Joint processing of V-bearing steelmaking slag and V-bearing black shale for vanadium and iron separation

L.-S. Wu a,*, C. Dai a, B.-J. Yan b, H.-C. Wang a, C.-J. Qi a

aSchool of Metallurgical Engineering, Anhui University of Technology, Maanshan 243032, Anhui, P. R. China
bSchool of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, P. R. China

1. Liushun Wu, E-mail: wuliushun@aliyun.com
2. Chao Dai, E-mail: 1007544321@qq.com
3. Baijun Yan, E-mail: baijunyan@ustb.edu.cn
4. Haichuan Wang, E-mail: which0555@163.com
5. Cunjun Qi, E-mail: 15755587980@139.com
*Corresponding author: Liushun Wu

E-mail: wuliushun@aliyun.com

Tel: +86 18155581066

 Declarations of interest: none

(Received 20 January 2020; Accepted 22 January 2021)

Abstract

To recycle vanadium from V-bearing steelmaking slag and V-bearing black shale, the both were jointly roasted to generate vanadium-rich phase, and then vanadium was separated by magnetic separation in this study. The compositions of samples were determined by X-ray fluorescence meter and the phases in the samples were characterized using X-ray diffractometer. Experimental results showed that, with increasing the ratio of CaO content to SiO$_2$ content in the samples, the vanadium separation efficiency first decreased, increased, and then decreased again. With increasing roasting temperature from 1423 to 1623 K, the vanadium separation efficiency increased. With increasing roasting time from one hour to four hours, the vanadium separation efficiency increased. The optimum conditions for vanadium recycling are the basicity of 1.2, roasting temperature of 1623 K, and roasting time of 4 hours. Under this condition, separation efficiency of vanadium reaches 71.6%, and the concentrate contains 3.67% V$_2$O$_5$ and 46.9% Fe$_2$O$_3$. A flow for joint processing of V-bearing steelmaking slag and V-bearing black shale was proposed, which involves vanadium separating, and tailings utilizing.
**Keywords:** Vanadium-bearing steelmaking slag; Vanadium-bearing black shale; Joint concentration; Separation efficiency

1 Introduction

Coulsonite and V-bearing black shale are the two most important vanadium ores, with more than 95% of vanadium produced from the two ores. Different methods are used to extract vanadium from the two ores because of the differences in their properties.

For coulsonite, pyrometallurgy is generally used to extract vanadium [1]. In the process of blast furnace smelting, most of the vanadium oxide and iron oxide in the ore are reduced, producing V-bearing hot metal. When the vanadium content in the hot metal is below 0.2%, the hot metal is directly used to produce steel in a converter furnace. Most of the vanadium in the hot metal is transferred to the slag in the process of steelmaking, forming V-bearing steelmaking slag.

Steelmaking slag is typically highly basic. The slag containing vanadium and iron is a valuable resource. However, the high basicity leads to instability, which restricts utilization of the slag, and the vanadium in the slag can cause heavy metal pollution [2–6]. Some metallurgists have attempted to recycle vanadium from high-grade vanadium slag by traditional methods, such as acid leaching [7–13], alkaline leaching [14–19], and bioleaching [20–22]. However, these methods do not apply to V-bearing steelmaking slag because of the low grade of vanadium.

Black shale containing 0.3–1.2% V\textsubscript{2}O\textsubscript{5} is a low-grade vanadium ore. The total reserves of vanadium are relatively large, and the reserves of vanadium in black shale are the second largest. It has promising prospects for development. Therefore, some researchers have performed experimental studies and proposed the following methods for vanadium separation: the direct acid-leaching method[23–33] and roasting–leaching method [34, 35]. However, these methods still have a lot of issues because of the low grade of vanadium, such as large consumption of reagent, severe water pollution, and treatment of the leaching tailings.

From the above discussion, methods to extract valuable metals from the two types of vanadium resources and utilization of the remaining tailings are difficult problems, so it is necessary to investigate new methods.

