



## ENGINEERING SCIENCES

# Reaction Mechanism of Magnesium in Roasting of Vanadium Slag

LIU DONG, XUE XIANGXIN & YANG HE

**Abstract:** The influence of magnesium on roasting vanadium slag was investigated by simulating the roasting process of vanadium by mixing  $V_2O_5$  and MgO. The calcination products of  $V_2O_5$  reacted with MgO at different temperatures which were characterized by X-ray diffraction (XRD), Thermogravimetry-differential scanning calorimetry (TG-DSC) and scanning electron microscope (SEM). There were two mass loss intervals, three endothermic peaks and one exothermic peak appearing during the reaction by the integrated thermal analysis as the temperature increased from room temperature to 1273.15 K. The samples of mixed  $V_2O_5$  and MgO began to melt at 573.15 K and reacted at 773 K, and the shape of the particles changed from block to ovoid or irregular sphere at 773.15 K. With increasing the reaction temperature from 973.15 to 1073.15 K, the intermediate of  $VO_2$  was produced, and  $MgV_2O_6$  was partially decomposed at 1073.15 K. During this process, the particle shape gradually returned to block shape. The conversion rate of vanadium is 99.4% with MgO of 1.65%.

**Key words:** vanadium slag, roasting, simulation, magnesium.

## INTRODUCTION

Up to now, about 88% reserves of vanadium in the world are extracted from vanadium-titanium magnetite (Qiu et al. 2011), and the rest of that is collected from various minerals such as stone coal, and spent catalyst (Moskalyk & Alfantazi 2003, Li et al. 2013).

Vanadium slag is a crucial raw material for preparing vanadium and steel material containing vanadium in the present research. For the traditional vanadium production process, the vanadium slag is used to be roasted with sodium salt or calcium salt (Voglauer et al. 2004, Gabra & Malinsky 1981, Bradbury 2002, Song et al. 2014, Li et al. 2015, Cao 2012, Chen et al. 2013), such as NaCl,  $Na_2CO_3$ , or  $Na_2SO_4$  in rotary kiln or multiple hearth furnace filled with oxidizing atmosphere at the temperature around 1023.15 to 1123.15 K.

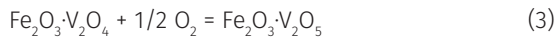
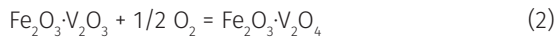
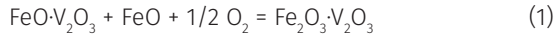
It is worth noting that various elements in the vanadium slag will affect the roasting process. Magnesium exists in vanadium slag in the form of spinel and complex oxides containing various metals (Wang 2011). Sodium magnesium slag has advantages over sodium slag for the next process to extract vanadium pentoxide (Sun 1995). However, there are few researches about effects of magnesium except chromium (Liu et al. 2016) and calcium (every 1% increase in CaO in slag will lose 4.7%–9.0% of  $V_2O_5$  (Peng et al. 2007)). Therefore, the effects of magnesium on salt roasting have been investigated and a theoretical basis for vanadium extraction was provided. The changes in the mineralogy of vanadium slag are studied by XRD, SEM, and TG-DSC. The effect of the roasting temperature on vanadium extraction and the characterization of leach residues are also discussed.

**MATERIALS AND METHODS**

Vanadium slag and the residue are from a steel group in Chengde, China. The vanadium slag is tail slag after the vanadium extraction from the converter, and the vanadium residue refers to the vanadium tailing obtained after the vanadium slag by sodium calcining-leaching-filtration.

The main mineral phases in vanadium slag are shown in Figure 1. The chemical compositions of vanadium slag and vanadium residue is given in Table I and Table II, respectively.

