	10.6	0.3	-	-	-
Ludwigite	30.0	0.4	15.0	1.5	24.0	-	-	-	-	7.0
RE-Nb- Iron ore	48.0	8.8	4.8	0.22	1.0	0.3	-	2.7	0.14	-

Table 2 Chemical composition of metallurgical slags (wt. %)

Slag	CaO	SiO_2	Al_2O_3	MgO	B_2O_3	TiO_2	REOx
Ti-slag	27-28	22-25	14-15	7-8	0	22-23	0
RE-slag	37-40	30-34	7-9	7-9	0	0	3.5-4.5
B-slag	5-10	5-35	5-10	35-45	12-15	0	0

A novel green technique to recovery VNMC from the slags was proposed, on which three continuous processes are involved in (Fig. 1): the selective enriching the dispersed VNMC into designed mineral phase in molten slag, the selective coarsening the designed mineral phase with lager grain, the selective separating the grown mineral phase from tailing by mineral dressing or hydrometallurgical process.

The features of the technique are clean, low-cost and a great capacity to deal with a large quantity of slags. In present paper the several case studies on the selective precipitating and recoverying VNMC were summarized respectively as examples of the technique's application.

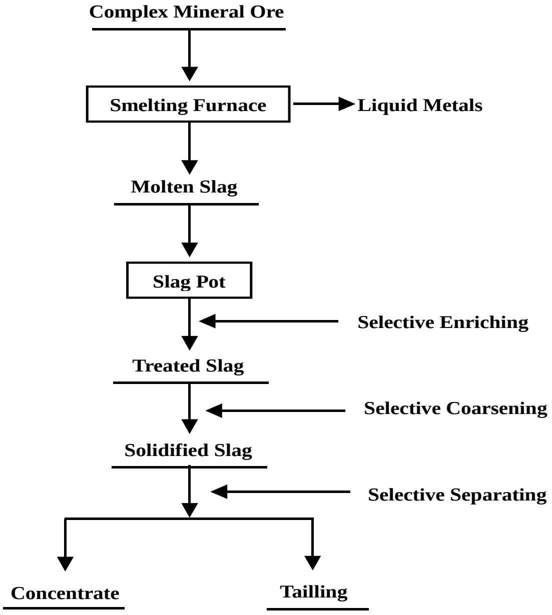


Fig. 1 Flow chart for the treatment of metallurgical slag by green technique

2. Titania recovery from Ti-slag

It was identified by EDXA and XRD that several mineral phases were occurred in Ti-slag[4-7], but titania was dispersed on different mineral phases as shown in Table 3[8].

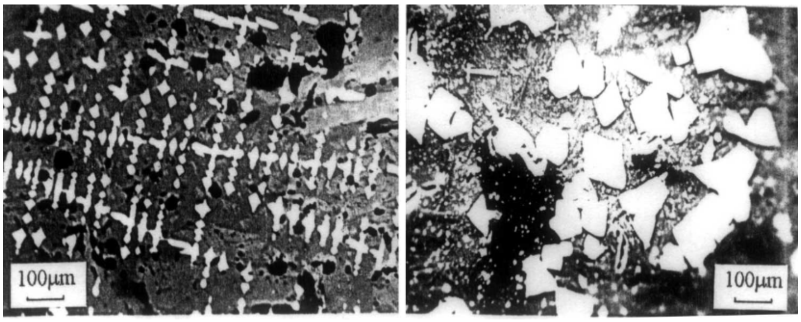
2.1 Selective enriching

Among others perovskite phase containing the largest amount of titania, it is reasonable to select perovskite as designed mineral phase into which the titania dispersed in various mineral phases will be possibly enriched[9]. After adjusting the chemical composition (basicity R=CaO/SiO_2) and injecting oxygen gas to molten slag, the morphology of perovskite phase of the slag was obviously varied (in Fig. 2) and a large amount of titania was enriched into perovskite phase. As a result, the enrichment of titania in perovskite phase was increased from 48% to 85%. The optimized composition was predicted by ANN (Artificial Neural Network) to be 30% CaO, 21.4% SiO_2, 26.0% TiO_2, 13.6 % Al_2O_3 and 9.0% MgO.

