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Thermodynamic and Experimental Studies of Selective Decomposition of Diopside in Ti-Bearing Blast Furnace Slag

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ABSTRACT: Titanium-bearing blast furnace slag (TBFS) is formed during the smelting of vanadium-titanium magnetite ore, containing more than 10 wt % Ti. The metal resource in TBFS has not yet been utilized because of the difficulty of extracting the objective phase from the complex eutectic. In this work, thermodynamic and experimental studies of selective leaching of diopside phase in TBFS in 20 wt % H_2SO_4 were conducted. The Gibbs free energy of reaction with H_2SO_4 calculated by applying a mechanical mixture model was in the order of Ti-bearing diopside < MgAl₂O₄ < Ti-rich diopside < CaTO₃. The extraction rate of Ti ions was controlled by the leaching temperature



and leaching time in 20 wt % H_2SO_4 . The extraction rate of Ti reached as high as 0.50 under optimal conditions. The diopside phases in TBFS were completely decomposed, while the perovskite (CaTiO₃) was almost unaffected by 20 wt % H_2SO_4 . The experimental results agreed with the trend of thermodynamic calculations, supporting their validity. The hydrolysis of TiOSO₄ showed the possibility of obtaining high-purity TiO₂. This work shows the selective leaching of the diopside phase in TBFS and suggests an environmentally friendly method for utilizing Ti-bearing blast furnace slag and waste acid.

1. INTRODUCTION

Titanium-bearing blast furnace slag (TBFS) is a byproduct formed during the production ofiron from vanadium-bearing titanomagnetite, with a high content of TiO_2 (21–25 wt %). It is estimated that 1 ton of TBFS is generated for every 1 ton of iron produced.1 The high content of TiO_2 in TBFS reduces the performance of building materials by breaking the bridge oxygen of SiO_4 tetrahedra, resulting in a low utilization rate (<3%) and significant slag accumulation (>100 million tons in total) of TBFS in the world.2 This may cause environmental pollution and also lead to the waste of titanium resources, making it necessary to accelerate Ti extraction from TBFS.

So far, there are challenges in extracting Ti from TBFS due to its mineral properties. TBFS is a complex mineral mixture formed by the rapid cooling of molten slag at approximatelyt 1600 °C, including some specialized minerals.3 The main Tibearing mineral phases in TBFS are perovskite, Ti-bearing diopside, and Ti-rich diopside, which contain over 90% Ti in TBFS.4 Perovskite (CaTiO₃) contains 37.9% Ti in TBFS and has a high TiO₂ content (55.8 wt %). The high TiO₂ content and high crystallinity of CaTiO₃ allow for direct beneficiation.5 Ti-bearing diopside and Ti-rich diopside (abbreviated as diopside) contain 53.7% Ti in TBFS but have a lower TiO₂ content (15–25 wt %). Ti, along with Si, Ca, Mg, and Al, forms a complex doped structure with low crystallinity in the diopsides, making it difficult to separate by direct beneficiation.4 Various methods for extracting Ti from TBFS have been proposed. A high-temperature carbonization and low-temperature chlorination process enables TBFS carbonization to form TiC at 1600–1800 °C and chlorinated at 400–600 °C to form TiCl₄.6 The alkali molten salt process uses strong alkalis such as NaOH to react with TBFS at 200–700 °C to form NaTiO₃, followed by leaching with strong acids such as HCl to form H₂TiO₃ and then calcination to form TiO₂.7 The acid leaching process uses concentrated acid, such as H₂SO₄ or HCl, to decompose TBFS to form TiOSO₄ or TiOCl₂; then, the titanium salts hydrolyze to form H₂TiO₃ and calcinate to form TiO₂.8 However, these methods do not take into account the differences between the mineral properties of CaTiO₃ and diopside, resulting in high energy consumption and long processes.