Vanadium extraction has been researched a lot by China and foreign scholars (Gabra & Malinsky 1981, Peng et al. 2007, Huang 2000, Wang et al. 1998, Wu 2008, Qiu et al. 2010, Li et al. 1994, Kozlov & Demidov 2000, Wen & Ding 1999, Fu et al. 2009, Shi et al. 2008). Vanadium pentoxide was extracted from vanadium slag using magnesium roasting technology in the study, and the reactions involving vanadium pentoxide and the reactions of spinel decomposition are as follows:

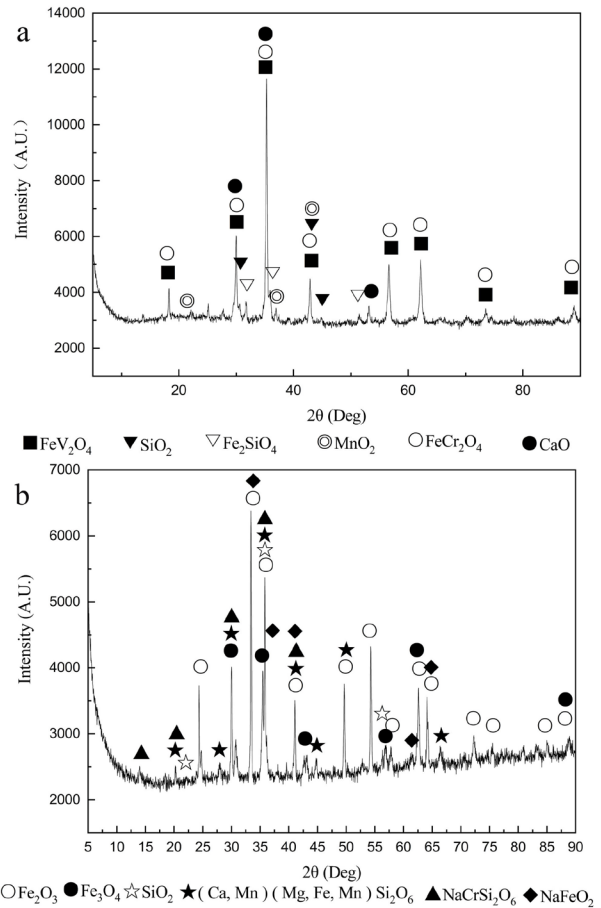


And the reactions involving magnesium and vanadium in the slag are as follows:

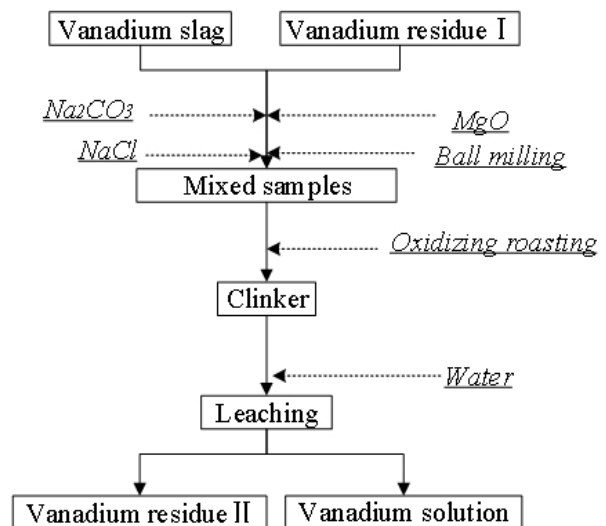


**Experimentation**

As shown in figure 2, the vanadium slag, vanadium residue, Na<sub>2</sub>CO<sub>3</sub>, NaCl and magnesium oxide were pretreated by mixing ingredients for 3 hours, subsequently were roasted with stirring in a vertical muffle furnace. The predetermined furnace temperature was maintained by a temperature controller. The furnace's door was



**Figure 1.** The XRD patterns of vanadium slag and vanadium residue. a: vanadium slag, b: vanadium residue.



**Figure 2.** Flow chat of experiment.

**Table I. Chemical compositions of vanadium slag (wt. %).**

Component	TFe	V	SiO <sub>2</sub>	CaO	Mn	MgO	TiO <sub>2</sub>	Cr	Na
wt. %	30.55	6.07	22.25	1.34	7.40	1.87	8.6	1.86	0.01

**Table II. Chemical compositions of vanadium residue (wt. %).**

Component	TFe	V	SiO <sub>2</sub>	CaO	Mn	MgO	TiO <sub>2</sub>	Cr	Na
wt. %	25.30	1.03	17.38	1.57	7.56	1.75	8.23	1.80	3.87

open to ensure the oxidizing atmosphere in the procedure above.

Cooled the roasted sample with water and heat the solution up to 353.15 K with stirring at 200 r/min, subsequently separate it via vacuum filtration. The concentration of vanadium in the solution was determined with ammonium ferrous sulfate titration.