Many investigations indicate that, black shale is an acidic ore mainly containing silica and alumina, and V-bearing steelmaking slag is a highly basic slag. The two are highly complementary in terms of chemical composition. Thus an assumption of combined treatment of the two at high temperature was proposed in our previous study [36]. If so, the carbon in the black shale would provide heat and maintain a reduction atmosphere, the valuable metals of iron and vanadium would form a V-bearing magnetic phase, and the high basicity of the steelmaking slag would decrease. The V-bearing magnetic phase and silicate phase in the roasted feed could be separated by magnetic separation to give a vanadium concentrate and tailings, which could be used as a vanadium source and to produce building materials, respectively. In the present work, the assumption was used for the first time, the factors that influence vanadium concentration and separation were investigated, such
as the shale to slag ratio and roasting temperature.

2 Experimental

Table 1 Experimental conditions

| No. | Ratio /mass % | Basicity | Temperature /K | Roasting time /hour |
|-----|--------------|----------|----------------|---------------------|
|     | Shale | Slag |                 |                     |
| 1   | 49.5  | 50.5 | 0.6             | 1473               | 2                   |
| 2   | 44.3  | 55.7 | 0.7             | 1473               | 2                   |
| 3   | 39.9  | 60.1 | 0.8             | 1473               | 2                   |
| 4   | 36.0  | 64.0 | 0.9             | 1473               | 2                   |
| 5   | 32.7  | 67.3 | 1.0             | 1473               | 2                   |
| 6   | 27.2  | 72.8 | 1.2             | 1473               | 2                   |
| 7   | 21.0  | 79.0 | 1.5             | 1473               | 2                   |
| 8   | 17.8  | 82.2 | 1.7             | 1473               | 2                   |
| 9   | 49.5  | 50.5 | 0.6             | 1573               | 2                   |
| 10  | 44.3  | 55.7 | 0.7             | 1573               | 2                   |
| 11  | 39.9  | 60.1 | 0.8             | 1573               | 2                   |
| 12  | 36.0  | 64.0 | 0.9             | 1573               | 2                   |
| 13  | 32.7  | 67.3 | 1.0             | 1573               | 2                   |
| 14  | 27.2  | 72.8 | 1.2             | 1573               | 2                   |
| 15  | 21.0  | 79.0 | 1.5             | 1573               | 2                   |
| 16  | 17.8  | 82.2 | 1.7             | 1573               | 2                   |
| 17  | 27.2  | 72.8 | 1.2             | 1523               | 2                   |
| 18  | 27.2  | 72.8 | 1.2             | 1623               | 2                   |
| 19  | 27.2  | 72.8 | 1.2             | 1623               | 3                   |
| 20  | 27.2  | 72.8 | 1.2             | 1623               | 4                   |
| 21  | 27.2  | 72.8 | 1.2             | 1623               | 1                   |
| 22  | 27.2  | 72.8 | 1.2             | 1423               | 2                   |

V-bearing black shale from Hunan Province, China and V-bearing steelmaking slag from Maanshan Iron & Steel Company, Ltd. (Maanshan, China) were ground for 2 h in a ball grinder. The obtained shale powder was dried at 383 K for 12 h in a drying oven.

The steelmaking slag to black shale ratio was determined based on the metallurgical basicity principle (R), i.e., the ratio of the CaO content to the SiO₂ content in the sample. The molar ratio of ferric oxide to carbon was fixed at 0.4 by adding graphite. Dried shale powder, slag powder, and graphite powder were mixed for 2 h in predetermined proportions in a blender mixer. The mixtures in industrial pure iron crucibles were placed in a sealed resistance furnace [36] and heated to the predetermined temperature at a rate of 5 K/min, roasted for a specified time at the temperature, cooled to room temperature at a rate of 5 K/min, and then the samples were removed from the furnace. Argon flow of 100 ml/min was maintained throughout the experiments. The experimental conditions for all of the samples are given in Table 1.
The roasted samples were ground into powder in a ball grinder. The powders were made into pulps by mixing them with tap water at a mass to volume ratio of 1:5. A magnetic tube (tube diameter: 50mm, head gap: 50mm, vibration frequency: 70 times/min, magnetic field strength: 0-200KA/m) was used to process the pulps to obtain magnetic concentrates and tailings (magnetic intensity of 100KA/m was adopted). The obtained concentrates and tailings were dried at 383 K for 12 h in a drying oven.

