A Novel Method to Extract Vanadium and Chromium from Vanadium Slag using Molten NaOH-$NaNO_3$ Binary System

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A new method using NaOH-$NaNO_3$ binary melts to treat vanadium slag is proposed. Vanadium and chromium can be simultaneously extracted in the leaching processes. Under the optimum reaction conditions, the recovery of vanadium and chromium can reach 93.7% and 88.2% in 6 h, respectively. The kinetics investigation indicates that the decomposition of vanadium slag is controlled by mass transfer in product layer. During the reaction, NaOH is believed to provide basic media and facilitate the dissolution of acidic oxides. $NaNO_3$ decomposes to produce a large amount of active oxygen species, such as O, O_2^{2-}, and O^{2-}. NaOH intensifies the decomposition of $NaNO_3$ to $NaNO_2$, but inhibits further decomposition of $NaNO_2$. $NaNO_3$ can be regenerated by oxidation of $NaNO_2$ using oxygen at high temperature. The apparent activation energy of $NaNO_2$ oxidation in the temperature ranging from 350 to 450°C is 105.5 kJ/mol. © 2012 American Institute of Chemical Engineers *AIChE J,* 59: 541–552, 2013
Keywords: vanadium slag, NaOH-$NaNO_3$, molten salt, liquid oxidation, mechanisms

Introduction

Vanadium is a high-melting point metal and is widely used in metallurgical industries due to its ability to enhance the mechanical properties such as tensile strength, hardness, and fatigue resistance of steels.[1,2] Iron and steel making industries consume about 85% of total vanadium production annually. There are about 65 types of vanadium-containing minerals in the world, and titanomagnetite is the main raw material for vanadium extraction, accounting for about 88% of vanadium production.[3,4] During steelmaking process using titanomagnetite ores, the vanadium compounds are oxidized and enriched into steel slag, which is called vanadium slag, and it is the direct source for vanadium extraction.[5]

At present, sodium salt roasting is the most commonly used technology for the treatment of vanadium slag, and vanadium (III) is oxidized to sodium metavanadate by oxygen in rotary kiln or multiple hearth furnace at high temperature (750–850°C). Sodium metavanadate is soluble and can be dissolved in water in the subsequent leaching steps. However, due to low-vanadium conversion rate (only 65–85%) of single roasting, multiple roasting processes have to be applied,[6–9] causing the consumption of a large amount of energy and resources. Furthermore, due to the decomposition of sodium salts such as Na_2CO_3, Na_2SO_4 and NaCl, a lot of harmful gases, such as Cl_2, SO_2 and HCl are emitted. To avoid the emission of toxic gases, calcium salt roasting technology is introduced to vanadium slag treatments.[10–12] Instead of sodium salt, CaO is used to react with vanadium oxide to form calcium vanadate at a relative higher temperature (850–950°C). Calcium vanadate is not water-soluble, but can be leached out using sodium or ammonium

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Table 1. Chemical Analysis of the Chengde Vanadium Slag

Component	V_2O_5	Cr_2O_3	FeO	SiO_2	TiO_2	CaO	MnO_2	Al_2O_3	MgO
Content, wt%	10.20	4.15	49.01	20.21	11.03	1.22	5.22	2.42	1.60

carbonate solutions[10] or acid such as sulfuric acid solutions.[12] The vanadium compounds in the solutions are further purified and extracted using ion exchange, followed by ammonia precipitation. The whole recovery of vanadium can reach 85–88%, slightly higher than multiple sodium salt roasting of 82–85%.[13] However, vanadium slag usually contains 3–6% chromium (III) oxide in the form of chromium spinel, which is thermodynamically more stable than vanadium spinel, not being able to be recovered at vanadium roasting temperatures.[14] The hazardous chromium compounds in tailings, therefore, greatly threat the environment. In this regard, it is imperative to develop a new and cleaner production process to improve the vanadium yield and recovery chromium simultaneously with low-energy consumption.

Recently, a novel KOH leaching process of extracting chromium was proposed by Zhang and coworkers.[15–18] This process has been named as submolten salt method and was first used for the treatment of chromite, in which a recovery of 99% was obtained and the residue amount was greatly reduced. A demonstration plant has been built in the Henan province and runs well. An additional new process was proposed by Sun et al.[19] to produce K_2CrO_4 by using the $KOH—KNO_3$-H_2O submolten system to lower the amount of KOH in the leaching process. Nevertheless, the high-cost of KOH restrains the application of extraction chromium. Molten $NaOH—NaNO_3$ salt liquid oxidation is an alternate approach to extract chromium and was first used to decompose chromite ore in 1974 by Kashiwase et al.[20] In their study, $NaNO_3$ was used as an oxidant to oxidize chromium (III), and the recovery reached 99% at 340°C in 3 h. However, the accumulation of $NaNO_2$ significantly deteriorated the reaction media, not only influencing the oxidation of chromium, but also causing heavy burden during the separation of chromium compounds from the leaching solutions. In another study, instead of $NaNO_3$, oxygen was used as an oxidant in molten NaOH media,[15,21–23] so that the formation of $NaNO_2$ was avoided. However, the reaction temperature had to be elevated to 500°C in order to extract chromium from chromite ore effectively.

In light of the foregoing, Zhang et al.[24] developed a new chromite ore oxidation process by combining the advantages of the aforementioned two approaches. Chromite ore was treated at 400°C in molten $NaOH—NaNO_3$ under continuous oxygen flow, and in such reaction system, $NaNO_3$ acted as oxidant and was reduced to $NaNO_2$. The recovery of chromium reached 99% and $NaNO_2$ was entirely oxidized by oxygen. Following the similar strategy, the new reaction media was considered to treat vanadium slag. The results showed that vanadium can be effectively extracted at a much lower temperature as compared with traditional sodium salt roasting process. Moreover, chromium can also be leached out in this new reaction system. The new process has been proven to be environmentally friendly, being able to avoid the generation of hazardous slag, wastewater, and exhaust gases.

In this study, the decomposition process of vanadium slag in binary $NaOH—NaNO_3$ melt under continuous oxygen flow was examined in detail, and the functions of $NaNO_3$ were investigated to clarify the nitrate oxidative mechanisms. Furthermore, the effect of various reaction conditions on the extraction of vanadium and chromium compounds was discussed, and a new vanadium slag treatment process was proposed.

Material and Experimental

Materials

All the chemical reagents used were of analytical grade and deionized water was used throughout the experiments. The vanadium slag was supplied by Chengde Iron and Steel Group Co., Ltd., Hebei, P.R. China. Vanadium slag was first dried in oven over night to remove moister, and then sieved to obtain particles of under 200-mesh for further treatment. The chemical and mineralogical analysis was performed using ICP—OES (PE Optima 5300DV, PerkinElmer), and X-ray diffraction analysis (Phillips PW223/30), respectively.

Apparatus and procedure

The batch reactor used in this work was a 500 mL SUS316 stainless steel container equipped with a thermometer and a mechanical stirrer. The temperature of reactor was controlled by a programmable temperature controller, with a precision of ±2°C.

The decomposition experiments of vanadium slag were carried out in the batch reactor. For each run, predetermined amount of NaOH and $NaNO_3$ was first put into the reactor, and about 50 mL deionized water was added to the reactor to produce a homogeneous slurry containing the alkali and salt under constant stirring. Then the slurry was heated at a rate of 12°C/min, and with the increase of temperature, water evaporation occurred. With completely evaporation of water, homogeneous $NaOH—NaNO_3$ molten salt mixture was formed. When the temperature reached the preset value and remained stable, the reaction gas was passed through the reactor and 50 g of vanadium slag was added to the reactor carefully. The slurry of all the reactants was intensively stirred to guarantee an adequate contact of slag particles with the reaction media. At a certain reaction time, approximate 2 g of the reacting slurry sample was taken out, and dissolved into 100 mL deionized water, followed by

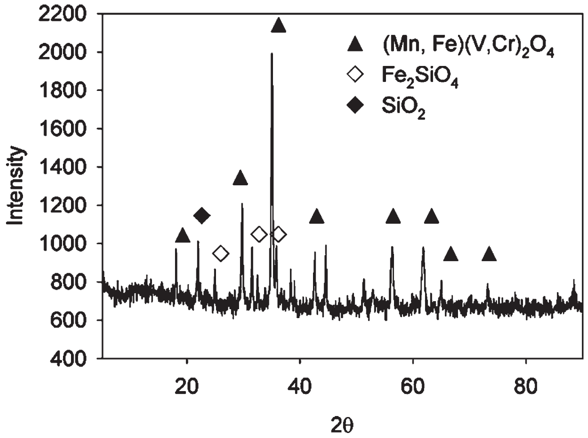

Figure 1. XRD patterns of the vanadium slag.