The vanadium conversion rate was calculated by:

$$\text{Conversion rate} = 1 - \frac{[V]_s}{[V]_0} \times 100\%$$

Where  $[V]_0$  is the mass of vanadium in the mixed sample, and  $[V]_s$  is the mass of vanadium in the vanadium residue II. The conversion rate was calculated using the concentration of leaching solution instead of the concentration of leaching residue, this is because it is difficult to determine the mass of all residues accurately. The parallel experiments were conducted 3 times and the obtained extraction data was averaged to ensure the validity.

MgO and V<sub>2</sub>O<sub>5</sub> were pretreated by mixing ingredients for 3 hours, subsequently were roasted with stirring in a vertical muffle furnace.

### Effect of MgO on vanadium conversion rate

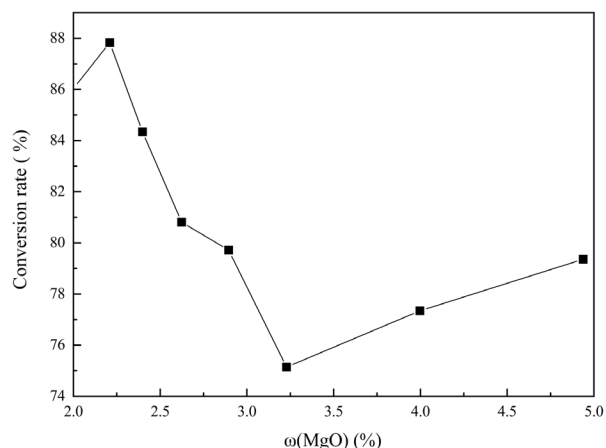
Table III shows that the mass ratios of Na<sub>2</sub>CO<sub>3</sub>/V<sub>2</sub>O<sub>5</sub> and Na<sub>2</sub>CO<sub>3</sub>/NaCl were 1.2 and 3.5, respectively. The vanadium content in the sample was kept

at 4.7% in the experiment, and the sample was kept at 1053.15 K for 100 minutes.

The silicate reacted with vanadium and additive to form glassy silicon vanadate, and there were 4 or 5 equivalents of vanadium moved into vitreous and insoluble vanadium compounds. Figure 3 shows that the conversion rate of vanadium decreased in the whole, with the increasing of the MgO content in the sample. The MgO content increased by 0.1% (with MgO in the range 1.65-3.23%), the rate of vanadium conversion decreased by 1.54%.

The conversion rate of vanadium sharply decreased from 99.4% to 75.14%, with the increase of MgO content from 1.65% to 3.23%. When the MgO content was less than 3.23%, the orthosilicate content was higher than metasilicate (olivine). However, the opposite situation occurred when the MgO content was more than 3.23%, and the destruction temperature of metasilicate (olivine) was higher than orthosilicate during the roasting process (the breaking temperature of (FeMgCa) SiO<sub>3</sub> needs to reach 1273.15 K (Chen 1993)), that was the reason why vanadium was difficult to diffuse in to diffuse in metasilicate (olivine). In addition, as the contact area between MgO and vanadium increased, the ability of MgO to react with vanadium to form magnesium vanadate increased, resulting in a slight increase in vanadium conversion rate.

Magnesium content at 1.65% was the control group without adding magnesium oxide.



**Figure 3.** Effect of MgO content on vanadium conversion rate.

In general, the addition of magnesium was detrimental to the conversion rate of vanadium in sodium roasting, since the increase of magnesium content in mixed slag would reduce the conversion rate of vanadium.

### Mechanism of magnesium on roasting vanadium slag

According to the research of vanadium slag calcined by sodium(or calcium) salt, when the ratio of sodium salt(or calcium salt) to vanadium pentoxide was 1, the primary product is metavanadate. When the molar ratio was 2, the main product is pyrovanadate. The main product was orthovanadate with increasing the molar ratio to 3 (Li et al. 2011, Gao et al. 2020, Zhang et al. 2015). Metavanadate was the most stable among them, followed by pyrovanadate, then orthovanadate. Orthovanadate was unstable and generally hydrolyzes after formation and was converted into pyrovanadate (Yang et al. 2014). In this experiment, magnesium metavanadate was used as the product. Magnesium oxide and the equal molar amount of vanadium pentoxide were roasted to study the reaction of magnesium on vanadium.