Waste acid is disposed in various industries, particularly in the production of TiO_2 pigments using the sulfate process. Approximately 6 tons of waste acid, which contains 20 wt % H_2SO_4 and 3 wt % Fe, is produced during the industrial production of 1 ton of $TiO_2.9$ The waste acid is usually

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Table 1. Approximate Composition of Main	Elements of TBFS	Measured by XR	F and Precise	Composition of	Fi, Al, Mg, and
Fe Measured by ICP					

XRF 23.4 16.4 7.4 5.3 3.5 3.3 0.44 0.76 0.46 0.29 ICD 11.7 7.6 4.2 20 20 11.7		Ca ,	Ti Si	Al	Mg	Fe	S	Mn	K	Na	V
ICP 11./ /.5 4.2 2.9	XRF ICP	23.4 1	16.4 7.4 11.7	5.3 7.5	3.5 4.2	3.3 2.9	0.44	0.76	0.46	0.29	0.18

neutralized with lime and converted into gypsum solid waste, which requires a more environmentally friendly treatment method. Currently, there are few studies on the extraction of Ti from TBFS using dilute acid leaching. Jiang et al.10 investigated the reaction between 10 and 60 wt % H_2SO_4 and two types of TBFS, including water-quenched slag (WQS) and naturally cooled slag (NCS). They found that Ti in both WQS and NCS was partially leached out, and the leaching rate of WQS was higher. This phenomenon may be related to the differences in the phase composition of WQS and NCS. Unfortunately, relevant studies have not been carried out.

In this study, we found that diopside in TBFS was completely dissolved by 20 wt % H_2SO_4 at 80 °C for 24 h, while CaTiO₃ in TBFS was barely decomposed. The Ti in the solution was finally hydrolyzed to form hydrated TiO₂. The estimated Gibbs free energy of the reaction, based on the mechanical mixture model, indicated that the decomposition of CaTiO₃ by H_2SO_4 is more difficult than that of diopsides. The relevant results provide a basis for the subsequent separation of titanium components.

2. EXPERIMENTS

2.1. Experimental Configuration. TBFS was obtained from Panzhihua Iron and Steel Group Co., Ltd. (China). The sample was ball milled, filtered by a 200-mesh sieve, and dried before experiments. Sulfuric acid was of analytical grade with a purity of 95.0-98.0% and purchased from Xilong Scientific Co., Ltd. (China). The dilute sulfuric acid used in leaching experiments was prepared by diluting H₂SO₄ with deionized water at a concentration of 20 wt %. The leaching experiment was conducted in a beaker. TBFS and the simulated acid were placed in the beaker with a slag/acid ratio of 1:10 to form a slag/acid slurry. The slag/acid slurry was heated in a silicone oil bath, with continuous stirring at 300 rpm, and maintained for a predetermined reaction time. The solution and the leaching residue were separated by centrifugation after the reaction was finished. The leaching residue was washed with deionized water, dried at 70 °C for 24 h, and ground before analysis. The solution was used to collect Ti under hydrothermal conditions in a 100 mL Teflon-lined stainless-steel autoclave (Beijing Xingde Instrument Equipment Co., Ltd., Beijing, China). The autoclave was sealed and fixed in a homogeneous reactor (Songling Chemical Equipment Co., Ltd., Yantai, China) and maintained at 120 °C for 4 h. The obtained solid and liquid were separated by centrifugation and analyzed, respectively.

2.2. Analysis Methods. The chemical composition of the TBFS raw material was identified using X-ray fluorescence (XRF, ARL PERFORM X, Thermo Fisher). The phase identification of the leaching residue was carried out with X-ray diffraction (XRD, D8 ADVANCE, Bruker Corporation) with a Cu-Ka (0.154178 nm) source. The diffraction data were collected at a speed of 5° /min in the region of $5-90^{\circ}$ with a step of 0.02° . The chemical composition of the leaching solution was analyzed by inductively coupled plasma-optical

emission spectrometry (ICP-OES, SPECTRO ARCOS, AMETEK, Inc.,)

2.3. Ti-Bearing Blast Furnace Slag. The approximate composition of main elements of TBFS measured by XRF and the more precise composition of the subject elements measured by ICP are presented in Table 1. There are errors between the ICP and XRF measurement results mainly due to sample heterogeneity and the measurement depth of XRF. TBFS contains more than 10 wt % Ti, which should be extracted in this study. TBFS mainly consists of diopside, CaTiO₃, and MgAl₂O (Figure 1). The compositions of Ti, Al, Mg, and Fe measured by ICP were used in the calculation of leaching rates in Section 3.



Figure 1. XRD pattern of TBFS.