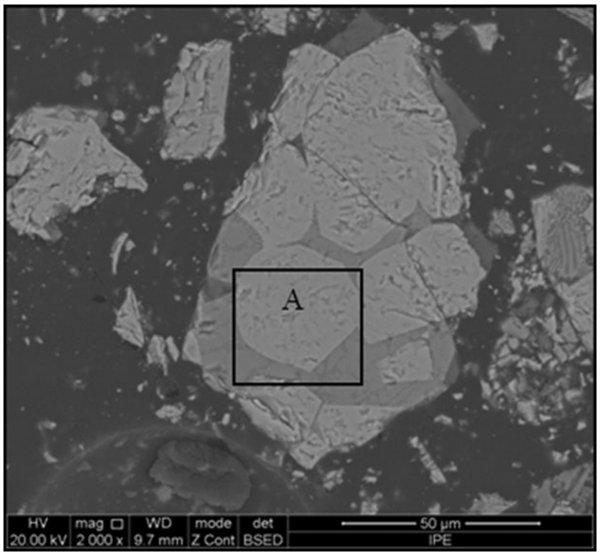

Figure 2. The backscattered electron image of vanadium slag particle.

filtration to obtain a filtrate and tailing. The concentrations of NO_3^- and NO_2^- in the filtrate were analyzed using ion chromatography (Dionex DX-500) to calculate the decomposition rate of $NaNO_3$. The chemical composition and morphologies of tailings were analyzed using ICP—OES and backscattered SEM (ZEISS EVO 18), respectively.

The decomposition experiments of $NaNO_3$ were also carried out in the batch reactor. However, to get quantitative information, the reactor was sealed with a cover with gas inlet and outlet holes. Before the $NaNO_3$ decomposition experiments, nitrogen gas was passed through the reactor with flow rate of 2.15 L/min to purge air. When the $NaNO_3$ started to decompose, the released gases were taken out with nitrogen gas flow and dried by passing through anhydrous potassium chloride particles. Then the concentrations of decomposition gases, such as O_2, NO, NO_2, were determined online using flue gas analyzing apparatus (Testo 350XL).

Results and Discussion

The vanadium slag decomposition process

Table 1 shows the chemical composition of typical vanadium slag, indicating that besides vanadium and chromium, iron, silicon, and titanium are the main elements. Figure 1 is the XRD patterns of the vanadium slag, clearly showing that the slag is mainly composed of vanadium and chromium spinels, quartz, and fayalite phases. Figure 2 is a backscattered electron image of a typical vanadium slag particle, and two obvious phases can be observed. To identify the chemical composition of the two phases, further examination of the element distribution of section A in Figure 2 using EDX has been performed, and the analysis results are illustrated in Figure 3. It is observed that the bright phase mainly contains V, Cr, and Ti, while the gray one mainly contains Si. Fe and Mn are uniformly distributed in these two phases. Because isomorphism widely exists in vanadium slag, the bright phase, therefore, is identified to be vanadium and chromium spinels which can be written as $(Fe,Mn)(V,Cr,Ti,Mn)_2O_4$ and the gray one mainly contains fayalite which can be written as $(Fe,Mn)_2SiO_4$. Furthermore, it is clearly that the spinel particles are randomly dispersed in fayalite phase, suggesting that before the oxidation of the vanadium and chromium spinels, the fayalite phase has to be decomposed first. Previous studies also revealed that silicon-containing phase is one of the major reasons impeding the decomposition of spinel.[1,25] Fayalite, made-up of acidic silicon oxide and low-valance amphoteric metal oxides, would readily react with strong base such as NaOH and strong oxidant such as $NaNO_3$ according to the following reactions

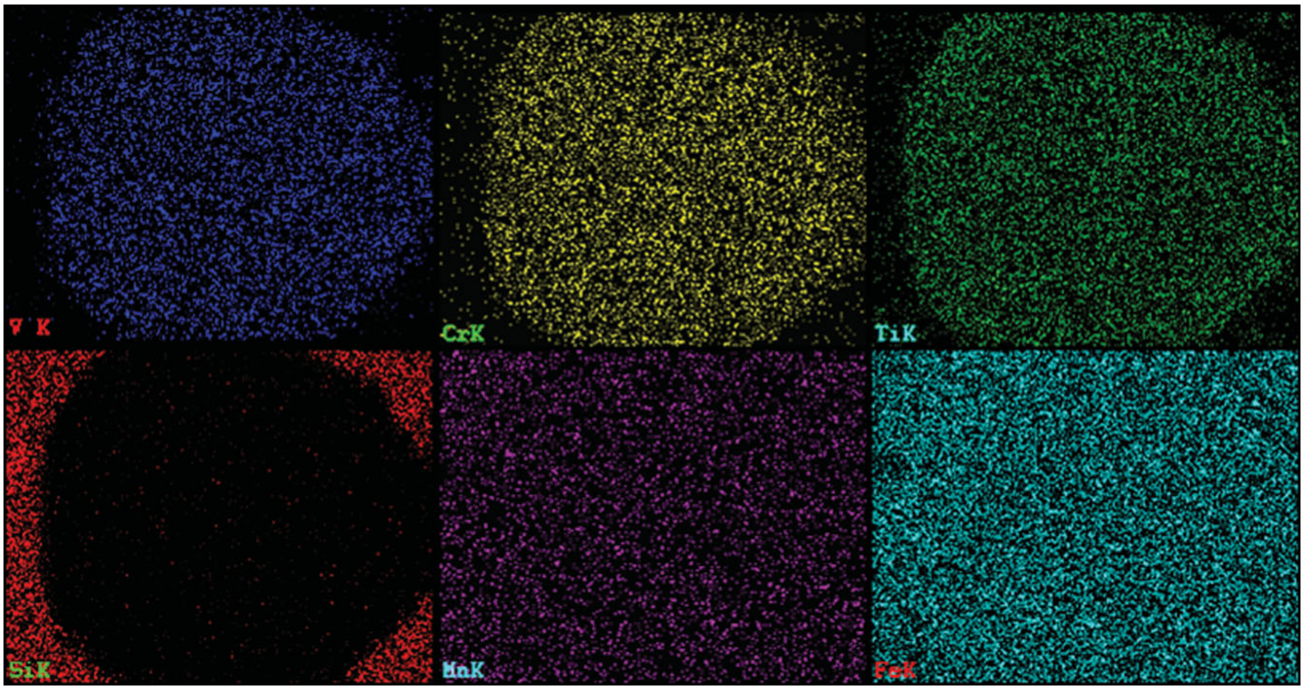

Figure 3. The elemental distribution image of Section A (in Figure 2) by EDX.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$Fe_2SiO_4 + 2NaOH + NaNO_3 \rightarrow Fe_2O_3 + Na_2SiO_3 + NaNO_2 + H_2O \tag{1}$$

$$Mn_2SiO_4 + 6NaOH + 4NaNO_3 \rightarrow 2Na_2MnO_4 + Na_2SiO_3 + 4NaNO_2 + 3H_2O \tag{2}$$

After the dissolution of fayalite, vanadium and chromium spinels is exposed to the reaction media for further reactions. In the presence of strong oxidant such as $NaNO_3$, the oxidation of vanadium and chromium spinel's occur rapidly to form water-soluble sodium vanadate and sodium chromate according to the following reactions (to simplify, only the main components of spinels, $FeO \cdot V_2O_3$ and $FeO \cdot Cr_2O_3$, are considered)

$$2FeO \cdot V_2O_3 + 12NaOH + 5NaNO_3 \rightarrow 5NaNO_2 + Fe_2O_3 + 6H_2O + 4Na_3VO_4 \tag{3}$$

$$2FeO \cdot Cr_2O_3 + 8NaOH + 7NaNO_3 \rightarrow 7NaNO_2 + Fe_2O_3 + 4H_2O + 4Na_2CrO_4 \tag{4}$$

Another main phase quartz, found to form a separated phase as suggested by the element distribution, would easily react with NaOH to form Na_2SiO_3

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O \tag{5}$$

It can be concluded that, to extract vanadium and chromium compounds effectively from the vanadium slag, the silicon-rich phases have to be first dissolved in molten salt, which can be achieved by reacting with NaOH. $NaNO_3$ accelerates this decomposition process by oxidizing iron (II) and manganese (II) to iron (III) and manganese (VI). Once vanadium and chromium spinels are exposed to the molten salt, the vanadium (III) and chromium (III) are rapidly oxidized by $NaNO_3$ to form water-soluble compounds. So the NaOH—$NaNO_3$ system in this regard provides favorable environment for the effective decomposition of vanadium slag.