The carbon content in the black shale was determined by loss on ignition. After grinding, the size distributions of the dried black shale powder, V-bearing steelmaking slag powder, and roasted samples were determined by the screening method. The chemical compositions of the dried black shale, V-bearing steelmaking slag, and dried concentrates and tailings were determined with an X-Ray fluorescence meter (ARL Advant’X Intellipower 3600). The phase compositions of the dried black shale, V-bearing steelmaking slag, and roasted samples were determined by X-ray diffractometry (Bruker D8 Advance X-ray diffractometer, Cu K).

Based on the compositions of the concentrates and tailings, the vanadium and iron separation efficiencies were calculated by the Hancock efficiency equation:

\[
E = \frac{(\beta - \alpha) \times (\alpha - \theta)(\beta_i - \theta_i)}{(\beta_i - \alpha)(\alpha - \theta)(\beta - \theta)} \times 100\%
\]

where \(E\) is the vanadium or iron separation efficiency (%), \(\alpha\) is the mass percentage of \(\text{V}_2\text{O}_5\) or \(\text{Fe}_2\text{O}_3\) in the roasted sample, \(\beta\) is the mass percentage of \(\text{V}_2\text{O}_5\) or \(\text{Fe}_2\text{O}_3\) in the concentrate (%), \(\theta\) is the mass percentage of \(\text{V}_2\text{O}_5\) or \(\text{Fe}_2\text{O}_3\) in the tailings (%), \(\beta_i\) is the ideal mass percentage of \(\text{V}_2\text{O}_5\) or \(\text{Fe}_2\text{O}_3\) in the concentrate (%), and \(\theta_i\) is the ideal mass percentage of \(\text{V}_2\text{O}_5\) or \(\text{Fe}_2\text{O}_3\) in the tailings (%). Based on the assumption that all of the vanadium and iron enter the vanadium–iron spinel, \(\beta_i\) was obtained by calculation and \(\theta_i\) was considered to be zero.

3 Results

| Table 2 Chemical compositions of the black shale and steelmaking slag /mass % |
|---------------------------|---|---|---|---|---|---|---|---|---|---|
| SiO₂ | CaO | MgO | Fe₂O₃ | Al₂O₃ | K₂O | S | P₂O₅ | V₂O₅ | MnO | C | Others |
| Shale | 65.61 | 6.86 | 2.45 | 2.86 | 7.70 | 2.27 | 1.52 | 0.83 | 0.98 | - | 7.59 | 1.33 |
| Slag | 9.06 | 39.97 | 10.36 | 31.14 | 2.24 | - | - | 2.33 | 0.86 | 2.49 | - | 1.56 |

The chemical compositions of the black shale and the steelmaking slag are given in Table 2. The black shale mainly consisted of silica and alumina. The steelmaking slag was composed of calcium oxide, iron oxide, silica, and magnesium oxide.
The XRD patterns of the shale and the slag are shown in Figure 1. The shale mainly consisted of mica and silica. The slag was composed of tricalcium silicate, dicalcium silicate, calcium oxide, RO and dicalcium ferrite. Besides the aforementioned phases, according to our previous studies, the slag contained a supercooled glass. The glass phase formed from molten slag without crystallization, consisting of CaO, SiO$_2$, FeO$_x$ and MgO.
According to the results of X-ray diffractometry for the samples roasted at 1573 K, the pattern of the sample with a basicity of 0.6 is closely to that of the sample with a basicity of 0.7, the patterns of the samples with basicity of 0.8, 0.9, 1.0, 1.2 and 1.5 are similar, and the pattern of the sample with 1.7 is quite different from the others. Thus, the XRD patterns of the samples can be split into three groups. Three representatives from the three groups are shown in Figure 2. As seen in the figure, the samples with lower basicities (0.6 and 0.7) mainly consist of aluminosilicate similar to muscovite, which indicates original structure of mica isn’t utterly destroyed, and the vanadium in the lattice of aluminosilicate isn’t released in full. The sample with a basicity of nearly 1.0 contains Ca₂MgSi₂O₇, KAl₂SiO₄, Fe and Fe₂O₄ (V-bearing spinel phase). In the sample with a basicity of 1.7, two crystalline phases of dicalcium silicate and composite silicate occur. V-bearing spinel phase wasn’t detected in the samples with low basicity and high basicity, which indicates that the formation of V-bearing spinel necessitates a moderate basicity.