### XRD Analysis

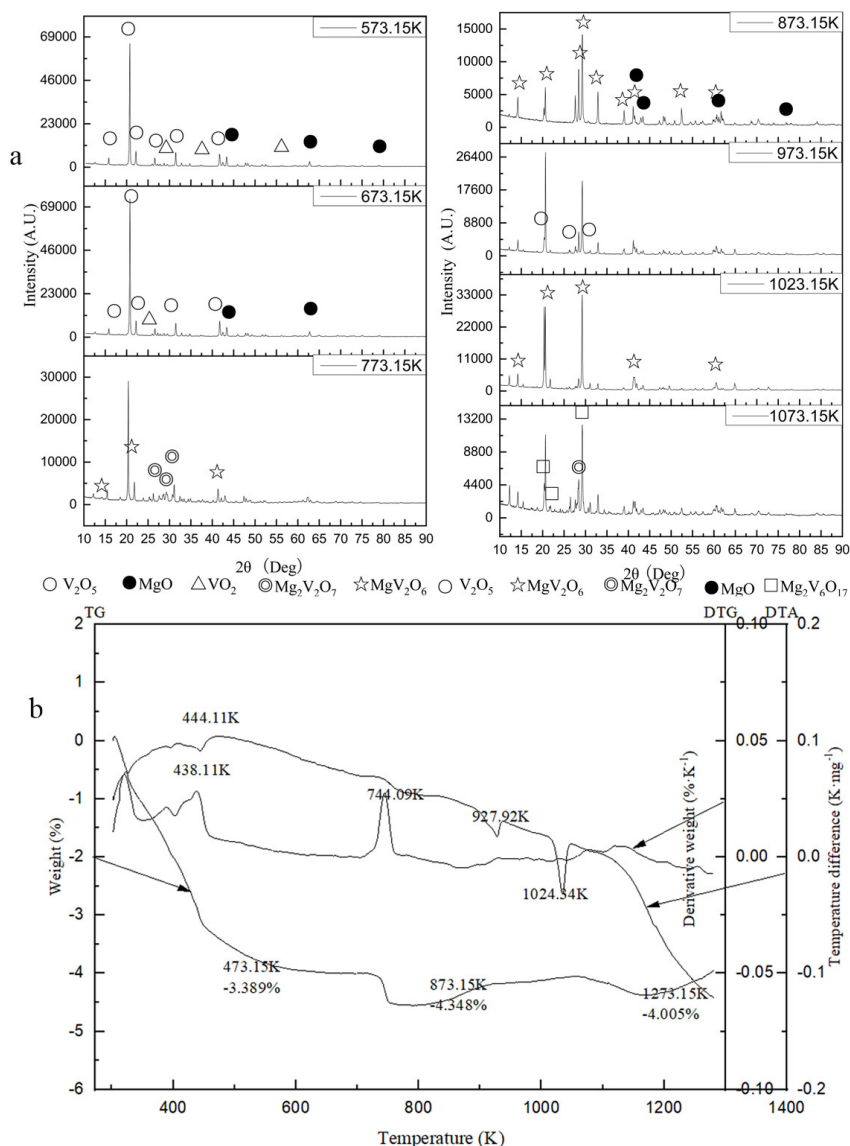
As shown in Figure 4a,  $V_2O_5$  did not react with MgO at the temperature below 673.15 K, while the appearance of  $VO_2$  indicated that  $V_2O_5$  decomposes at low temperature. When the temperature rose to 773.15 K, the phase peaks of  $MgV_2O_6$  and  $Mg_2V_2O_7$  appeared nevertheless, the phase peak of  $V_2O_5$  was still the strongest. Furthermore, the phase peak of  $VO_2$  disappeared, indicating that  $VO_2$  was mesophase.

When the temperature increased to 873.15 K, the intensity of the diffraction peak of  $MgV_2O_6$  increased sharply and became the main peak with the disappearance of  $V_2O_5$  and MgO, indicating that MgO and  $V_2O_5$  reacted vigorously and consumed several samples at 773.15 ~ 873.15 K. The phase peak of MgO disappeared and the peak intensity of  $V_2O_5$  continuously attenuated with the increase of temperature to 973.15 K, which indicated that the reaction between  $V_2O_5$  and MgO basically completed within the temperature range of 873.15 ~ 973.15 K. In addition, the intensity of the main peak of  $MgV_2O_6$  increased and shifted, indicating that the change of magnesium vanadate crystal form.