Table 3 Distribution of titania in various mineral phases (wt. %)

Name of mineral phases (Formula)	Content of titanium in mineral phases	Distribution of total titania in mineral phases	Percent of titania in mineral phases

Perovskite: $(Ca_{0.93}\ Mg_{0.04}\ Al_{0.03}\ Fe_{0.01})_{1.01}\ (Ti_{0.94}\ Al_{0.04}\ Si_{0.02})_{1.00}\ O_3$	55.8	48.0	11.6
Titanaugite: $(Ca_{0.96}\ Mg_{0.53}\ Ti_{0.46}\ Fe_{0.04}\ M_{0.01})_{2.00}\ (Si_{1.28}\ Al_{0.72})_{2.00}O_6$	15.5	37.9	9.1
Ti-rich Diopside: $(Ca_{0.35}\ Mg_{0.66}\ Ti_{0.45}\ Fe_{0.03}\ Mn_{0.01})_{2.00}\ (Si_{0.93}Al_{0.84}\ Ti_{0.23})_{2.00}O_6$	23.6	5.7	1.4
Spinel: $(Mg_{1.007}\ Fe_{0.018}\ Ca_{0.010}\ Mn_{0.005})_{1.040}\ (Al_{1.741}\ Ti_{0.131}\ Si_{0.032}\ V_{0.008}\ Cr_{0.001})_{0.913}\ O_4$	7.2	1.1	0.3
Titanium Carbide: Ti(C, N)	95.7	4	1.0
Sum		100	23.4

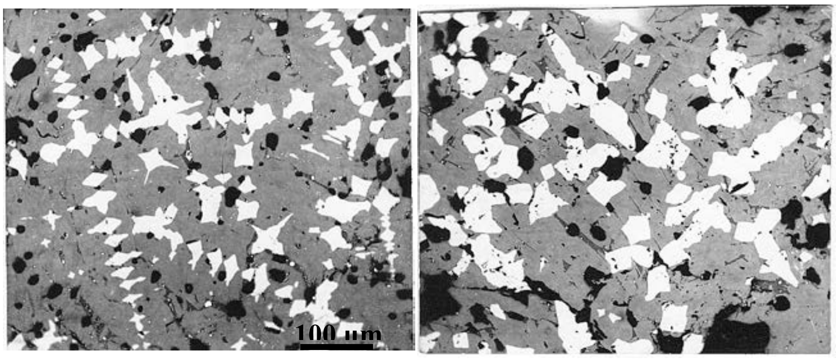


(a) (b)

Fig. 2 The morphology of perovskite phase as (a) R=1.0 and (b) R=1.4

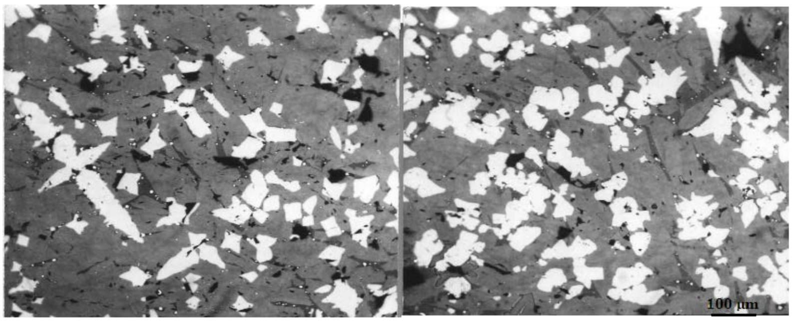
2.2 Selective coarsening[5, 8, 10-11]

The growing and coarsening perovskite phase in molten slag can be achieved by optimizing start-blowing temperature and time of oxygen injection as shown in Fig. 3 and Fig. 4, respectively. It was determined by imagine analysis that the average grain size of perovskite phase was changed from 10 μm to 60~80 μm after the optimizing treatment.