The particle size distribution of the shale powder was as follows: the 75–150, 48–75, and <48 μm fractions accounted for 11.6%, 41.8%, and 46.6% of the total mass, respectively. In the steelmaking slag powder obtained by grinding, the 75–150, 48–75, and <48 μm fractions accounted for 26.1%, 18.7%, and 55.2% of the total mass, respectively. Although the roasted samples were grounded for the same time, the particle size distributions were different because of the mineral composition difference. This difference was relative small, and the 75–150, 48–75, and <48 μm fractions accounted for 30%, 19%, and 51% of the total mass, respectively.
Table 3  Fe$_2$O$_3$ and V$_2$O$_5$ contents and separation efficiencies

| No. | Concentrates $\beta$ /wt% | Tailings $\theta$ /wt% | Original grade $\alpha$ /wt% | Ideal grade $\beta_i$ /wt% | Efficiency /% |
|-----|---------------------------|------------------------|-----------------------------|---------------------------|--------------|
|     | Fe$_2$O$_3$ | V$_2$O$_5$ | Fe$_2$O$_3$ | V$_2$O$_5$ | Fe$_2$O$_3$ | V$_2$O$_5$ | Fe$_2$O$_3$ | V$_2$O$_5$ |
| 1   | 36.74 | 0.82 | 7.10 | 0.77 | 0.79 | 17.41 | 4.33 | 95.67 | 1.8 | 47.2 |
| 2   | 35.37 | 0.70 | 7.60 | 0.79 | 0.73 | 24.93 | 2.86 | 97.14 | -3.9 | 35.2 |
| 3   | 35.37 | 0.67 | 11.38 | 0.81 | 0.74 | 23.88 | 2.99 | 97.01 | -6.3 | 33.3 |
| 4   | 37.38 | 0.68 | 9.64 | 0.82 | 0.75 | 23.15 | 3.15 | 96.85 | -6.1 | 39.3 |
| 5   | 35.19 | 0.67 | 8.96 | 0.8 | 0.72 | 24.28 | 2.90 | 97.10 | -5.8 | 35.0 |
| 6   | 26.67 | 1.02 | 11.23 | 0.77 | 0.88 | 17.88 | 4.68 | 95.32 | -8.6 | 26.1 |
| 7   | 28.54 | 0.91 | 11.42 | 0.82 | 0.86 | 19.91 | 4.16 | 95.84 | 3.3 | 27.1 |
| 8   | 27.11 | 0.96 | 15.78 | 0.86 | 0.91 | 21.03 | 4.13 | 95.87 | 3.5 | 17.2 |
| 9   | 45.06 | 1.66 | 1.31 | 0.38 | 0.68 | 11.59 | 5.55 | 94.45 | 38.5 | 77.3 |
| 10  | 45.45 | 1.68 | 1.11 | 0.35 | 0.71 | 13.21 | 5.12 | 94.88 | 43.0 | 77.4 |
| 11  | 29.50 | 1.24 | 3.32 | 0.44 | 0.77 | 14.00 | 5.19 | 94.81 | 29.6 | 53.0 |
| 12  | 23.62 | 1.19 | 1.56 | 0.34 | 0.67 | 10.23 | 6.18 | 93.82 | 33.8 | 57.7 |
| 13  | 22.36 | 1.11 | 1.46 | 0.32 | 0.66 | 10.53 | 5.92 | 94.08 | 33.0 | 54.9 |
| 14  | 38.11 | 1.67 | 2.51 | 0.28 | 0.73 | 13.97 | 4.95 | 95.05 | 48.9 | 65.2 |
| 15  | 30.57 | 1.39 | 4.30 | 0.52 | 0.92 | 16.28 | 5.33 | 94.67 | 28.4 | 48.3 |
| 16  | 29.87 | 1.21 | 5.51 | 0.62 | 0.96 | 19.57 | 4.68 | 95.32 | 18.9 | 38.2 |
| 17  | 28.68 | 1.28 | 8.86 | 0.60 | 0.78 | 14.25 | 5.22 | 94.78 | 20.2 | 32.4 |
| 18  | 35.96 | 2.09 | 3.05 | 0.31 | 0.71 | 10.52 | 6.36 | 93.64 | 49.3 | 61.8 |
| 19  | 40.82 | 2.74 | 1.67 | 0.13 | 0.74 | 10.83 | 6.40 | 93.60 | 71.4 | 73.3 |
| 20  | 46.90 | 3.67 | 1.53 | 0.17 | 0.75 | 9.11 | 7.65 | 92.35 | 71.6 | 76.9 |
| 21  | 31.30 | 1.31 | 6.34 | 0.32 | 0.68 | 15.50 | 4.22 | 95.78 | 40.2 | 44.6 |
| 22  | 23.42 | 0.73 | 17.45 | 0.83 | 0.78 | 20.28 | 3.72 | 96.28 | -4.0 | 9.3 |