The peaks shifted again at 1023.15 K. The intensity of the main peak of  $MgV_2O_6$  became weakly at the temperature of 1073.15 K, and the phase peaks of  $Mg_2V_2O_7$  and  $Mg_2V_6O_{17}$  appeared, indicating that  $MgV_2O_6$  partially decomposed to insoluble  $Mg_2V_2O_7$  and  $Mg_2V_6O_{17}$  at temperature from 1023.15 to 1073.15 K. The experimental results were consistent with the conclusions of R.C. Kerby (Kerby & Wilson 1973).

### Comprehensive thermal analysis

Figure 4b shows that the first weight loss section appeared due to the removal of adsorbed water from room temperature up to 473.15 K. The second weight loss section appears due to deoxygenation from 673.15 K to 873.15 K.



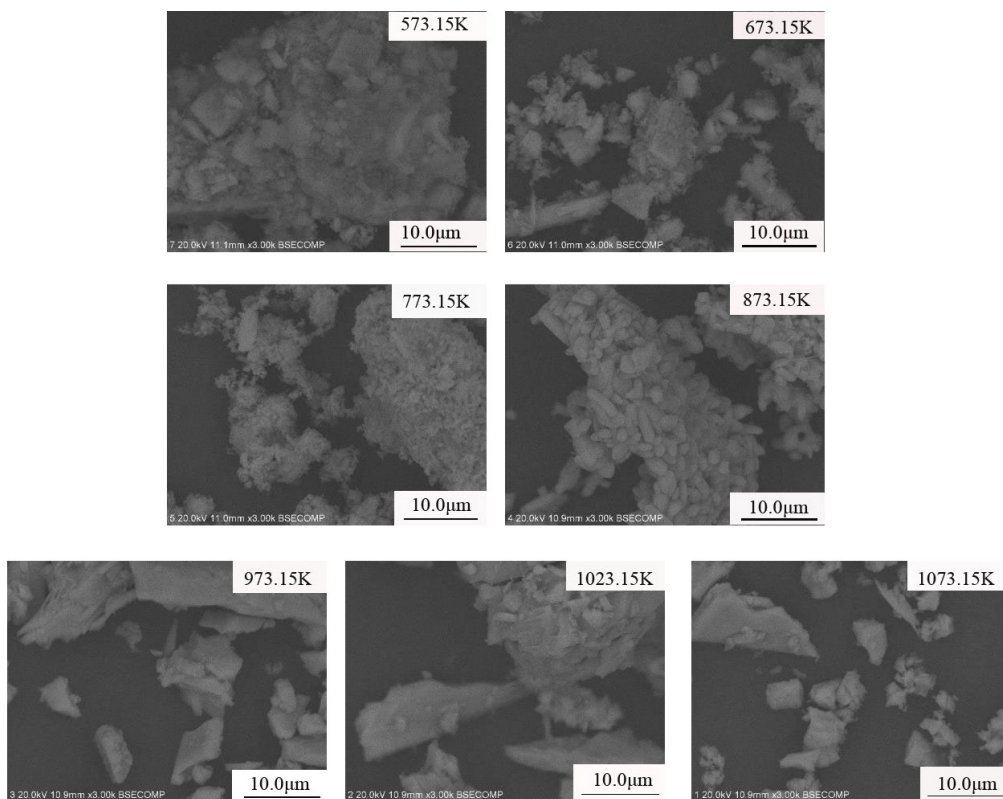
**Figure 4.** (a)The XDR pattern and (b) TG-DTG-DTA curve of sample roasted at different temperatures for 1 hour with the molar ratio of  $V_2O_5$  - MgO is 1:1. Instrument Name: SDT 2960 Simultaneous DSC-TGA (USTA Instruments).

The differential thermal analysis (DTA) figure 4b shows that the endothermic peak near the temperature of 443.15 K was due to the dehydration reaction, and the exothermic peak appears around the temperature of 743.15 K was due to the formation of  $MgV_2O_6$  and crystal transformation of  $V_2O_5$ . The endothermic peak near 923.15 K was due to the crystal transition of  $MgV_2O_6$ . In addition, the endothermic peak near 1033.15 K was due to the transition from  $MgV_2O_6$  to  $Mg_2V_2O_7$  and  $Mg_2V_6O_{17}$ .