3. RESULTS AND DISCUSSIONS

3.1. Thermodynamic Calculation. A thermodynamic study was conducted to understand the mechanism of the decomposition of TBFS by dilute sulfuric acid. No thermodynamic data have been reported for diopside phases due to their complex compositions. The mechanical mixing model was employed to simplify the materials with complex structures and to estimate the Gibbs free energy of the formation of diopsides. The chemical formulas of diopside phase were reported to be Ti-bearing diopside $((Ca_{0.96}Mg_{0.53},Ti_{0.46}Fe_{0.04},Mn_{0.01})(Si_{1.28},Al_{0.72})O_6)$ and Ti-rich diopside $((Ca_{0.35},Mg_{0.66},Ti_{0.45},Fe_{0.03},Mn_{0.01})(Si_{0.93},Al_{0.84},Ti_{0.23})$ - O_6). It is appropriate to use the two compositions reported by them as representatives in our study, as TBFS used by other researchers originates from the same place as the one used in this study. According to the mechanical mixture model, these components were considered as a mixture of simple chemicals. Each coefficient was determined by the least-squares method to minimize the sum of the squares of the residual for the composition of each original material.

The Gibbs free energy of the formation of Ti-bearing diopside and Ti-rich diopside are described as

$\Delta G^0_{f(Ca_{0.96}Mg_{0.53}Ti_{0.46}Fe_{0.04}Mn_{0.01})(Si_{1.28}Al_{0.72})O_6}$

$$= 0.16\Delta G_{fCaMgSi_2O_6}^{0} + 0.80\Delta G_{fCaO}^{0} + 0.37\Delta G_{fMgO}^{0} + 0.45\Delta G_{fTiO_2}^{0} + 0.02\Delta G_{fFe_2O_3}^{0} + 0.01\Delta G_{fMnO_2}^{0} + 0.3\Delta G_{fAl_2O_3}^{0} + 0.95\Delta G_{fSiO_2}^{0}$$
(1)

 $\Delta G^0_{f(Ca_{0.35}Mg_{0.66}Ti_{0.45}Fe_{0.03}Mn_{0.01})(Si_{0.93}Al_{0.84}Ti_{0.23})O_6}$

$$= 0.16\Delta G_{fCaMgSi_2O_6}^{0} + 0.22\Delta G_{fCaO}^{0} + 0.53\Delta G_{fMgO}^{0} + 0.73\Delta G_{fTiO_2}^{0} + 0.02\Delta G_{fFe_2O_3}^{0} + 0.05\Delta G_{fMnO_2}^{0} + 0.43\Delta G_{fAl_2O_3}^{0} + 0.66\Delta G_{fSiO_2}^{0}$$
(2)

The calculated ΔG_T^0 for Ti-bearing diopside and Ti-rich diopside are shown in Figure 2. This indicates the chemical stability of the diopsides.



Figure 2. Calculated Gibbs free energy of formation for Ti-bearing diopside and Ti-rich diopside.

The major reactions for the decomposition of Ti-bearing components with H_2SO_4 can be written as reactions (3)–(6) as written in Table 2. Figure 3 shows the calculated Gibbs free

Table 2. Reactions of Main Components in TBFS and $\rm H_2SO_4$

reactions	no.
$(Ca_{0.96}Mg_{0.53}Ti_{0.46}Mn_{0.01})(Si_{1.28}Al_{0.72})O_6 + 3.1H_2SO_4$	(3)
$\rightarrow 0.46 \mathrm{TiOSO_4} + 0.96 \mathrm{CaSO_4} + 0.53 \mathrm{MgSO_4} + 0.02 \mathrm{Fe_2(SO_4)_3}$	
+ 0.01 MnSO ₄ + 0.36 Al ₂ (SO ₄) ₃ + 1.28 SiO ₂ + 3.1 H ₂ O	
$(Ca_{0.35}Mg_{0.66}Ti_{0.45}Fe_{0.04}Mn_{0.01})(Si_{0.93}Al_{0.84}Ti_{0.23})O_6+3.0H_2SO_4$	(4)
$\rightarrow 0.35 \text{TiOSO}_4 + 0.35 \text{CaSO}_4 + 0.66 \text{MgSO}_4 + 0.02 \text{Fe}_2(\text{SO}_4)_3$	
+ 0.01 MnSO ₄ + 0.42 Al ₂ (SO ₄) ₃ + 0.93 SiO ₂ + 3.0 H ₂ O	
$CaTiO_3 + 2 H_2SO_4 \rightarrow TiOSO_4 + CaSO_4 + 2 H_2O$	(5)
$\mathrm{MgAl}_{2}\mathrm{O}_{4} + 4\mathrm{H}_{2}\mathrm{SO}_{4} \rightarrow \mathrm{MgSO}_{4} + \mathrm{Al}_{2}(\mathrm{SO}_{4})_{3} + 4\mathrm{H}_{2}\mathrm{O}$	(6)

energy changes of the reactions. The thermodynamic data of substances except diopsides were taken from references.11 The gibbs free energy change of thee reaction was in the order of (3) < (6) < (4) < (5), suggesting the high chemical stability of CaTiO₃ compared to other Ti-bearing components in H₂SO₄ solution.

