Vaporization of Vanadium Pentoxide from CaO-SiO₂-VO_x Slags During Alumina Dissolution

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The vaporization of vanadium pentoxide from CaO-SiO₂-VO_x ternary slags using different gas treatment regimens and parallel vacuum gas extirpation to treat V-bearing slags at 1873 K has been developed in the present study. The novelty of the present study is to monitor the effect of parallel alumina dissolution on the vaporization phenomenon. Vanadium pentoxide has high vapor pressure at the temperatures over 1500 K. When CaO-SiO₂-VO_x ternary slags, kept in dense alumina crucibles, are injected with oxygen, V₂O₅ gas bubbles are formed which are forced out by using vacuum extirpation. The vanadium pentoxide could be then collected in the exhaust gases. The mechanism of the process phenomenon is described as the formation of V₂O₅ gas phase resulting from the oxidation of the lower-valent oxides present in the slag. This gas phase would form microbubbles in the molten slag bulk phase due to low surface tension between the gas phase and the slag, thereby increasing the contact surface. At the same time, the crucible material would dissolve in the slag causing an increase in the slag viscosity. Due to the high slag viscosity of the bulk slag, these microbubbles formed would have difficulty in coalescing and reaching the slag surface. The escaping of the bubbles into the gas phase is enabled by the vacuum extirpation.

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I. INTRODUCTION

DURING the production of metals, especially iron and steel, considerable amounts of slags are generated every year all over the world. The annual amount of the slag produced in steelmaking industry exceeds 400 million tones.^[1] Vanadium bearing steelmaking slags are classified as environmentally hazardous substances, which require special handling, storage, and restricted landfill, since vanadium higher oxide may be harmful for biological organisms.^[2] At the same time, vanadium-containing silicate melts are valuable secondary sources for the recovery of vanadium in some cases containing up to 24 pct vanadium.^[3] The concentration of vanadium in the fly ash collected in the furnace off-gas cleaning system after combustion process can be as high as to 40 pct in a form of V₂O₅.^[4]

The interest to recover vanadium and its oxide from different sources is high. Particularly, in metallurgical industry, vanadium is widely used due to its ability to increase the strength and hardness of steel. Addition of vanadium to steel increases its corrosion resistance. Vanadium is considered as a strategic material by EU. Particularly, Germany, being the largest European steel producer reaching crude steel output as high as 39.7 million metric tons in 2019,^[5] is also the largest consumer of vanadium and its alloys in EU. Total import of vanadium to Germany amounts approximately 15,000 t/a.^[6] Further, vanadium is an important element for Ti-6Al-4V alloy widely-used in additive manufacturing.^[7]

Several methods to recover vanadium have already been reported as for example, direct acid leaching,^[8] sodium salt roasting,^[9] hot slag reduction,^[10] and bioleaching.^[11] During vanadium extraction, the disadvantages such as large amount of waste after leaching, high salt consumption at roasting, and substantial energy consumption during hot slag reduction make those methods energy-inefficient, expensive, time consuming, and environmentally polluting. Bioleaching is also a very slow process requiring days of slag treatment.

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In 2012, the first research efforts were made towards developing alternative ways of vanadium extraction. Authors of present work^[12,13] have obtained positive experimental results of V_2O_5 evaporation from thin-film slag samples. At the same time, Yang *et al.*^[14] have successfully studied kinetics of pure vanadium pentoxide evaporation under different atmospheres. These works indicated a prospective way of vanadium extraction from the slags *via* evaporation treatments.

The aim of present work is to study the effects of various technical conditions and parameters on the vaporization route of vanadium extraction as vanadium pentoxide. In the present work, the technique of vacuum extirpation of exhaust gases has been adopted for the first time in the context of vanadium recovery from secondary sources.

II. THERMODYNAMIC CONSIDERATIONS

The vapor pressure of vanadium pentoxide (V_2O_5) in equilibrium with pure liquid V_2O_5 as a function of temperature, reported in literature,^[15] is presented in Figure 1.