(a) (b)

Fig. 3 Micrographs of the samples with various blowing temperature of oxygen injection (a)1400℃, (b) 1430℃



(a) (b)

Fig. 4 Micrographs of the samples with various blowing time of oxygen injection (a) 2 min, (b) 6 min

2.3 Selective separating[12]

Based on study of mineralogy, distribution of perovskite phase and interfacial combination with other mineral phases in the treated slag, flotation was conducted for upgrading titania of the slag, in which the average grain size of perovskite was 40μm. Flotation performance was researched by investigating the amount of collector oil acid, collector A, inhibitor sodium silicate and CMC at 25 ℃. The effect of collector oil acid, collector A, and inhibitor sodium silicate, CMC on TiO_2 grade in purpose mineral was studied. Both collector oil acid and collector A could be used for the flotation of the slag, but flotation performance of collector A was better; both inhibitor sodium silicate and CMC could inhibit the gangue, but sodium silicate could also inhibit perovskite, therefore CMC was more suitable for the flotation. The optimized flotation process was the amount of collector A of 600g/t and CMC of 1500g/t. TiO_2 grade in concentrate and tailings was 41.64% and 10.98%, respectively, and the recovery of concentrate was 32.67%. The concentrates and taillings were obtained by dressing separation (Table 4). The concentrates have already been used as feedstock for producing the titania-enriched material (Table 5) which will be raw material for making titanium dioxide pigment by chloride route, and the tailings for cement filler.

Table 4 Chemical composition of the concentrates and tailings (wt. %)

product	TiO_2	CaO	MgO	FeO	Al_2O_3 + SiO_2
Concentrates	35-45	30-35	8-9	3-5	18-6
taillings	8-11	15-25	8-10	7-10	60-4-

Table 5 Chemical composition of titania-enriched material(wt. %)

	TiO_2	CaO	MgO	Al_2O_3	SiO_2	Fe_2O_3
Titania-enriched material	92-95	0.05	0.05	2.65	0.82	1.17

3. Boron recovery from B-slag[4, 13-15]

It was found by experiments that the efficiency of extraction of boron (EEB) from slag was directly related to both the operation conditions like slag's composition and heat-treatment temperature as well as the precipitating characteristics of the boron compounds, such as amorphous or crystalline phases.

The EEB was low when the molten slags were quickly cooled and then the most of the boron compounds existed in the form of amorphous phases, while the EEB was high when slags were slowly cooled and then the boron compounds were in the form of crystalline phase-suanite ($2MgO{\cdot}B_2O_3$), which was reasonably chosen to be the designed mineral phase.

3.1 Chemical composition

It can be seen in Fig. 5 that the composition of slags having high EEB are just located along the line between $2MgO{\cdot}SiO_2$ and $2MgO{\cdot}B_2O_3$. The farther the composition deviates from the line, the lower the EEB is.