The oxidation behavior of $NaNO_3$

Previous studies have suggested that in the presence of strong oxidant such as alkali nitrates, chromite could be efficiently oxidized in basic melt, and alkali nitrates were believed to exhibit catalytic characteristics during the oxidation of chromium (III) oxides.[19] However, the functions of alkali nitrates in molten alkali hydroxides have not been fully investigated. To obtain further information regarding the nitrate oxidation mechanisms, the decomposition behavior of $NaNO_3$ was systematically investigated in pure $NaNO_3$ and NaOH—$NaNO_3$ binary systems, and the effect of reductive oxides was also considered. Figure 4 demonstrates the decomposition behaviors of $NaNO_3$ in pure $NaNO_3$NaOH—$NaNO_3$ binary (weight ratio 1:1), $NaNO_3$—Cr_2O_3, and NaOH—$NaNO_3$-Cr_2O_3 systems with temperature ranging from 300°C to 600°C, and the formation rates of O_2, NO and NO_2, are expressed as $mol_{(O_2,NOorNO_2)} \cdot mol^{-1}_{(NaNO_3)} \cdot h^{-1}$.

Pure $NaNO_3$ System. In general, the outlet gas amount increases with treatment temperature, suggesting high temperature is in favor of the decomposition of $NaNO_3$. Further examination Figure 4 reveals that in pure $NaNO_3$ melt NO and O_2 almost simultaneously start to be formed at approximately 450°C, and become appreciable at temperatures higher than 550°C, which is inconsistent with a previous study.[26] As suggested by Hoshino et al. the main decomposition reactions of $NaNO_3$ could be described as follows[26–28]

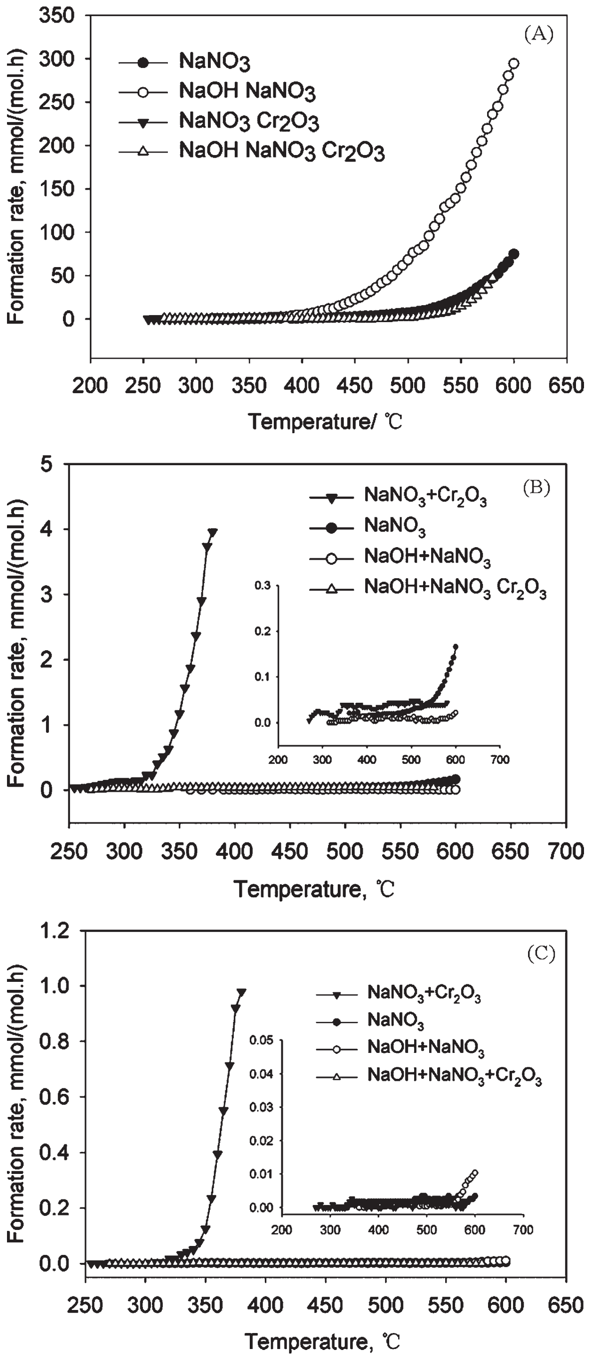

Figure 4. The formation rate of O_2 (A), NO (B), and NO_2(C) in $NaNO_3$, NaOH—$NaNO_3$, $NaNO_3$-Cr2O3 and NaOH—$NaNO_3$-Cr_2O_3 systems with temperature ranging from 250 to 600°C.

$$NaNO_3 \rightarrow NaNO_2 + O \tag{6}$$

$$O + O \rightarrow O_2 \uparrow \tag{7}$$

$$2NaNO_2 \rightarrow Na_2O_2 + 2NO \uparrow \tag{8}$$

It is noticed, that the Reaction 6 proceeds much further than Reaction 8 as indicated by the much higher (two- to

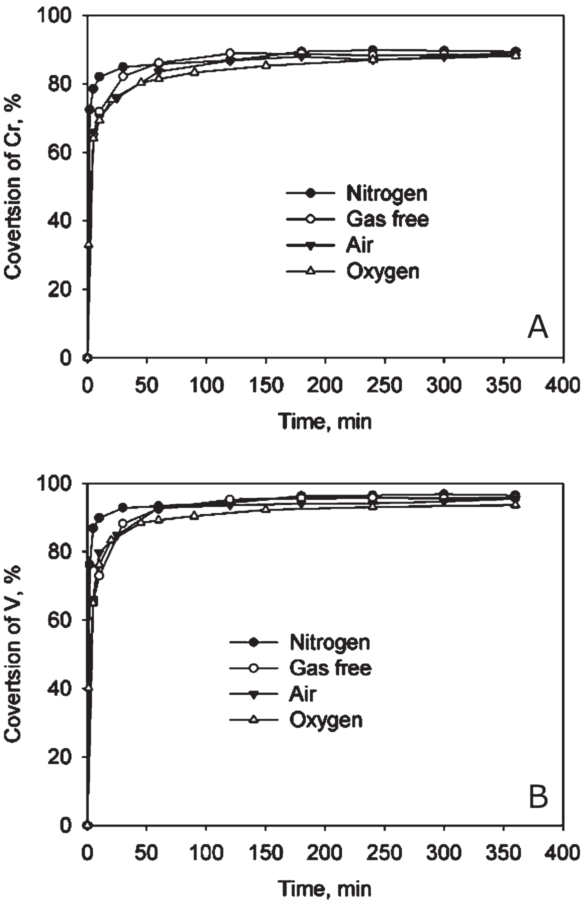

Figure 5. The effect of oxygen partial pressure on the conversion of vanadium and chromium.

three-orders higher) O_2 concentration in comparison with the NO concentration. So O_2 is the main product of $NaNO_3$ decomposition reaction at low temperatures. When the temperature is elevated above 550°C, these decomposition reactions are intensified and a small amount of NO_2 is formed, which may be interpreted by the following reaction

$$NO + O \rightarrow NO_2 \tag{9}$$

The $NaNO_3$-NaOH System. However, with the presence of NaOH in the fused $NaNO_3$, the decomposition behavior of $NaNO_3$ obviously changes. The formation of O_2 is remarkably intensified and initiated at a lower temperature of 320°C (Figure 4A). It is because the N—O bond in NO_3^- is significantly polarized by OH^- in NaOH melt, and NO_3^- becomes more prone to decompose with increase of temperature.[28] Moreover, there is equilibration of OH^- and O^{2-} in NaOH molten salt,[29] and the latter may react with O to generate higher active oxygen species such as O_2^{2-} and O_2^- according to the following equations

$$2OH^- \rightarrow O^{2-} + H_2O\uparrow \tag{10}$$

$$O^{2-} + O \rightarrow O_2^{2-} \tag{11}$$

$$O_2^{2-} + O_2 \rightarrow 2O_2^- \tag{12}$$

It has been confirmed that superoxide and peroxide ions are stable in basic media and exhibit high-oxidizing activity. Especially peroxide, which is believed to have higher oxidizing ability than $NaNO_3$.[28] Therefore, with the induction of OH^-, these reactive oxygen species such as O, O_2^{2-}, and O^{2-} are significantly generated in NaOH—$NaNO_3$ melts, and are expected to be responsible for the strong oxidizing ability of the binary melts.[30,31] The strong oxidizing ability of the mixed melts has also been confirmed by Abe et al. in their study using electrochemical methods.[27]

Another noticeable feature in Figure 4B and 4C is that the generation of NO and NO_2 is greatly inhibited in the binary melts, and these gases are scarcely detected even at temperatures exceeding 550°C. This is because when $NaNO_2$ decomposes, NO is formed accompanied with Na_2O_2 as suggested by Reaction 8. Na_2O_2 is a basic oxide, and the presence of NaOH obviously increases the basicity of the melts, affecting the equilibrium of Reaction 8 to move toward the reverse direction. Consequently, the formation of NO and Na_2O_2, as well as NO_2 is inhibited.