It is to be noted that vanadium in the slag can exist in two different valence states, *viz.* V^{3+} and V^{+4} in the slag.^[16,17] At low oxygen levels, the trivalent vanadium will be the dominating species. The low valent oxides (existing as silicates in the slag) need to get oxidized to the pentavalent state before they can escape as vapor. The corresponding chemical reaction will be

The ΔG° which is $-77,038$ kJ for this reaction (calculated at $T = 1873$ K, oxides are pure state and O_2 is considered at 101.3 kPa.) was calculated using HSC Chemistry 9.0 Software.^[18]

The thermodynamics of V_2O_3 in CaO - SiO_2 - MgO - Al_2O_3 slags has been measured by Dong *et al.*^[19] These authors report that the thermodynamic activity of V_2O_3 (as $VO_{1.5}$) is a function of the mol fraction of $VO_{1.5}$ in the above-mentioned slag. From Figure 5 in their publication, the equation for the activity-composition relationship was derived in the present work and represented as in Eq. [2].

$$a_{VO_{1.5}} = 88.3736X^2 + 0.02513X + 0.00005, \quad [2]$$

where X refers to the mol fraction of $VO_{1.5}$ in the slag. The standard state is pure solid $VO_{1.5}$. These authors have also given the variation of the activity coefficient of $VO_{1.5}$ as a function of slag basicity.

From Eq. [2], it can be seen that the activity of $VO_{1.5}$ shows a positive deviation from ideality. This would imply that the oxidation of V^{3+} in the slag according to Reaction [1] will be difficult in the solution state. V^{+4} in the slag can also get oxidized to V^{5+} in a similar way. If the experiments could be designed to promote the oxidation of lower-valent vanadium in the bulk slag to the pentavalent state and if the gaseous V_2O_5 could be transported to the surface, it should be possible to capture the vanadium as condensate. Thus, the objective

Fig. 1—Vapor pressure of V_2O_5 in equilibrium with liquid V_2O_5 as a function of temperature.

of the present work is to design an experimental method to get the vanadium pentoxide into the vapor phase so that an elegant separation of vanadium by condensation of the gas phase is enabled. As the transportation of the vanadium pentoxide formed in the bulk slag is dependent on the bulk viscosity of the slag, it was planned that the slag viscosity could be gradually increased by the dissolution of alumina from the crucible into the ternary slag monitoring, at the same time the vaporization of V_2O_5 .

III. EXPERIMENTAL

A. Samples Preparation

In the present study, the synthetic ternary (CaO - SiO_2 - VO_x) slag samples with different oxide combinations were investigated (See Table I). Prior to the experiments, pure oxides were prepared and mixed in appropriate proportions. CaO was made from $CaCO_3$ by heating it to 1273 K in a muffle furnace for 10 hours and cooling the sample in a desiccator with silica gel as the dehydrant. SiO_2 and V_2O_5 were heat-treated at 383 K for 5 hours to remove moisture. The chemicals were mixed in appropriate proportions in an agate mortar and pressed into tablets weighing 0.022 kg each. The prepared series of oxide mixtures were stored in a desiccator before use.

B. Experimental Setup and Procedure

1. Choice of crucible

The choice of the crucible for holding the slag is very crucial in the present experiments. It would be natural to choose a metallic crucible. As the experiments are conducted with oxygen purging, the only metallic crucible resistant to oxidation at the experimental temperature would be those made out of Pt. 30 Rh. Preliminary experiments elsewhere had indicated that these could crack during the experiments due to the contact with metal which could be reduced from the slag with the subsequent dissolution in the crucible. An alternative would be to use ceramic crucible, either Al_2O_3 or MgO . One of the aims of the present study is to

investigate the effect of the increase of the slag viscosity on the evaporation process. Hence, in the present experiments, the slag samples were melted in dense alumina crucibles ($h = 0.037$ m, $d_t = 0.037$ m, $d_b = 0.017$ m) supplied by Giess-Technische-Sonderkeramik GmbH & Co. KG chosen to hold the slags at the experimental temperature.

2. Experimental set-up

Cold Crucible Induction Melter (CCIM) supplied by LINN High Therm GmbH was employed in the present work for melting the slags. Usually this equipment is used for melting of high-temperature reactive materials (e.g., steels, pure metals, TiAl 6-4, CoCr, etc.). The equipment was re-designed to have an additional controlled oxygen inflow system, a suction device for drawing off exhaust gases connected to vacuum chamber for collecting the condensing vapor species, graphite heating element, and thermocouple type B for temperature control (see Figure 2). As mentioned earlier, alumina crucibles were used in the present study.

3. Experimental procedure

A schematic illustration of the cross-sectional view of the experimental setup is presented in Figure 3.

For each slag composition, a series of experiments was conducted. The influence of different factors on vanadium extraction from the slag samples were monitored by each series, varying the parameters such as total pressure in a chamber and oxidizer (O_2) flow rate (see Table II).