3.2. Chemical Composition of Leaching Solution. The effect of the leaching temperature was investigated. The



Figure 3. Calculated Gibbs free energy of reactions (3)-(6).

leaching temperatures were set as 20, 40, 60, and 80 $^{\circ}$ C, and the leaching time was set as 4 h. Figure 4a shows the effect of



Figure 4. Extraction rate of (a) Ti and (b) Mg, Al, and Fe at different reaction temperatures for 4 h in 20 wt % H₂SO₄.

the temperature on the extraction rates of Ti in TBFS. The extraction rates were calculated using the following equation.

$$= \frac{\text{amount of extracted metal in solution}}{\text{metals contained in raw TBFS}}$$
(7)

As the leaching temperature increases, the extraction rate of Ti increases from 0.057 to 0.40. The reaction temperature of 20 °C was not sufficient for the reaction with 20 wt % sulfuric acid. The titanium extraction rate increased significantly because the viscosity of the sulfuric acid solution decreased with increasing temperature, which favored the transfer to the slag surface. In addition, as described in the next section, the precipitation of Ti due to hydrolysis did not dominate the extraction at a reaction temperature of 80 °C with a reaction time of 4 h, which also led to an increase in the extraction rate. Increasing the leaching temperature favored the acid decomposition of TBFS. The extraction rates of Mg, Al, and Fe are presented in Figure 4b. The extraction of Fe was effective even at 20 °C, and the rate was as high as 0.73, which increased to 0.90 by increasing the reaction temperature. The extraction rates of Mg and Al were linearly increased from 0.004 and 0.057 to 0.81 and 0.76, respectively. To investigate the effect of leaching time, the leaching times were set as 0.5, 1, 2, 3, 4, 6, 8, 12, 16, and 24 h, and the leaching temperature was set as 80 °C. The extraction rate of Ti is displayed in Figure 5a. The extraction rate of Ti showed a peak in 6 h and decreased in the next 10 h. The decline in the concentration of Ti ion is due to the hydrolysis of TiOSO₄ in the relatively low acid concentration and high reaction temperature and the



Figure 5. Extraction rate of (a) Ti and (b) Mg, Al, and Fe in different reaction times in 20 wt % H_2SO_4 at 80 °C.

formation of $\text{TiO}_2 \cdot \text{H}_2 \text{O}^{12,13}$ The reaction of hydrolysis is written below. The decomposition of TBFS and hydrolysis of TiOSO₄ proceeded simultaneously, and the Ti content in the solution reached its maximum after 6 h.

$$\text{TiOSO}_4(\text{aq}) + \text{H}_2\text{O} \rightarrow \text{TiO}_2 \cdot \text{H}_2\text{O}(\text{s}) + \text{H}_2\text{SO}_4 \tag{8}$$

Figure 5b shows the extraction rates of Mg, Al, and Fe. The extraction of Fe progressed rapidly within 1 h, and the rate reached 0.95, with little change after that hour. The extraction rate of Mg and Al increased significantly in the first 4 h and continued increasing slowly. The extraction rate reached 0.90 and 0.80 for Mg, and Al, respectively. From the trends in the extraction rate of Mg, Al, and Fe, it appears that the decomposition of TBFS was completed within 6 h at 80 °C.