The $NaNO_3$-Cr_2O_3 System. Vanadium slag contains a large amount of reductive oxides such as V_2O_3, Cr_2O_3, FeO, etc., it was reported that when the reductive oxides were added to the fused nitrate, the decomposition of $NaNO_3$ would be promoted and the decomposition temperature would be decreased.[26,32] In this regard Cr_2O_3, one of the representative oxides, is added to the aforementioned two systems to examine its effects on the decomposition of $NaNO_3$. Figure 4A verifies the aforementioned conclusions and shows that the decomposition of pure $NaNO_3$ is significantly intensified due to the addition of Cr_2O_3. The formation of NO and NO_2 becomes obvious at temperature

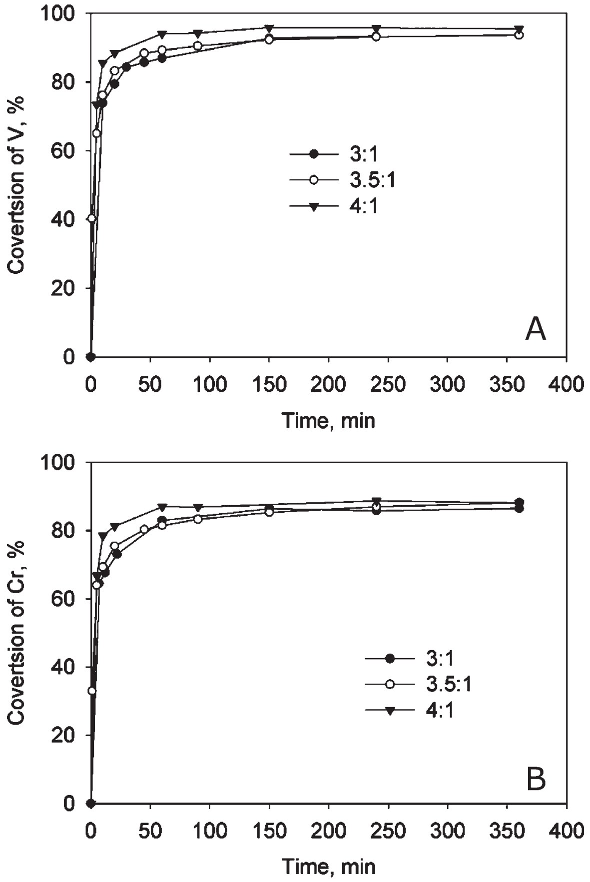

Figure 6. The effect of liquid-to-solid mass ratio on the conversion of vanadium and chromium.

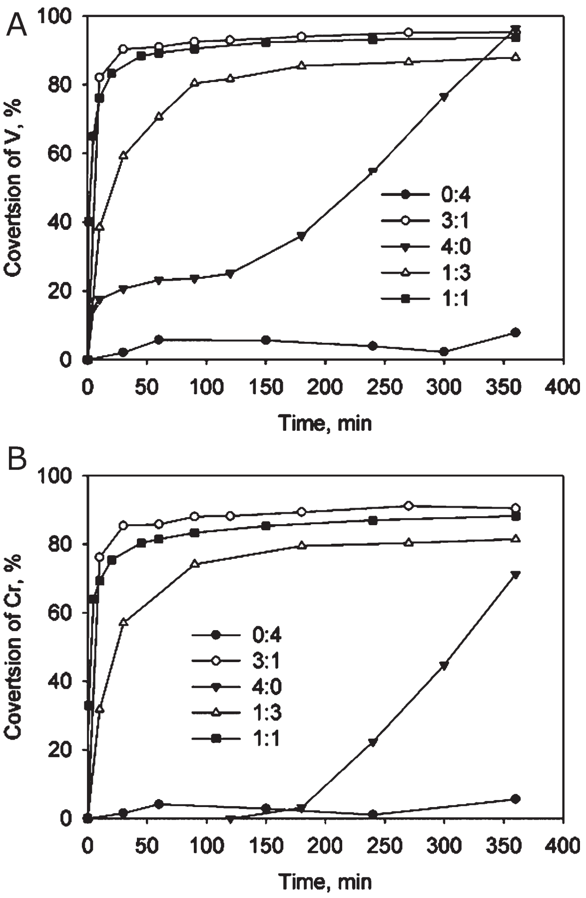

Figure 7. The effect of base-to-salt mass ratio on the conversion of vanadium and chromium.

exceeding 320°C, and the concentrations of NO and NO_2 rapidly reach the detection limits (3,000 ppm for NO and 500 ppm for NO_2) of the flue gas analyzing apparatus at 375°C (Figure 4B and 4C). This is due to the fact that the acidic reductive Cr_2O_3 is first oxidized by $NaNO_3$, promoting the decomposition of $NaNO_3$ (Reaction 6), and then react with basic oxides, originated from the decomposition of $NaNO_2$ (Reaction 8), to form Na_2CrO_4 due to the acid–base neutralization reaction. In pure $NaNO_3$ melt, Na_2O_2 acts as basic oxide to react with acidic oxide to form oxysalt.[27] Thus, the decomposition process (Reaction 8) from $NaNO_2$ to NO and Na_2O_2 is greatly intensified and the reactions can be expressed

$$3NaNO_3 + Cr_2O_3 \rightarrow 2CrO_3 + 3NaNO_2 \quad \text{(Oxidation reaction)} \tag{13}$$

$$2Na_2O_2 + 2CrO_3 \rightarrow 2Na_2CrO_4 + O_2\uparrow \quad \text{(Acid – base reaction)} \tag{14}$$

The $NaNO_3$-$NaOH$—Cr_2O_3 System. However, in the NaOH—$NaNO_3$ melt, NaOH will replace $NaNO_2$ to provide basic oxide for the aforementioned acid–base reaction (Reaction 14), and, consequently, the further decomposition of $NaNO_2$ is, therefore, expected to be inhibited. Figure 5 confirms this hypothesis and shows that even with the presence of reductive oxide Cr_2O_3, the release of NO and NO_2 maintains at a very low level. In summary, in $NaNO_3$-NaOH binary melts, $NaNO_3$ and NaOH provide oxidant and base, respectively, to react with acidic reductive oxide Cr_2O_3 according to the following reactions

$$3NaNO_3 + Cr_2O_3 \rightarrow 2CrO_3 + 3NaNO_2 \quad \text{(Oxidation reaction)} \tag{15}$$

$$2NaOH + CrO_3 \rightarrow Na_2CrO_4 + H_2O\uparrow \quad \text{(Acid – base reaction)} \tag{16}$$

In vanadium slag, vanadium and chromium exist as low-valence oxides in spinels, and acid–base neutralization and oxidation reactions simultaneously occur in the decomposition process. NaOH and $NaNO_3$ function to provide basic oxides and oxidant, respectively, establishing beneficial environment for the decomposition of vanadium slag and avoiding the generation of toxic nitrogen oxides.

The extraction of V and Cr under different reaction conditions

In previous sections, the oxidation mechanisms of vanadium and chromium compounds in vanadium slag have been discussed in detail, and to establish the optimal reaction conditions for process development, critical parameters including oxygen partial pressure, reaction temperature, liquid-to-solid ratio, and base-to-salt ratio, were systematically studied with results being discussed in the following sections.