After placing crucible with the sample in the CCIM reaction chamber, the air in the system was pumped out and the chamber was filled with inert gas (Ar of 99,999 pct purity from a liquid argon tank with typical 2 to 3 ppm of O_2) to a fixed total pressure in a CCIM chamber (50, 85, or 100 kPa). The oxygen blowing was then launched and kept constant for different time sequences (0, 5, 10, 20, 60 minutes). Oxygen flow rates used in experiments were 250 and 500 $cm^3\ min^{-1}$. Pulsating vacuum extirpation enabled the removal of the oxidized layer during oxygen treatment. The total pressure in CCIM was controlled by closing and opening an outlet tap connected to vacuum chamber for 5 to 7 seconds with intervals of about 20 seconds. For comparison of the results, some experiments were conducted without oxygen treatment after melting the sample, but under argon for the same time periods as with oxygen. Pulsating vacuum extirpation was also used to remove the exhaust gases during gas treatment.

Table I. Chemical Composition of Slags			
	CaO (wt pct)	SiO ₂ (wt pct)	V ₂ O ₅ (wt pct)
CSV1	44.61	47.29	8.10
CSV2	44.37	49.53	6.09
CSV3	44.35	49.52	6.12

After each experiment, chemical compositions of synthetic slags were analyzed using XRF. The results were recalculated, excluding the alumina addition from alumina crucible so that a comparison of the final slag composition with the weighed-in amounts could be enabled. Amount of Al_2O_3 pick-up depends on the treatment time and composition, achieving a maximum of 23.3 pct of Al_2O_3 in one of the experiments at 60 minutes of treatment (See Figure 4).

IV. EXPERIMENTAL RESULTS

The present results indicate that vanadium could be extracted from the slag by evaporation using the combined oxygen injection and vacuum extirpation method. Preliminary experiments showed that vanadium escape from the slag was quite low without the vacuum extirpation treatment. On the other hand, the vanadium extraction rate became significant with the application of vacuum extirpation and increased as a function of time.

A. CaO-SiO₂-VO_x Slag System

The sample denoted as CSV1 was pre-melted at 1873 K in argon atmosphere with total pressure in chamber of 85 kPa. It was then treated with oxygen for different time sequences (0, 5, 10, 20, 60 minutes). Oxygen flow rate was 250 $cm^3\ min^{-1}$. The results of vanadium pentoxide extraction rate are presented in Figure 5. As shown in this figure, the V_2O_5 extraction rate increases linearly as function of time in the initial stages up to 20 minutes, after which the slope decreases. The highest fraction of V_2O_5 (over 77 mass pct) is extracted at the longest experimental period at 60 minutes.

The images of cross-sectional view of CSV1 sample after 5 minutes oxygen treatment show high concentration of foam-like surface with V-rich bubbles formation (See Figure 6(a)). The SEM/EDX analysis reveals that the flat cross-section surface contains the traces of vanadium and the bubbles contain high amounts of vanadium. On the contrary, the sample after 20 minutes of oxygen treatment has a glassy structure (See Figure 6(b); Table III).

An experimental series with the higher oxygen flow rate and slightly different composition was conducted. This sample, denoted as CSV2, was pre-melted at 1873 K in argon atmosphere with total pressure of 850 mbar in the chamber. It was then treated with oxygen for different time sequences (0, 5, 10, 20, 60 minutes). Oxygen flow rate was 500 $cm^3\ min^{-1}$. The results indicate that more than 45 pct of V_2O_5 was removed from the liquid slag during the 60 minutes of oxygen treatment. In order to confirm the reproducibility of the results, another series of experiments under the same conditions and almost identical slag composition was carried out. The sample was denoted as CSV3. A comparison of CSV2 and CSV3 treatments shows that the obtained results are reproducible (Figure 7).

Fig. 2—(a) Experimental setup (re-designed Cold Crucible Induction Melter); (b) Inner view of setup.

Fig. 3—Schematic illustration of cross-sectional view of a method for recovering V₂O₅ from a slag.

Additional experiments with 20 and 60 minutes of time sequence for comparison of influence of inert gas use and pressure increase on V₂O₅ recovery were conducted. The sample treated 20 and 60 minutes in argon atmosphere showed that vanadium pentoxide extraction decreased by half in comparison with the same with oxygen blowing (Figure 8). An increase of total pressure in a chamber to 1 atm also halved the V₂O₅ extraction indicating that higher chamber pressure hindered V₂O₅ evaporation. The results also indicate that changes of vanadium content of the slag at ambient chamber pressure would point to the emission of toxic vanadium-containing vapor from molten vanadium-containing slags in steel mills.