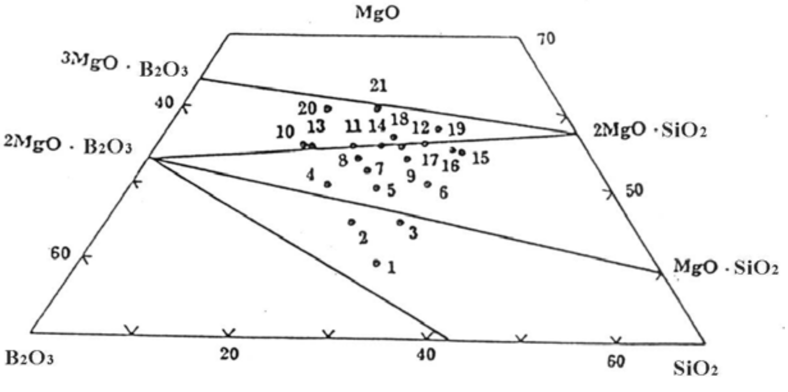


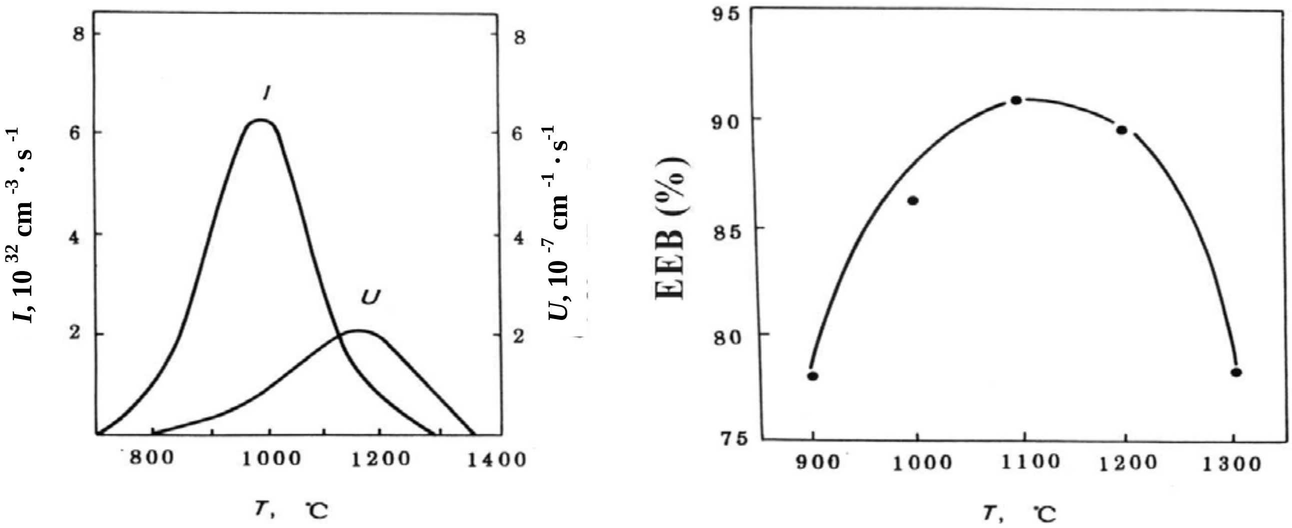
Fig. 5 Composition of $MgO\text{-}B_2O_3\text{-}SiO_2$ system

3.2 Temperature of heat treatment

During cooling process a precipitation of crystalline is dependent on the nucleation rate *I* and crystal growth rate *U*, which are a function of temperature[2].

$$I = \frac{kTN_0}{3\pi a^3\eta}\exp\left(-\frac{b\alpha^3\beta}{T_x\Delta T_x^2}\right) \quad (1), \qquad U = \frac{kTf}{3\pi a^2\eta}\left[1-\exp\left(-\frac{\beta\Delta T_x}{T_x}\right)\right] \quad (2)$$

When the temperature was in the range of 1100-1240℃, according to the kinetic calculation[13], both *I* and *U* can approach to higher value simultaneously. Therefor, for Suanite crystalline, 1100°C is the optimum temperature for heat treatment. The calculated optimum temperature is in good agreement with the experimental results (Fig. 6).

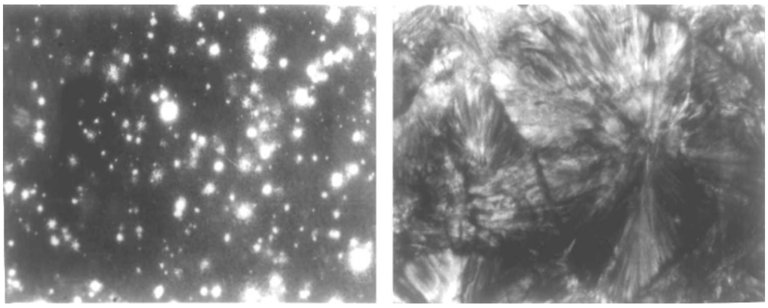


(a) Calculated results (b) Experimental results

Fig. 6 Effect of heat treatment temperature on I - U and EEB

3.3 Additive

The microstructure of the sample without any additive is shown in Fig. 7 (a). The most of the visual field was covered by amorphous phase in which a small quantity of crystalline was distributed. The additive caused the reducing amorphous phase from 80% to 60% and the growing crystalline to large host grains as shown in Fig. 7 (b), so the EEB was increased by 8-11%.