Effect of Oxygen Partial Pressure. It has been reported that the vanadium and chromium spinels in vanadium slag could be oxidized by oxygen in the NaOH melt, and a

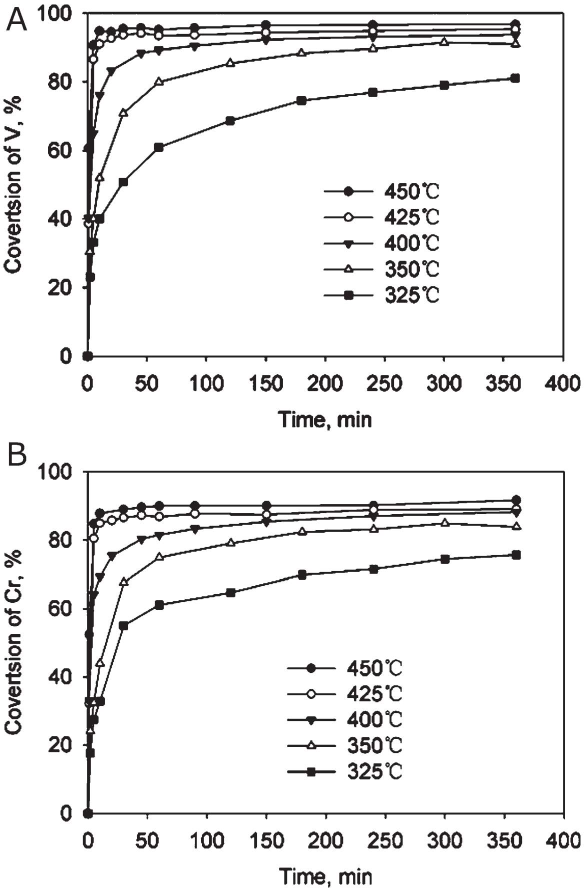

Figure 8. The effect of temperature on the conversion of vanadium and chromium.

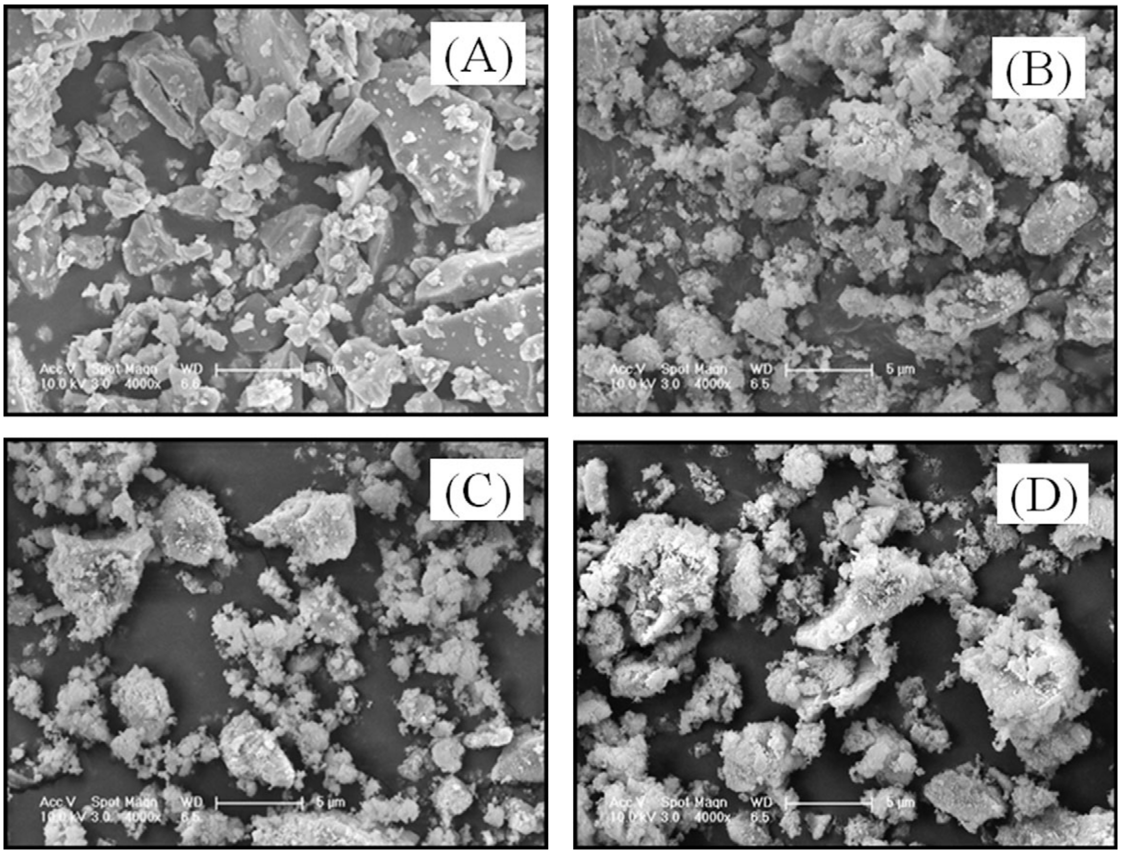

Figure 9. SEM images of leaching residue at different conversion time (A) 0 min, (B) 5 min, (C) 20 min, and (D) 6 h.

higher oxygen partial pressure is then expected to promote the vanadium slag decomposition. So the effect of oxygen partial pressure was studied with results summarized in Figure 5. However, it is clear that the oxidation and decomposition of vanadium slag are not dependent on the oxygen partial pressure as indicated by the high vanadium and chromium extraction rates under oxygen, air, and air-free atmospheres. Even under inert environment by passing nitrogen through the reaction slurry, the extractions of vanadium and chromium can still reach 92 and 83% in 1 h, respectively. Consequently, it is reasonable to believe that under ambient pressure, $NaNO_3$ is the main oxidant and the decomposition of vanadium slag mainly relies on the active oxygen species released by the decomposition of $NaNO_3$, rather than the oxygen dissolved in the melt. Oxygen plays only a negligible role in terms of vanadium slag oxidation; however, it functions to reoxidize $NaNO_2$, which will be further discussed in the following section.

Effect of Liquid-to-Solid Ratio on Extraction. At the examined reaction temperatures, which are higher than the NaOH and $NaNO_3$ eutectic point (273°C), NaOH and $NaNO_3$ exist as liquid and vanadium slag as solid. A higher liquid-to-solid ratio is, therefore, believed to decrease the viscosity of the reacting slurry and facilitate the mass transfer of reactants and products during reaction. To obtain the optimal reaction conditions, the ratios of 3:1, 3.5:1 and 4:1 were tested to investigate the effect of the amount of molten liquid on extraction, and the results are summarized in Figure 6. It demonstrates that the extractions of vanadium and chromium do not change significantly with the increase of liquid-to-solid mass ratio, and only a slight improvement of the conversion rate is observed. In summary, at the examined liquid-to-solid ratio levels, mass transfer is not the rate determining parameter for the decomposition of vanadium slag due to the fact that the vanadium slag particles are well soaked in the binary melts with strong stirring, and the active oxygen species existed in the binary melts can achieve well to interact with vanadium slag particles, guaranteeing the full oxidation of vanadium and chromium spinels. In this study, liquid-to-solid ratio of less than 3:1 was not considered mainly due to the fact that with such a low ratio, the slurry would become too viscous to be mechanically stirred, impossible for reaction controlling. However, the liquid-to-solid ratio will influence the oxidation of $NaNO_2$ due to its effect on oxygen solubility and diffusivity, and a relative high ratio is, consequently, recommended.

Effect of Base-to-Salt Ratio on Extraction. Both NaOH and $NaNO_3$ are important for the efficient decomposition of vanadium slag as confirmed by the aforementioned discussion. The base-to-salt ratio, therefore, is expected to be influential on the recovery of vanadium and chromium compounds. To obtain the optimal conditions, base-to-salt (NaOH to $NaNO_3$) ratios of 4:0, 3:1, 1:1, 1:3, and 0:4 were tested under the liquid-to-solid ratio of 4:1, with the results shown in Figure 7.