A series of experiments with a ceramic (Boron-Nitride) lid on the top of the crucible were also conducted (Figure 9) in order to study the effect of the same on vanadium evaporation. The experimental results of V₂O₅ extraction rate as a function of time reveal that the addition of ceramic lid prevents the evaporation process. As shown in Figure 10, the period of treatment up to 60 minutes shows no significant change of vanadium content. As mentioned earlier, the outlet gas tap is not constantly evacuating the chamber, therefore, the explanation for the evaporation process should be divided into two various conditions (with and without outlet gas under the crucible lid):

a) The process under the lid with evacuation of atmosphere:

Since the diameter of outlet gas tube is much larger than that of the inlet oxygen tube, a lower experimental pressure is created by the high outlet gas velocity. To equilibrate the pressure difference, the oxygen gas will be drawn out from the inlet gas before contacting with the liquid slag and a fraction of argon gas can be drawn into the crucible from the gaps between the ceramic tubes and ceramic cover. Although a fraction of oxygen gets in contact with liquid slag and V₂O₅ is formed at the surface of liquid slag, in comparison to the density of oxygen and argon gas at the same experimental conditions, the density of V₂O₅ is several times higher than that of oxygen and argon ($\rho_{V_2O_5} = 8.12 \text{ kg/m}^3$, $\rho_{O_2} = 1.48 \text{ kg/m}^3$ and $\rho_{Ar} = 1.784 \text{ kg/m}^3$ at room temperature). Consequently, instead of drawing out the V₂O₅, argon is likely to be drawn.

b) The process under the lid without evacuation of atmosphere:

Table II. Various Treatment Sequences Used for Experiments (Temperature: 1873 K)

Sample	Total Pressure in a Chamber (kPa)			Gas Atmosphere in CCIM Chamber During Heating and Melting	Oxygen Top Blowing ($\text{cm}^3 \text{cm}^{-1}$)	
	50	85	100	Argon	250	500
CSV1		x		x	x	
CSV2		x		x		
CSV2		x		x		x
CSV2			x	x		x
CSV3	x			x		x
CSV3		x		x		x
CSV3		x		x

Fig. 4—Evolution of alumina content in the sample with the treatment time (Temperature: 1873 K).

Fig. 5—Vanadium pentoxide extraction rate as a function of oxygen treatment time (O_2 flow rate = $250 \text{ cm}^3 \text{min}^{-1}$, total pressure in a chamber = 850 mbar, $T = 1873 \text{ K}$).

Oxygen gas left the area between the ceramic and surface of liquid slag from the gaps between gas tubes and ceramic cover. Therefore, it was presumed that the extraction of vanadium as well as evaporation of vanadium without ceramic lid occurs partially from the free surface of liquid. The outlet gas tube would enable the withdrawal of the V_2O_5 vapor from the chamber and equilibrating the chamber pressure.

V. DISCUSSION

In present experiments, alumina crucibles were used for containing the sample. Post-treatment chemical analysis showed considerable increase of alumina content in the slags. Al_2O_3 behaves as amphoteric oxide and can both increase and decrease slag viscosity depending on its amount and the presence of other slag constituents.^[20,21] The calculations of viscosities in present studies were performed with FactSage 7.2.^[22] In Figure 11, it can be seen that the viscosity of the slag due to dissolution of alumina considerably increases initially at 5 minutes of oxygen treatment, then gradually decreases until 20 minutes and again increases at further treatment. Alumina being an amphoteric oxide is not expected to contribute to the evaporation process of V_2O_5 . However, in comparative series of CSV2 and CSV3 slags, it can be noted that, under similar treatment conditions (See Figures 4 and 7, treatment 20 minutes), higher vanadium extraction corresponds to higher alumina content while at 10 minutes of treatment time showed the opposite effect of Al_2O_3 .

As it can be seen from Figure 11, the viscosity is relatively high (220 to 420 mPa s) which would hinder the coalescence and rising of gas bubbles. Thus, the vacuum treatment is essential for the vaporization of V_2O_5 .

The chemical composition before and after the experiments confirmed the loss of element vanadium. This loss is attributed to the volatilization of the vanadium pentoxide vapor from slag samples as mentioned in the heading “Thermodynamic considerations.” Changing of the chamber conditions such as the experimental pressure and velocity of oxygen flushing may favor the evaporation rate.