### SEM analysis

Figure 5 shows that the sample was in the form of irregular powder melts and sticks at the temperature of 573.15 K. The sample consisting of clastic particles was collected with fine powders at the temperature of 673.15 K. Combined with XRD analysis, the sample was mainly composed of  $V_2O_5$ , MgO, and a few  $VO_2$  below 673.15 K.

At the temperature of 773.15 K, the sample consisted of massive particles with the attachment of abundant fine powders. The



**Figure 5.** The SEM images of sample roasted at different temperatures for 1 hour with the molar ratio of 1:1 between  $V_2O_5$  and  $MgO$ .

sample roasted at 873.15 K consisted of ovoid and irregular sphere particles with a few filamentous particles and clear surface. Combined with XRD analysis, the sample roasted at 773.15 K was mainly composed of  $V_2O_5$ ,  $MgO$ , a small quantity of  $MgV_2O_6$  and  $Mg_2V_2O_7$ , while the sample roasted at 873.15 K was mainly composed of  $MgV_2O_6$ , a few  $V_2O_5$ , and  $MgO$ .

Samples at 973.15 K mainly consisted of massive and ribbon-like particles with different particle sizes. The sample was composed of massive particles at 1023.15 K, where the large particles were breakable and could be further made into small particles. The sample at 1073.15 K was composed of different sized massive particles that were aggregated to form larger clusters. Combined with XRD analysis, the sample roasted at 973.15 K and 1023.15 K mainly consisted of  $MgV_2O_6$  and a small amount of

$V_2O_5$ . In addition, the sample roasted at 1073.15 K consisted of water-insoluble  $Mg_2V_2O_7$  and  $Mg_2V_6O_{17}$ .

## CONCLUSION

$V_2O_5$  in the sample did not react with  $MgO$  below 673.15 K, however reacted at 773.15 K to produce  $MgV_2O_6$ , which was decomposed into insoluble  $Mg_2V_2O_7$  and  $Mg_2V_6O_{17}$  at 1023.15 K to 1073.15 K.

From room temperature to 473.15K, the weight loss was mainly caused by dehydration, and the weight loss in the temperature range of 473.15 ~ 873.15 K was caused by the deoxidation reaction. The endothermic peak was observed at 444.11 K due to the dehydration reaction, and the exothermic reaction peak around 744.09 K was observed to the reaction of  $MgV_2O_6$  generating

**Table III. Experimental schemes for the effects of MgO on vanadium conversion.**

No.	vanadium slag/%	vanadium residue/%	Na <sub>2</sub> CO <sub>3</sub> /%	NaCl/%	MgO/%
1	76.38	6.19	10.91	3.12	4.94
2	76.18	7.34	10.91	3.12	4.00
3	76.02	8.28	10.91	3.12	3.23
4	75.95	8.69	10.91	3.12	2.89
5	75.90	9.03	10.91	3.12	2.62
6	75.81	9.53	10.91	3.12	2.21
7	75.77	9.79	10.91	3.12	2.00
8	75.68	10.29	10.91	3.12	1.65

and crystal transformation of V<sub>2</sub>O<sub>5</sub>. Furthermore, the endothermic peak around 927.92 K was due to the crystal transition of MgV<sub>2</sub>O<sub>6</sub>, and the endothermic peak at around 1024.34 K was observed to the conversion of MgV<sub>2</sub>O<sub>6</sub> to Mg<sub>2</sub>V<sub>2</sub>O<sub>7</sub> and Mg<sub>2</sub>V<sub>6</sub>O<sub>17</sub>.

The samples began to melt at 573.15 K and reacted at 773 K, and the shape of the particles changed from block to ovoid or irregular sphere. As the reaction temperature increased from 973.15 K to 1073.15 K, the particle shape gradually returned to block shape.

The conversion rate of vanadium is 99.4% with the addition of 1.65% MgO -under optimal conditions.

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Xue Xiangxin provided the project, guided the experiment. Yang He supported the experiment and participated in the review of the article. Liu Dong designed the experiment and did the experiment, analyzed the characterization data, and wrote the article.