In pure NaOH melt, the vanadium and chromium can be oxidized and extracted by reacting with oxygen in the melt, but the reactions exhibit slow reaction kinetics and stepwise characteristics as suggested by the slow increase of extraction rate in the first 2 h of reaction, and fast increase of extraction rate afterward. This observation can be explained by the structure of vanadium slag particle in which the vanadium and chromium spinels are wrapped by fayalite as previously discussed. The decomposition of fayalite is achieved

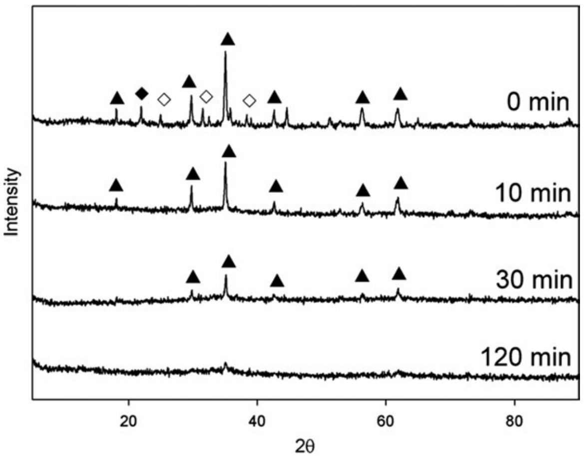

Figure 10. XRD patterns of leaching residue at different conversion time: ▲: (Mn,Fe)(V,Cr)$_2$O$_4$; ◇: Fe$_2$SiO$_4$; ◆: SiO$_2$.

due to two reactions, and the first one is the neutralization reaction to form sodium silicate, which proceeds fast in NaOH melt. The second one is the oxidation reaction of converting iron (II) and manganese (II) to iron (III) and manganese (VI) compounds, which is slow in kinetics due to the low solubility and diffusivity of oxygen in basic melt. Because the oxidation of vanadium and chromium spinels can only occur after the decomposition of fayalite wrapping around the spinels, the extraction of vanadium and chromium compounds proceeds slowly in the first stage. After reacting for 2 h, once the silicon-rich phases are totally decomposed, appreciable increase of vanadium and chromium conversion is observed, and the amount of vanadium and chromium compounds extracted increases monotonically with time, further suggesting that the oxidation reaction is governed by the diffusion of oxygen. After reacting for 6 h, vanadium and chromium recoveries reach nearly 94 and 70%, respectively.

When NaNO$_3$ is present in the NaOH melt, significant increase of vanadium and chromium conversion rates is observed, and a high base-to-salt ratio obviously improves the oxidation of both vanadium and chromium compounds. Theoretically, to oxidize all the low-valance oxides in the vanadium slag to their highest valance compounds, for each unit of vanadium slag, only about 0.4–0.5 unit of NaNO$_3$ is needed. Thus, a small amount of NaNO$_3$ in the binary melts would be enough to guarantee the complete oxidation of the vanadium and chromium compounds. So at ratios of 3:1 and 1:1, high vanadium and chromium conversion rates are observed. However, when the base-to-salt ratio decreases to 1:3, the final conversions of vanadium and chromium are dropped to 86 and 74%, respectively, which is due to increasing slurry viscosity and decreasing reactants diffusivity, as well as decreasing NaOH reactivity in low NaOH containing binary melts.

In pure NaNO$_3$ melt, however, due to the lack of a strong basic environment to react with acidic oxides such as fayalite and quartz, vanadium and chromium spinels cannot be exposed even after reacting for 6 h, therefore, both vanadium and chromium compounds are scarcely extracted.

In summary, NaOH is essential for the decomposition of vanadium slag due to its ability of decomposing acidic oxides. Furthermore, the presence of NaNO$_3$ intensifies the vanadium slag decomposition process, and equivalent amount of NaNO$_3$ would provide enough oxidant to satisfy the decomposition of vanadium slag.

Effect of Temperature on Extraction. Temperature is usually an important parameter for chemical reactions by controlling the reaction equilibrium and kinetics. In this regard, the effect of temperature on the vanadium and chromium compounds extraction rate was examined, and the results are shown in Figure 8. It is clear that the extraction of vanadium and chromium compounds exhibits obvious temperature dependence with a similar trend in the temperature range between 325 and 450°C. In general, the recoveries of vanadium and chromium gradually increase with the extension of reaction time. However, when reaction temperature is above 400°C, fast increase of vanadium and chromium compounds conversion is observed in a very short reaction time (within 30 min). Obviously, it is inconsistent with the results of decomposition of NaNO$_3$ in NaOH—NaNO$_3$ melts, indicating NaNO$_3$ is greatly decomposed to produce a large amount of active oxygen species at above 400°C (Figure 4A). Therefore, the vanadium and chromium spinels are simultaneously decomposed by the mixed melts.

The morphological features of the vanadium slag particle treated at 400°C for different times is illustrated in Figure 9. It can be seen that the untreated slag particles are featured as compact solids with a smooth surface, and the surface of the particle becomes rough and porous after reacting for 5 min due to the decomposition reactions. Furthermore, the particle size decreases significantly as the reaction proceeds as suggested by particle size analysis results, which show that the average particles size decreases from 29.95 μm to 13.18 μm after reacting for 1 h. The spinel particles are destroyed by the mixed melts to form tiny ferric oxide particles mainly containing in the tailings.

The phase change of vanadium slag is shown in Figure 10. The diffraction patterns of quartz and fayalite are quickly disappeared after reacting for 10 min, indicating that silicon-phases are easily dissolved in NaOH—NaNO$_3$ melts. However, the decomposition of vanadium and chromium spinels proceeds progressively. The complete oxidation of vanadium (III) and chromium (III) can only be observed after 2 h of reaction, which is suggested by the vanishing of spinel structural diffraction peaks, leaving amorphous-like tailings eventually. The typical composition of tailing is listed in Table 2. In comparison with Table 1, the vanadium and chromium contents are obviously decreased to low values, below 1% in terms of their oxides.

The morphology and chemical analysis of vanadium slag and tailings illustrates that the extraction of vanadium and chromium from vanadium slag can be described by the unreacted shrinking core model. The basic equation as shown in Eq. 17 is used to describe the extraction macrokinetic of vanadium slag[19,24]

Table 2. Typical Composition of the Vanadium Residue

Component	V_2O_5	Cr_2O_3	FeO	SiO_2	TiO_2	CaO	MnO_2	Al_2O_3	MgO	Na_2O
Content, wt%	0.62	0.47	57.23	10.01	12.91	1.17	6.34	1.15	1.58	7.93

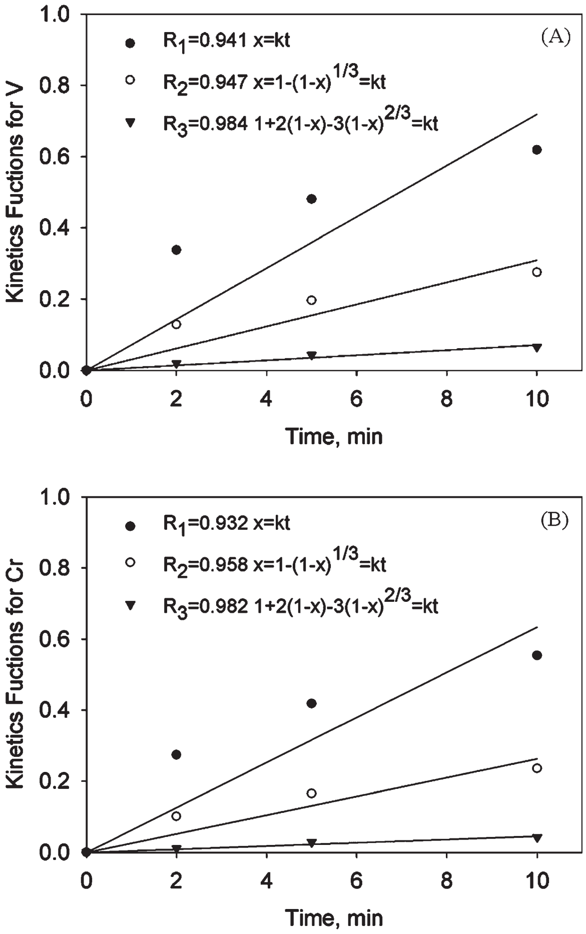

Figure 11. Vanadium (A) and chromium, (B) extraction rate vs. time at 325°C fitted by three kinetics equations.

$$\frac{1}{3\mathrm{k_M}}x+\frac{R_0}{6D_e}[1-3(1-x)^{2/3}+2(1-x)]+\frac{1}{k_{rea}}\times[1-(1-x)^{1/3}]=\frac{MC_0}{\sigma\rho R_0}t \quad (17)$$

where x is the extraction rate of chromium or vanadium, k_M is the mass-transfer coefficient of the reactant from reagents in liquid boundary layer, R_0 is the radius of the vanadium slag particle, D_e is the mass-transfer coefficient of the reactant in the product layer, k_{rea} is the reaction rate constant, t is the reaction time, M is the molar weight of vanadium slag, C_0 is the concentration of the reactant at $t = 0$, ρ is the density of vanadium slag, and σ is the coefficient of NaOH.