Firstly, the evaporation rate of V_2O_5 is increased with the decrease of the chamber pressure which is predicted by Eq. [3].^[23] The diffusion of the element in the gas phase shows a negative tendency to pressure. In the work of Savov *et al.*^[23] and Zaitsev *et al.*,^[24] the evaporation process of steel tramp element—copper and tin—was studied at various pressures in the vacuum range. In their experiments, a similar correlation between pressure and evaporation rate was found.

Fig. 6—CSV1 sample after (a) 5 min of oxygen treatment; (b) after 20 min of oxygen treatment.

$$D_{V_2O_5-Ar} = \frac{\text{const}}{P}, \quad [3]$$

where $D_{V_2O_5-Ar}$ is the diffusion of V_2O_5 vapor in argon ($\text{m}^{-2} \text{s}^{-1}$), P is pressure (bar).

Secondly, as shown in Figure 12, a condensate slag layer circa 1 cm is observed, on the experimental crucible wall. Apparently, this part of slags was pulled up by the capillary force, which marks the interaction between surface tension of liquid slag and adhesive force between liquid slag and crucible wall. The value of liquid height h on the crucible wall can be expressed by Jurin's law^[25]

$$h = \frac{2\gamma \cos \theta}{\rho g r_o}, \quad [4]$$

where h is the height of the top of the layer to the liquid surface (m); θ is the contact angle of the liquid on the crucible wall; γ is the surface tension of the liquid (mN m^{-1}); ρ is the density of the liquid (kg m^{-3}); g is the gravitational acceleration and r_o is the crucible radius (m).

The evaporation rate of the V_2O_5 heavily depends on the free surface of the liquid slag. However, the liquid slag layer on the crucible wall caused by capillary effect extends the free surface area for evaporation process

Table III. SEM/EDX Analysis of CSV1 Sample

Spot 1		Spot 2		Spot 3		Area 1		Area 2	
Element	Atomic Pct	Element	Atomic Pct	Element	Atomic Pct	Element	Atomic Pct	Element	Atomic Pct
O K	51.86	O K	35.33	O K	45.30	O K	43.60	O K	45.04
Al K	2.81	Al K	1.16	Al K	0.31	Al K	0.51	Al K	0.76
Si K	21.54	Si K	15.07	Si K	25.87	Si K	23.13	Si K	26.52
Ca K	8.80	Ca K	17.16	Ca K	21.92	Ca K	21.35	Ca K	20.17
V K	5.16	V K	13.19	V K	0.36	V K	2.14	V K	1.72

Fig. 7—Comparison of the results of CSV2 and CSV3 slag systems (Temperature: 1873 K).

Fig. 9—Top view on the crucible with additional cover.

Fig. 8—Additional experiments with different pressures in CCIM chamber (Temperature: 1873 K) compared with the aggregated trend line for all data points of CSV2 and CSV3 shown in Fig. 7.

which favors the evaporation. The parameters shown in Eq. [4] are constants or available. During the present investigations, the surface tension of liquid slags can be changed by the oxygen flushing and the V_2O_5 evaporation.

Fig. 10—Experiments with additional cover on top of the crucible (O_2 flow rate = $250 \text{ cm}^3/\text{min}$, total pressure in a chamber = 850 mbar, $T = 1873 \text{ K}$).

The modeling of slag properties was carried out in the present work using the modeling tables developed by Mills.^[26] Due to the absence of data for V_2O_5 for modeling of surface tension values and assuming that vanadium in the bulk should be in a form of V^{3+} or V^{4+} , its content was recalculated as V_2O_3 . In order to calculate optical basicity of the slag, V_2O_3 was assumed to have the same properties as Cr_2O_3 . The increase of surface tension in the bulk of the slag can be affected due to dissolution of alumina from the crucible (See Figure 13).

Fig. 11—Viscosity of the slag as a function of treatment time and chemical composition of the samples including the dissolved alumina calculated in FactSage 7.2.

Fig. 12—Thermocapillary effect.

As reported by Badger *et al.*,^[27] the surface tension of liquid slag with the composition 17.4 pct Na₂O–10.1 pct CaO–SiO₂ was decreased by 23 pct with small addition of V₂O₅ at 1473 K and 1623 K. Thus, the formation of V₂O₅ at the liquid slag surface due to oxygen flushing is expected to reduce surface tension significantly. It is reported^[28] that, at steelmaking temperatures, V₂O₅ amounts as in the present study reduce surface tension to about 40 mN m^{−1}. SEM/EDX analysis of slag cross-section reveals higher concentration of vanadium in the bath surface.