3.3. Phase Composition of Residue. The XRD diffraction patterns of leaching residues at various temperatures are shown in Figure 6. Diopside phases and $CaTiO_3$ have no



Figure 6. XRD patterns of leaching residue at different reaction temperatures for 4 h in 20 wt % H_2SO_4 .

obvious change in their characteristic diffraction peaks at 20– 40 °C for 4 h. The diffraction peaks of diopsides slightly weakened, and the peaks of $CaSO_4$ ·2H₂O appeared at 60 °C due to the decomposition of the diopsides which contain CaO of more than 20 wt %.14 The diopside phases were mostly decomposed; in contrast, CaTiO₃ was difficult to be decomposed by 20 wt % H₂SO₄ at 80 °C. As shown in Figure 3 where the concentration of H_2SO_4 was not considered in the calculation, the Gibbs energy changes for the reactions of diopside, CaTiO₃, and MgAl₂O₄ with H_2SO_4 are all negative, indicating that all reactions proceed. However, the reaction Gibbs energy change of CaTiO₃ is smaller than that of the other phases and its reactivity is relatively low. This difference affected the reaction speed under the relatively mild conditions of 20 wt % H_2SO_4 , atmospheric pressure, and 80 °C.

The XRD patterns of the raw TBFS and leaching residues with different reaction times at 80 °C are shown in Figure 7.



Figure 7. XRD pattern of leaching residue at different reaction times in 20 wt % H_2SO_4 at 80 °C.

The clear peaks of CaSO₄·2H₂O appeared after the leaching experiment when the reaction times were shorter than 4 h. The dehydration of CaSO₄ occurred after 6 h of reaction, and CaSO₄·0.66H₂O and CaSO₄ were produced. The diopsides were completely decomposed in 8 h in 20 wt % H₂SO₄ at 80 °C. The diopside was completely decomposed in more than 6 h, and no peaks were observed from XRD. Perovskite was not completely decomposed even after 24 h, suggesting the stability of CaTiO₃ in 20 wt % H₂SO₄. The peaks of TiO₂· H₂O could not be detected from the XRD patterns while changes in the Ti concentration of the solution (Figure 5a) indicated the hydrolysis of TiOSO₄ and formation of TiO₂· H₂O with a reaction time of 6 h or more. This is because TiO₂· H₂O exhibits a very weak diffraction peak compared with other compositions due to the low crystallinity and small amount.

3.4. Hydrolysis of the Ti Ion. The leached Ti can be collected by hydrolysis under hydrothermal conditions. The leaching solution with the highest Ti content, extracted for 6 h, was treated under hydrothermal conditions at 120 °C. The reaction of hydrolysis is described as in ref 8, and a white powder was obtained. The XRD pattern of the obtained powder, shown in Figure 8, fits well with TiO₂ anatase, and the sample was defined as metatitanic acid (TiO₂·H₂O). The precipitation yields of Ti, Mg, Al, and Fe ions measured by ICP were 0.97, 0.013, 0.0082, and 0.061, respectively. Other studies have reported that the presence of magnesium and aluminum ions promotes the formation of Ti–O–Ti and hydrolysis of TiOSO₄.15 This result showed the possibility of producing high-purity TiO₂ from TBFS treated with 20 wt % sulfuric acid.



Figure 8. XRD pattern of the sample after hydrothermal treatment of the leaching solution.

Manufacturing TiO_2 for industrial use requires processes to remove impurities and control factors such ascrystal shape and particle size. In a case where TBFS was decomposed using 90% sulfuric acid, it was reported that Fe and V ions could be removed by controlling the hydrolysis conditions,16 and it is possible that impurities can be removed using a similar approach under our conditions.

4. CONCLUSION

Thermodynamic and experimental studies of the selective leaching of diopside phase in TBFS in 20 wt % H₂SO₄ were conducted. The thermodynamic property was revealed by applying the mechanical mixture model. The Gibbs free energy of reaction with H_2SO_4 was in the order of $MgAl_2O_4 < Ti$ bearing diopside < Ti-rich diopside < CaTO₃, suggesting that CaTiO₃ was more stable than other components in H₂SO₄ solution. The extraction rate of Ti was controlled by the leaching temperature and leaching time in 20 wt % H₂SO₄. Perovskite (CaTiO₃) was almost completely undecomposed even at a leaching temperature of 80 °C. Diopside phases were fully decomposed, and the extraction rate of Ti reached 0.50 in 6 h at 80 °C. The hydrolysis of TiOSO₄ occurred over a longer reaction time, with the precipitation of amorphous H₂TiO₃ leading to a decrease in the Ti concentration in the solution. Further hydrothermal treatment of the solution also showed the possibility of obtaining high-purity TiO2. This study provides ideas and theoretical basis for utilizing resources in blast furnace slag and waste acid.

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Notes

The authors declare no competing financial interest.

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