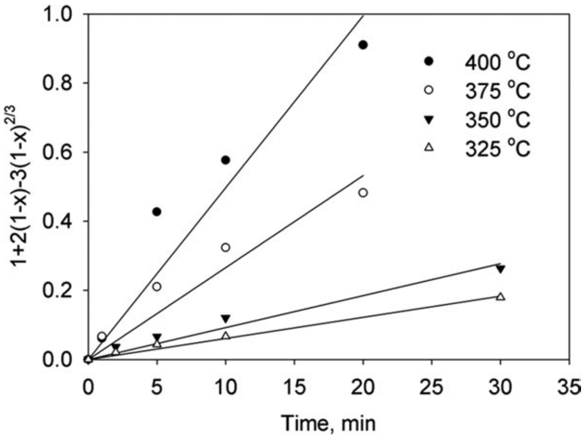

Figure 12. Plot of extraction kinetics under various reaction temperatures.

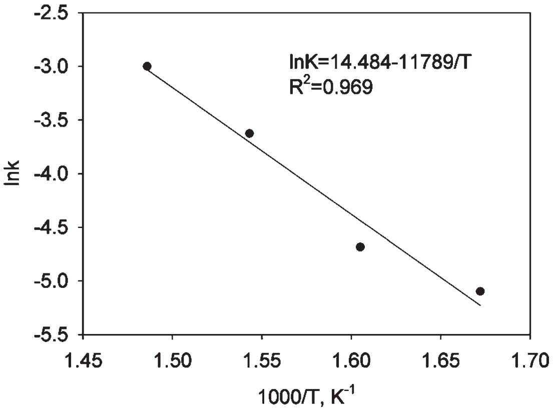

Figure 13. Nature logarithm of reaction rate constant vs. reciprocal temperature.

Under different process control, the kinetics equations can be simplified as[24]:

1. Liquid boundary layer diffusion control

$$\mathrm{x}=\frac{3k_M MC_0}{\sigma\rho R_0}t \quad (18)$$

2. Solid-product layer diffusion control

$$1+2(1-x)-3(1-x)^{2/3}=\frac{6\mathrm{D_e}MC_0}{\sigma\rho R_0^2}\mathrm{t} \quad (19)$$

$$1-(1-x)^{1/3}=\frac{\mathrm{k_{rea}}MC_0}{\sigma\rho R_0}\mathrm{t} \quad (20)$$

To reveal the controlling step of the vanadium and chromium extraction, the conversion data of vanadium and chromium at 325°C in Figure 8 is fitted into Eqs. 18, 19, and 20 as shown in Figure 11. The results show that $1 + 2(1 - x)-3(1 - x)^{2/3} = kt$ fits the experimental data well for vanadium and chromium, where k is the rate constant, $k = \frac{6\mathrm{D_e}MC_0}{\sigma\rho R_0^2}$. Therefore, mass transfer in the residue layer, which consists of iron, titanium and manganese oxides, is the determined step of the reaction. Any method can improve inner mass transfer in the residue layer would enhance the decomposition, such as the increase of temperature and decrease of particle size.[19]

Conversion rates of vanadium with different temperatures are fitted (Figure 12) and the value of k is obtained. Then the specific apparent activation energy can be calculated based on Arrhenius equation as shown in Figure 13

$$lnk=lnA-\frac{E}{R}\times\frac{1}{T} \quad (21)$$

where E is the apparent activation energy, A is the pre-exponential factor, and R is the molar gas constant.

The apparent activation energy of vanadium extraction is calculated to be $E = 98.02$ kJ/mol. Similarly, the apparent activation energy of chromium extraction is calculated to be $E = 102.90$ kJ/mol, which is a bit higher than that of vanadium, indicating a slower reaction process.

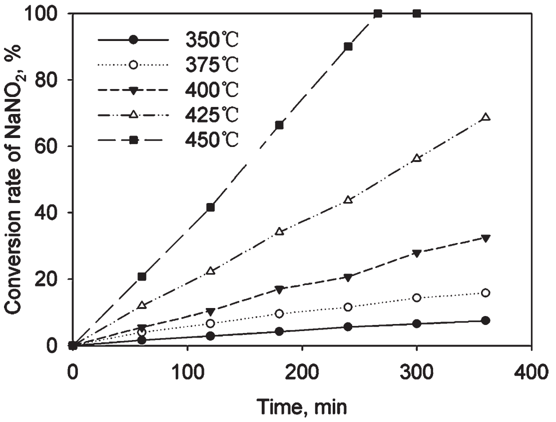

Figure 14. Effect of reaction temperature on the oxidation of $NaNO_2$.

The regeneration of $NaNO_3$

During the oxidation of low-valance amphoteric metal oxides in vanadium slag, $NaNO_3$ is reduced to $NaNO_2$. The accumulation of $NaNO_2$ in the system not only influences the purity of sodium vanadate and sodium chromate products, but also affects the oxidation and decomposition of vanadium slag in the next cycle. In this regard, the produced $NaNO_2$ needs to be reoxidized to $NaNO_3$, which is accomplished by passing oxygen through the reaction media continuously during the reaction. The oxidation of fused $NaNO_2$ has been investigated previously,[33] but in $NaOH$—$NaNO_3$ melts it has not been systematically studied so far, therefore, deserving much study to understand its oxidation characteristic infused NaOH. In this research, a series of carefully designed and executed experiments were performed to investigate the reoxidation of $NaNO_2$. 81 g of $NaNO_2$ (equivalent to 100 g $NaNO_3$ in molarity) was mixed with 100 g of NaOH, and under O_2 flow rate of 1 L/min, the oxidation rate of $NaNO_2$ at 350, 375, 400, 425 and 450°C was examined, and the results are summarized in Figure 14. Clearly, the oxidation rate of $NaNO_2$ is greatly dependent on temperature, and increase with temperature, which is in good agreement with a previous study about the oxidation of $NaNO_2$ in pure fused $NaNO_3$ system.[33]

In addition, the oxidation of $NaNO_2$ strictly follows one-order reaction kinetics. The relationship between conversion rate Y, and reaction time t, can be simply expressed as $Y = kt$, in which k is the reaction rate constant. By liner fitting, the value of k is obtained and then the specific apparent activation energy can be calculated based on Arrhenius equation (Eq. 21).

The apparent activation energy is calculated to be $E = 105.5$ kJ/mol, and the kinetics equation of the oxidation of $NaNO_2$ can then be written as