The capillary height h of the liquid slags on the crucible wall gets reduced, which results in less surface area for the V₂O₅ evaporation. With the higher velocity of flushing gas, more quantity of V₂O₅ will accumulate at the surface layer of liquid phase leading to the lower surface tension.

Fig. 13—Surface tension of CSV1 slag as a function of time.

Thirdly, there is a dependency of evaporation of V₂O₅ on the velocity of oxygen flushing. The mainstream understanding of evaporation would indicate that the flow velocity favors the evaporation process. In the previous evaporation work of Jung *et al.*^[29] it was reported that, with the higher flow velocity, the evaporation rate is increased. Moreover, the variation of the flow velocity is directly changing the velocity of the vapor in vicinity of liquid droplet surface. Consequently, it enhances the parameters which play significant role on evaporation, such as the pressure on the surface of liquid droplet, shear stress, and concentration gradient of the evaporating vapor. However, the present results of V₂O₅ evaporation are in contrast with the mainstream understanding between evaporation rate and flow velocity. The evaporation rate of V₂O₅ at 250 cm³ min^{−1} is much higher than at 500 cm³ min^{−1}. The oxygen flushing at 250 cm³ min^{−1} was the best value for favoring the evaporation rate of V₂O₅. The evaporation process may be affected by many other factors; some of them may limit the evaporation process. For example, the oxygen flushing may increase the pressure around the droplet surface and enhance the Marangoni effect by varying the surface tension of the liquid slag. For understanding the evaporation process of V₂O₅ in the present investigation, the kinetic and mechanism of evaporation must be studied in detail.

The reaction steps may be as follows:

1. Penetration of oxygen molecule in the bulk slag.
2. Oxidation of V₂O₃ (or VO₂) in the bulk slag forming the V₂O₅ gas bubble.
3. The gas bubble is entrapped without coalescence due to high slag viscosity and low interfacial tension.
4. Application of vacuum pulls the bubbles to the surface.
5. The V₂O₅ reaching the surface is pulled into the gas phase.

As this is a “chain reaction,” higher oxygen flow may not be very effective in oxidizing the V^{3+} or V^{4+} in the bulk and escape directly into the gas phase without reaction. Thus, an optimum balance between the oxygen inflow and vacuum would be required. Higher oxygen flow may be less effective.

A. Formation and Rising of V_2O_5 Bubbles

V_2O_5 bubbles are formed as the result of oxidation of V_2O_3 (or VO_2) in the bulk slag. Formation of the bubble in the slag takes place on the surface of the crucible and on the surface of solid particles. Also, some amount of oxygen may be entrapped by the liquid slag in form of bubbles and work as a liquid–gas interface for gaseous V_2O_5 evaporation. Movement of the bubble starts when the buoyancy force exceeds the surface force. According to Mersmann,^[30] the bubble size can be calculated as follows.

The buoyancy force is

$$F_g = \frac{\pi}{6} d_B^3 g (\rho_L - \rho_G) \approx \frac{\pi}{6} d_B^3 g \rho_L, \quad [5]$$

where d_B is the equivalent diameter of the bubble, assumed to be spherical; g is gravitational acceleration; ρ_L is the density of the liquid; ρ_G is the density of gas.

The surface force is

$$F_\sigma = \pi d_n \sigma, \quad [6]$$

where d_n is the nozzle diameter; σ is the interfacial tension.

Depending on the gas flow, three different ranges arise^[31]:

1. At low gas flow rate, the size of the bubble is determined by the buoyancy force of the gas and the surface force. Inertial force has no effect.
2. At high gas flow rate, the size of the bubble is defined by the buoyancy of the bubble and inertial force of the liquid. Surface force has no effect.
3. In other cases, all the forces have to be considered.

In the present study, gas flow rate is relatively low, therefore, the size of the bubble is defined as the equilibrium between the buoyancy and the surface forces. The bubble diameter is expressed by equation.^[32]

$$d_B = \left(\frac{6\sigma d_n}{g\rho_L} \right)^{\frac{1}{3}}. \quad [7]$$

Modeling proposed by Wang *et al.*^[33] was applied to current work to describe the physico-chemical phenomena for gas–liquid reactions. The modeling is done in the following steps:

- 1) Transfer of V^{3+} from the bulk liquid slag to gas–liquid interface
- 2) Transfer of O_2 from the gas phase to gas–liquid interface
- 3) Transfer of V_2O_5 from the interface to the bulk gas phase