The V$_2$O$_5$ and Fe$_2$O$_3$ contents in the concentrates and tailings, and the calculated separation efficiencies are given in Table 3. The results indicate that the basicity, roasting temperature, and roasting time have large effects on the vanadium and iron separation efficiencies from the roasted samples.

4 Discussion

4.1 Theoretical analysis of V-concentrating phase formation

According to our previous study [36, 37], the vanadium in the shale is mainly located in the mica, and the vanadium in steelmaking slag exists in a glass phase and dicalcium silicate. In the process of roasting, mica in the shale first broke down into silicate and water. The silicate and silica in turn reacted to calcium oxide, dicalcium silicate, tricalcium silicate, a glass phase mainly consisting of calcium ferrite and RO
in the slag at higher temperature.

**Fig. 3.** Variation of standard Gibbs energy for several reactions with temperature

Standard Gibbs free energy for the possible reactions were plotted against temperature in Figure 3. The free energies are much less than zero, which indicates that the reactions may take place at 1273K to 1873K in term of thermodynamics. The reactions make the structures of mica, dicalcium silicate and the glass phase decompose. Vanadium oxide in the glass phase and crystal lattice of mica and dicalcium silicate was released, and iron oxide got liberated from glass phase and RO phase. In the study, the targeted compound of vanadium is V–bearing spinel (Fe$_{3-m}$V$_m$O$_4$). The released vanadium oxide and iron oxide need further interact each other, forming V–bearing spinel (Fe$_{3-m}$V$_m$O$_4$).

Vanadium and iron are the elements with variable valency and their valence is severely affected by oxygen partial pressure in atmosphere. Therefore, controlling oxygen partial pressure in atmosphere within an appropriate range is essential for obtaining the targeted compound. High pure argon gas can ensure the atmosphere.[36]

Binary chemical basicity, i.e. the ratio of calcium oxide content to silica content, is another key factor influencing occurrence state of vanadium. With increasing the basicity, vanadium attempts to form high valence oxides, combining to calcium oxide. Our previous studies demonstrated that vanadium was contained in dicalcium silicate (Ca$_2$Si$_{1-x}$V$_x$O$_4$ or Ca$_2$SiO$_4$·nCa$_3$V$_2$O$_8$) in the slags with high basicity [36]. Lower basicity improves the transform of iron element from high valence to low valence, reacting to acid oxides. In the studied system, FeSiO$_3$ would be generated in substantial amounts, which restrains the generation of the spinel. Influences from the two aspects would leads to an optimal basicity.

**4.2 Effect of the basicity**
The effect of the basicity on the vanadium and iron separation efficiencies is shown in Figure 4. For the samples roasted at 1473 K, with increasing basicity, the V$_2$O$_5$ separation efficiency remained low (even less than 0), i.e., the V$_2$O$_5$ content in the concentrate was less than that in the tailings. The Fe$_2$O$_3$ separation efficiency decreased with increasing basicity, and it also maintained a low level. For the samples roasted at 1573 K, with increasing basicity, the V$_2$O$_5$ separation efficiency first decreased, increased, and then decreased, reaching a maximum when the basicity was 1.2. This are consistent with theoretical analysis of V-concentrating phase formation. The variation trend of the Fe$_2$O$_3$ separation efficiency was similar to that of the V$_2$O$_5$ separation efficiency.

![Figure 4](image_url)

**Fig. 4.** Effect of the basicity on separation efficiencies of vanadium and iron

### 4.3 Effect of the roasting temperature

![Figure 5](image_url)

**Fig. 5.** Effect of roasting temperature on separation efficiencies of vanadium and iron.
The Fe₂O₃ and V₂O₅ separation efficiencies are plotted against the roasting temperature in Figure 5. With increasing roasting temperature from 1423 to 1623 K, the Fe₂O₃ separation efficiency increased and then decreased, reaching a maximum at 1573 K. The V₂O₅ separation efficiency greatly increased with increasing roasting temperature from 1423 to 1573 K, and it slightly increased when the roasting temperature increased from 1573 to 1623 K.