(a) without additive (b) with additive

Fig. 7 Micrographs of B-slag samples treated without (a) and with (b) additive

4. Vanadium recovery from converter slag[16]

At present, V-Ti-Magnetite concentrates have been treated by conventional process in Panzhihua Iron & Steel Company as shown in Fig. 8. Exhausted converter slags containing vanadium-oxide (in Table 6) contaminate environment as waste as 0.135 million tons /year.

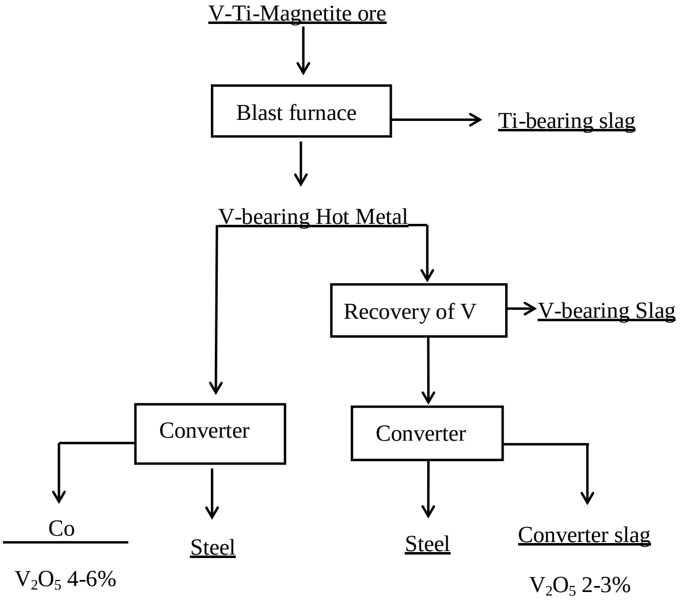


Fig. 8 Process for iron and steel making in Panzhihua Company

Table 6 Chemical composition of V-bearing converter slag (wt. %)

V_2O_5	CaO	TFe	MgO	SiO_2	MnO	P
2.65	53.3	15.25	7.66	8.54	2.04	0.353

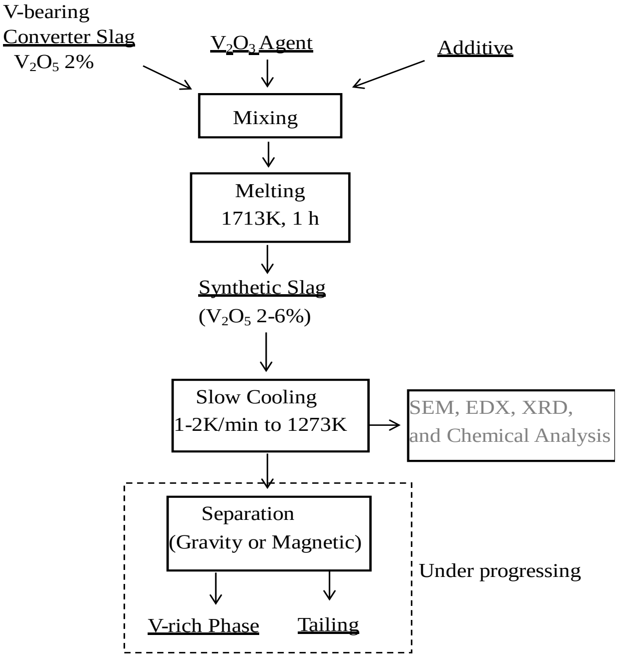
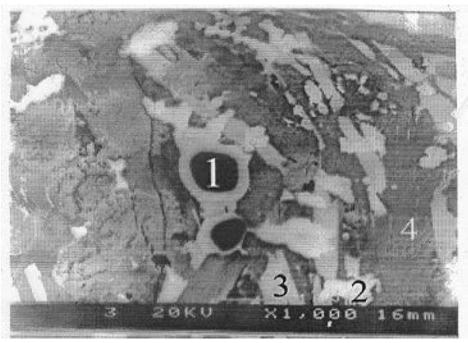