Mathematically it can be described as follows:

$$n_{V_2O_3} = \frac{A_b k_m^{V_2O_3} \rho_m}{100 M_{V_2O_3}} (\text{wt pct } V_2O_3^B - \text{wt pct } V_2O_3^*) \quad [8]$$

$$n_{O_2} = A_b k_g^{O_2} (C_{O_2}^B - C_{O_2}^*) \quad [9]$$

$$n_{V_2O_5} = A_b k_g^{V_2O_5} (C_{V_2O_5}^B - C_{V_2O_5}^*), \quad [10]$$

where n_i is the rate of transfer of species i ; A_b is the surface area of the bubble; k is the mass transfer coefficient (“m” and “g” refer to liquid and gaseous phases, respectively); ρ_m is the density of liquid slag; C_i is the concentration in the gas phase (“B” and “*” refer to bulk and gas–liquid interfaces, respectively).

Equilibrium constant at the gas–liquid interface for the reaction

is as follows:

$$K = \frac{P_{V_2O_5}^*}{\text{wt pct } V_2O_3^* \cdot f_{V_2O_3} \cdot P_{O_2}^*}, \quad [12]$$

where $f_{V_2O_3}$ refers to Henrian activity coefficient of V_2O_3 ; $P_{O_2}^*$ is oxygen partial pressure in gas–liquid interface.

As it can be seen from Eq. 12, the model calculations can add oxygen partial pressure as a parameter. This will enable to apply the model in oxidizing vanadium in the slag using air as the oxidizing medium.

The absorbed oxygen regarded as incoming force is the factor which can affect the liquid convection phenomenon. Inside the bulk liquid, a gaseous V_2O_5 is formed. Therefore, the liquid slag convection is also affected by the buoyancy effect. In Figure 14, the illustration of vortices and V_2O_3 concentration gradient is shown. The reduction of V_2O_5 as well as the reduction of the V_2O_3 creates the concentration gradient in liquid slag, consequently, the liquid convection is enhanced by the Marangoni force. The present treatment does not consider probable turbulence effects in the bulk due to gas injection.

B. Escape of V_2O_5 Gas Bubble from the Slag Surface

As it is shown in Figure 15, the pressure on the surface of liquid slag consists of two parts P1 and P2. P1 indicates the pressure on the surface area under the oxygen flushing and P2 indicates the normal pressure on the rest of liquid slag. Equations [13] and [14] show that the pressure under the oxygen flushing P1 is greater than P2. The greater surface pressure heavily reduces the diffusion of volatile species, consequently, reduces the overall evaporation rate. A small black vector indicates the direction of V_2O_5 vapor and the length of vectors represents the evaporation scale.

$$P = \frac{F}{S} \quad [13]$$

$$F = \frac{m \cdot v}{t}, \quad [14]$$

where P indicates the pressure (Pa), F indicates the force (N), S indicates the surface (m^2), m indicates the mass (g), v indicates speed (m s^{-1}), and t indicates time (s).

Kabov *et al.*^[34,35] studied the evaporation convection in a horizontal liquid with gas flow. The results in their investigation are in a good agreement with the mainstream understanding that the gas flow can enhance the evaporation process. They obtained the equations for the shear stress on the liquid surface caused by Marangoni effect τ_{sur} and shear stresses on the liquid surface induced by gas flow τ_g . The correlated equations are shown in Eqs. [15] and [16].

$$\tau_{\text{sur}} = \frac{\delta\sigma}{\delta T} \cdot \frac{\delta T}{\delta x}, \quad [15]$$

where τ_{sur} is a shear stress caused by Marangoni effect on the liquid surface (N m^{-2}); $\frac{\delta\sigma}{\delta T}$ is a temperature coefficient of surface tension (N mK^{-1}); $\frac{\delta T}{\delta x}$ is a velocity gradient (K m^{-1}).

$$\tau_g = \eta \frac{dv}{dy} = -\frac{H}{2} \cdot \frac{\delta p}{\delta x}, \quad [16]$$

where τ_g is a shear stress caused by gas flow on the liquid surface (N m^{-2}); η is dynamic ($\text{m}^2 \text{s}^{-1}$); $\frac{dv}{dy}$ is the velocity gradient (m s^{-1}); H is the distance between end of the inlet gas tube and the liquid slag surface (mm); $\frac{\delta p}{\delta x}$ is the pressure gradient (m^2).