The reasons for the above trends are as follows. On the one hand, high temperature favors formation and growth of the vanadium–iron spinel phase, which is favorable for vanadium and iron separation. On the other hand, higher temperature leads to more liquid phase forming, and more vanadium oxide and iron oxide dissolve in the liquid phase, which results in an increase in the iron oxide content in the tailings.

4.4 Effect of the roasting time

The vanadium and iron separation efficiencies are plotted against the roasting time in Figure 6. With increasing roasting time from 1 to 3 h, the vanadium separation efficiency dramatically increased from 40.2% to 71.4%, and slightly increased to 71.6% when roasting time increased from 3 to 4 h. With increasing roasting time from 1 to 4 h, separation efficiency of iron gradually increased from 44.6% to 76.9%.

Generally, a long roasting time promotes crystal grain growth. Large crystal grains are conducive to separation, resulting in high separation efficiency. The experimental results are consistent with this principle.

4.4 Processing flow
Joint processing of V-bearing black shale and V-bearing steelmaking slag can be performed in two steps. In the first step, the mixture of the two is roasted. In the second step, after grinding, vanadium and iron are separated from the roasted material by magnetic separation, producing a concentrate and tailings.

The obtained concentrate mainly consisting of iron and vanadium can be used to produce V$_2$O$_5$ or vanadium–iron spinel. The tailings were mainly composed of calcium aluminosilicate and had high stability because of an appropriate basicity. Furthermore, the remaining vanadium in the tailings was present in the trivalent state in the form of spinel, which is relatively stable and non-toxic. Therefore, it can be used as building materials.

5 Conclusions

Based on investigation of joint roasting of V-bearing steelmaking slag and V-bearing black shale followed by magnetic separation, the effects of the roasting conditions on the vanadium and iron separation efficiencies can be summarized as follows.

1. With increasing basicity, in the samples roasted at 1573 K, the vanadium and iron separation efficiencies first decreased, increased, and then decreased, reaching a maximum when the basicity was 1.2. The vanadium and iron contents in the obtained concentrates showed a similar variation trend to the separation efficiencies.

2. Increasing the roasting temperature greatly affected the vanadium and iron separation efficiencies. The vanadium separation efficiency increased with increasing roasting temperature from 1423 to 1623 K. The iron separation efficiency increased with increasing roasting temperature from 1423 to 1573 K, and slightly decreased when the roasting temperature was increased from 1573 to 1623 K.

3. The roasting time had a significant effect on the vanadium and iron separation efficiencies. The vanadium separation efficiency increased from 40.2% to 71.4% when the roasting time was increased from 1 to 3 h, and it slightly increased from 71.4% to 71.6% when the roasting time was increased from 3 to 4 h. The iron separation efficiency increased from 44.6% to 76.9% when the roasting time was increased from 1 to 4 h.

4. Comprehensive evaluation of the vanadium and iron separation efficiencies and their contents in the concentrate showed that appropriate conditions are basicity of 1.2, roasting temperature of 1623 K, and roasting time of 4 h.

Acknowledgments

Financial support from the National Natural Science Foundation of China through Project Nos. 51774001 and 51534001 is gratefully acknowledged. We thank
Liwen Bianji, Edanz Editing China (www.liwenbianji.cn/ac), for editing the English text of a draft of this manuscript.

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Figure captions

**Fig. 1.** X-ray diffraction patterns of black shale and steelmaking slag.
**Fig. 2.** X-ray diffraction patterns of the samples roasted at 1573 K.
**Fig. 3.** Variation of standard Gibbs energy for several reactions with temperature
**Fig. 4.** Effect of the basicity on separation efficiencies of vanadium and iron
**Fig. 5.** Effect of roasting temperature on separation efficiencies of vanadium and iron.
**Fig. 6.** Effect of roasting time on separation efficiencies of vanadium and iron
Table lists

**Table 1** Experimental conditions
**Table 2** Chemical compositions of the black shale and steelmaking slag /mass %
**Table 3** Fe$_2$O$_3$ and V$_2$O$_5$ contents and separation efficiencies