Fig. 9 Flow chart for V-bearing converter slag treatment

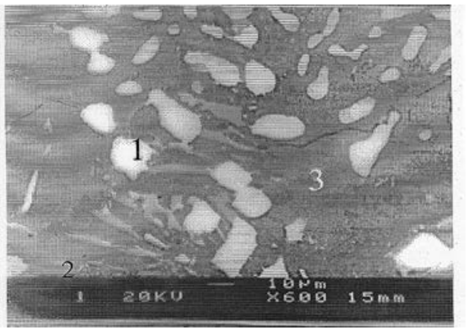
However, it is difficult to recovery vanadium-oxide from the converter slag by conventional process due to its high lime content. An experimental process was conducted to recovery vanadium-oxide from the converter slag by the precipitation technique (in Fig. 9).

The synthetic slag samples with 3.4% and 6.0% of V_2O_5 were respectively melted at 1713 K and kept constant temperature for 60 min and then slow cooled to 1273 K in the cooling rate of 2 K/min. After that, the samples were cooled in the furnace to room temperature. The phases in the treated slag were analyzes by SEM, EDX and XRD respectively (in Fig. 10).



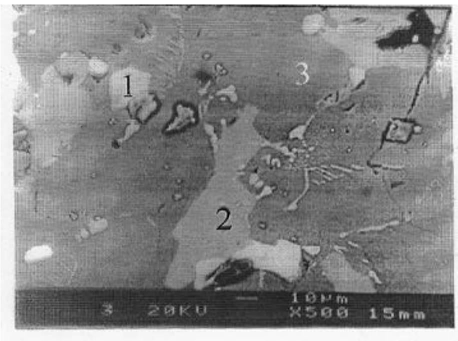
Phase 1: Magnesia
Phase 2: Magnesio wustite
Phase 3: Lime solid solution containing1.3% V_2O_5
Phase 4: Tricalcium silicate containing 3.0% V_2O_5

(a) as received V-bearing converter slag containing 2 % V_2O_5



Phase 1: Magnesio wustite
Phase2: Tricalcium silicate containing 11% V_2O_5
Phase3: Dicalcium silicate containing trace V_2O_5

(b) synthetic slag containing 3.4 % V_2O_5



Phase 1: Wüstite
Phase 2: CaV_2O_6-$Ca_2P_2O_7$ solid solution containing 30.3% V_2O_5
Phase 3: Dicalcium silicate containing 1.1 % V_2O_5

(c) synthetic slag containing 6.0 % V_2O_5

Fig. 10 Photograph of the samples

It was found that the vanadium-oxide was distributed both in lime solid solution and the tricalcium silicate in the as received V-bearing converter slag; in the synthetic slag the vanadium-oxide existed mainly in the Ca_3SiO_5 for the slag containing 3.4% of V_2O_5, but for the slag containing 6.0% of V_2O_5, the vanadium-oxide existed in the form of CaV_2O_6- $Ca_2P_2O_7$ solid solution in which the V_2O_5 content was as high as 30%. Obviously the selective enrichment of vanadium-oxide from V-bearing converter slag is possible if vanadium-oxide content in the slag is higher than 3.4% V_2O_5.

5. Conclusions

It was confirmed by the experimental results that the VNMC can be enriched into a designed mineral phase, such as perovskite for titania, susanite for borate and sincosite for vanadium oxide by proper operation factors like the slag composition and so on. During solidification of molten slags, the precipitating behavior of VNMC could be artificially controlled by proper operation conditions like temperature of heat-treatment, cooling rate, and additives so as to approach the selective coarsening of perovskite in Ti-slag , saunite in B-slag and sincosite in V-slag.

The goal of separating the grown mineral phases from taillings can be fulfilled by dressing or hydrometallurgical process. These facts may come to the conclusion that the novel technique to recover VNMC from the waste slags is available.

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