The main principle of the present investigation is the formation of volatile species of V_2O_5 , when the oxygen flushing flows on the surface of liquid slag and fraction of oxygen is absorbed in the liquid slag. The formed V_2O_5 evaporates on the liquid slag surface with the oxygen flushing, consequently, the surface tension on the surface liquid layer is changed by the loss of V_2O_5 . The SEM/EDX analyses of the cross-section of CSV1 after 5 minutes of oxygen treatment (See Figure 6) reveals that the size of bubbles in vicinity of surface slag layer is smaller than the bubble in the deeper part of the slag, this phenomenon clearly indicates that the V_2O_5 concentration gradient and as well the slag surface tension gradient have been created by the losses of V_2O_5 . The variation of surface tension of liquid slag produces the shear stress on the surface liquid layer as shown in Eq. [16]. In the study of Kabov,^[34] the gas flow channel was settled in parallel with the liquid layer with the height H of 0.005 m and the gas flow channel in the present investigation was settled with inclination angle 70 deg with the same height of 0.005 m. However, the gas flow on the surface of liquid slag can reflect (bounce) back by the contact between crucible wall and liquid slag. Therefore, H for the present study was settled as $H \cdot n$ (where n is parameter for modifying the height H).

Fig. 14—Schematic convection illustration for the inside liquid.

Fig. 15—Schematic illustration of liquid slag surface system surface of liquid slag system.

However, actual $H \cdot n$ is difficult to obtain due to the complex structure of experimental system. As the variation of the orientation of inlet gas tube can substantially affect the flow velocity and shear stress in vicinity of liquid surface,^[36] the inclination angle of the inlet gas tube is considered to be constant in all experimental trials.

$$\tau_g = \eta \frac{dv}{dy} = -\frac{H \cdot n}{2} \cdot \frac{\delta p}{\delta x} \quad [17]$$

The evaporation kinetics indicate that, over the liquid surface, the vapor layers as well as concentration gradient will be created by the reduction of element's energy. For higher diffusivity as well as further motion with higher vapor concentration, more energy is

Fig. 16—Schematic illustration of liquid slag surface.

required. Therefore, when the gas flow penetrates the surface of the liquid, the velocity increases and the concentration gradient is rebuilt. In Figure 16, the flushing oxygen flow is the pushing force on the partial surface of liquid slag, and gas flow turns to the horizontal driving force which is shear stress on the liquid slag τ_g induced by gas flow. Line 1 represents a concentration gradient; line 2 represents oxygen flushing velocity gradient; and line 3 represents pressure gradient. The direction of vectors is from high value to the low value. The total mass flow N is a combination of the diffusion flux of V_2O_5 , J and convective process as shown in Eq. [19], the diffusion flux of V_2O_5 in argon atmosphere can be expressed by the Fick's law of diffusion Eq. [18]:

$$J = D_{V_2O_5-Ar} \cdot \frac{\delta C}{\delta x}, \quad [18]$$

where $D_{V_2O_5-Ar}$ is interdiffusivity of V_2O_5 vapor in Ar gas ($m^2 s^{-1}$); $\frac{\delta C}{\delta x}$ is the concentration gradient (mol/m^4)

$$N = \text{Diffusion} + \text{Convection} = D_{V_2O_5-Ar} \cdot \frac{\delta C}{\delta x} + Cv, \quad [19]$$

where N is a total mass flow ($mol m^{-2} s^{-1}$); v is the vapor flux velocity ($m s^{-1}$).

VI. CONCLUSIONS

The investigations on vanadium extraction under various gas pressure and oxidizer flow rate from variable slag compositions with increasing alumina content in the ternary $CaO-SiO_2-VO_x$ slag are conducted. The results indicated the following:

1. Vanadium can be successfully removed from the slag using vacuum extirpation technique (pulsating oxidation).
2. The decrease of total pressure in a chamber favors the removal of vanadium from slag.
3. Reduction of oxidizer flow rate improves the removal of vanadium.
4. Neutral atmosphere without oxidizer source halves the removal rate of vanadium oxides from the slag.
5. The increased oxygen flushing elevates the pressure on the fraction of evaporation surface and the greater

oxygen concentration introduced in the liquid slag may decrease the surface tension as well as the capillary effect, consequently, the free surface for evaporation is reduced. In result, the extraction rate of V_2O_5 is limited.

6. The increase of alumina content has only a marginal effect on the evaporation process.

The most of parameters in the present investigation cannot be measured or are complicated for computation, the 3D simulation is suggested for deeper and more complete discussion in the future work.

VII. FUTURE WORK

The future work will be focused on studying the influence of different oxides addition to V-bearing slags as well as extraction of V_2O_5 from industrial slags.

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