$$Y = 1.49 \times 10^5 \, e^{-\frac{105500}{RT}} \cdot t \qquad (22)$$

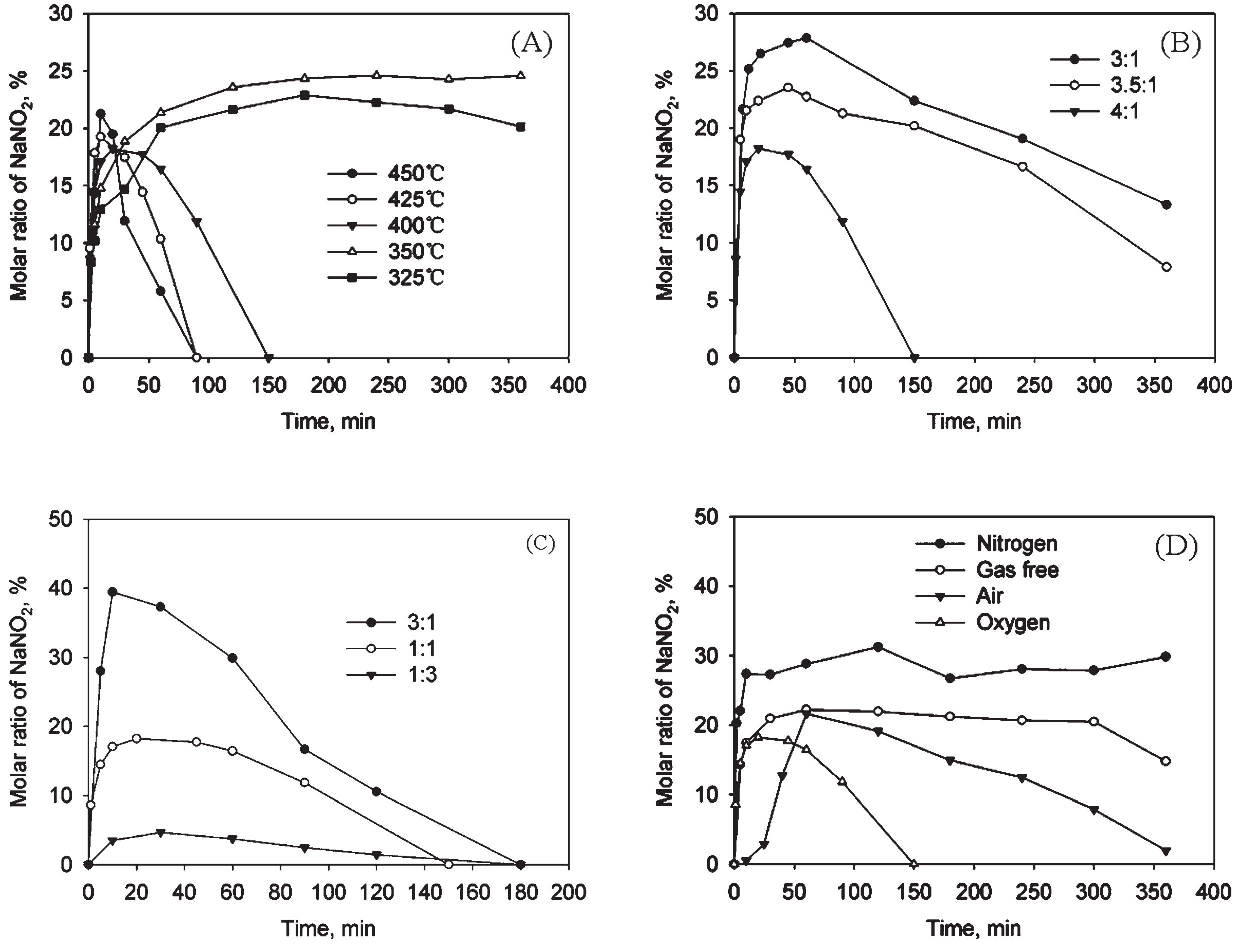

Figure 15. The effect of various parameters on the decomposition rate of $NaNO_3$ (A) temperature, (B) liquid-to-solid mass ratio, (C) base-to-salt mass ratio, and (D) oxygen partial pressure.

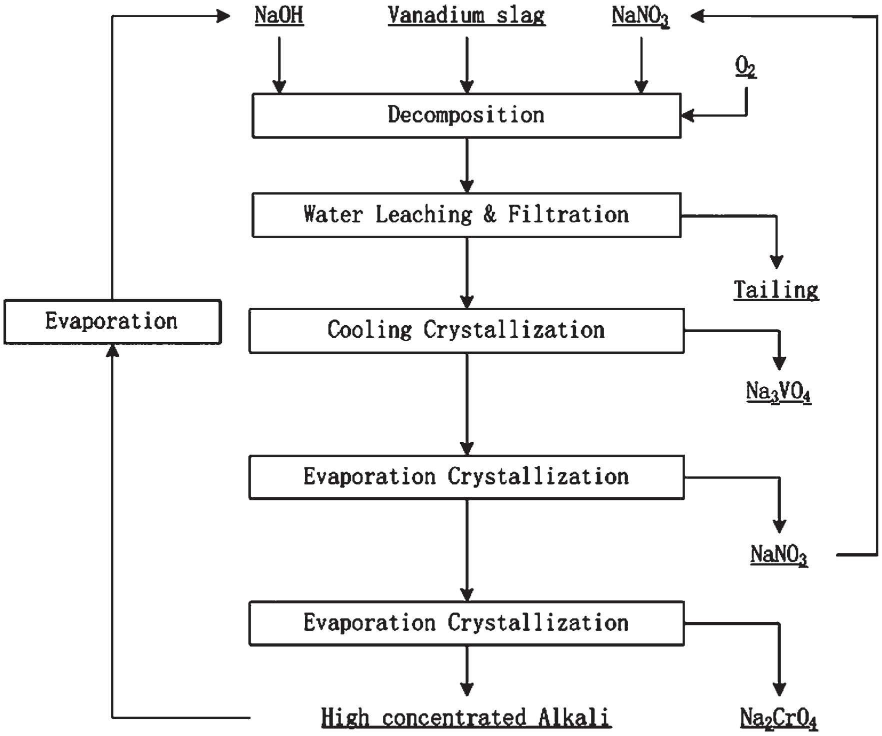

Figure 16. Flow sheet for the leaching and recovery of vanadium and chromium.

The oxidation of $NaNO_2$ in practical extraction was also investigated. Figure 15 illustrates the dependence of $NaNO_3$ decomposition rate on temperature (A), liquid-to-solid ratio (B), base-to-salt ratio (C), and oxygen partial pressure (D). It is clear that the decomposition of $NaNO_3$ is a rapid process, while the oxidation of $NaNO_2$ is a slow one. The decomposition rate of $NaNO_3$ reaches a maximum value in the first stage (first 30 min), during which the vanadium and chromium spinels are mostly oxidized, suggesting the dominant role of $NaNO_3$ in the oxidation process. The oxidation of $NaNO_2$ proceeds gradually and is dependent on the aforementioned listed parameters. Conditions favoring the diffusion and solubility of oxygen molecules including high temperature, liquid-to-solid ratio, and oxygen partial pressure would significantly improve reaction kinetics.

Development a new method of extraction of V and Cr from vanadium slag

Based on previous theoretical and experimental results, a new process for extracting vanadium and chromium compounds from vanadium slag by NaOH—$NaNO_3$ molten salt has been proposed and the process flow sheet is plotted in Figure 16. This mixed system exhibits intense decomposition effect for vanadium slag, and vanadium and chromium can be simultaneously extracted in short reaction time, converting to Na_3VO_4 and Na_2CrO_4, respectively. Then the reaction slurry is diluted by addition of water to form concentrated alkaline solutions containing Na_3VO_4, Na_2CrO_4, and the reaction media. Na_3VO_4 and Na_2CrO_4 products can be separated by cooling and evaporation crystallization, respectively. The high-alkali concentration mother liquor is evaporated for the next leaching process.

Conclusions

A new NaOH—$NaNO_3$ melt reaction system for the extraction of vanadium and chromium compounds from vanadium slag is proposed and proven to be effective in this work.

1. $NaNO_3$ is considered to be the dominate oxidant for the oxidization of vanadium (III) and chromium (III) in vanadium slag in the mixed melts. Being polarized by OH^- in NaOH, $NaNO_3$ is easily decomposed to generate a large amount of active oxygen species, such as O, O_2^{2-}, and O^{2-}, exhibiting strong oxidizing ability. NaOH inhibits the further decomposition of $NaNO_3$ to toxic NO and NO_2 and facilitates the dissolution of acidic oxides in the vanadium slag decomposition process. NaOH and $NaNO_3$ provide an excellent environment for the decomposition of vanadium slag.

2. Various parameters for the extraction of vanadium and chromium are investigated. Temperature and alkali-to-salt ratio are two of the most significant factors on the conversion process, while oxygen partial pressure and liquid-to-solid ratio play minor roles. Under the optimal conditions of liquid-to-solid ratio 4:1, base-to-salt ratio 1:1, decomposition temperature 400°C, oxygen flow rate 0.5 L/min, and reaction time 6 h, the recoveries of vanadium and chromium reach up to 93.7% and 88.2%, respectively. The macrokinetics investigation indicates that a unreacted shrinking core model can be used to describe the decomposition process, which is controlled by mass transfer in the product layer. The apparent activation energy of vanadium and chromium extraction is calculated to be 98.02 kJ/mol and 102.90 kJ/mol, respectively.

3. The oxidization of $NaNO_2$ by oxygen exhibits slow reaction kinetics and temperature dependence. It is found that high temperature obviously accelerates the oxidization of $NaNO_2$. The apparent activation energy of $NaNO_2$ oxidation in the temperature ranging from 350 to 450°C is 105.5 kJ/mol. Under optimal conditions, the $NaNO_2$ can be entirely oxidized by oxygen and the net consumption of $NaNO_3$ is zero.

Acknowledgments

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