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Effects of roasting pretreatment on zinc leaching from complicated zinc ores

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Abstract: Roasting pretreatment and ammonia leaching were performed to extract zinc from complicated zinc ores. The residue of the unroasted ore showed that the zinc containing phase $ZnCO_3$ cannot be effectively leached in the ammonia leaching system. Mineral phase transformation of $ZnCO_3$ takes place at a roasting temperature of 673 K, and this is the reason for the improvement of zinc leaching recovery. Additionally, the parameters that can influence the leaching rate of zinc such as the calcined temperature, the total ammonia concentration, the ratio of liquid to solid, the stirring speed and the leaching time were also investigated. Zinc leaching recovery from the complicated zinc ores could reach 84.7% under the following optimized experiment conditions: roasting temperature of 673 K, leaching temperature of 298 K, stirring speed of 500 rpm, total ammonia concentration of 6 mol/l, liquid to solid ratio of 11:1 and leaching time of 60 min. Compared to the zinc leaching recovery from unroasted ore (49.7%, ammonia concentration 6 mol/l), roasting pretreatment and optimization of process parameters can increase the zinc leaching recovery by 70.4%.

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Keywords: ammonia leaching; complicated zinc ores; mineral phase transformation; roasting.

1 Introduction

Zinc is widely used in the galvanizing and battery manufacturing industries [1]. Currently, zinc is mainly produced from zinc sulfide ores owing to the fact that sulfides can be easier to separate from gangue minerals; in addition, sulfides are easily concentrated by conventional flotation techniques [2]. With the depletion of zinc sulfide ores, the utilization of low grade oxide zinc ores and other complicated zinc ores became an effective way to alleviate the shortage of raw materials in zinc companies [3, 4].

There is an abundance of complicated zinc ores in Yunnan Province of China, and the zinc reserve in the ores exceeds 10 million tons. However, mineralogical studies of complicated zinc ores show that the hemimorphite ($Zn_4Si_2O_7[OH]_2{\cdot}H_2O$) and smithsonite ($ZnCO_3$) are relatively difficult to be leached under inorganic acid conditions owing to the high silica content [5, 6]. Moreover, large amounts of inorganic acid will be consumed because a large amount of alkali gangue such as CaO and MgO exists in complicated zinc ores [7, 8]. Therefore, extensive research has been carried out on the new hydrometallurgical methods for extracting zinc from complicated zinc ores [9], and Zhang et al. [10] developed an ammonium chloride solution leaching technology to extract zinc from the zinc ores.

However, the mineral composition of low grade zinc oxide ores is complicated, and several kinds of zinc-containing phases exist in it, such as ZnO, $ZnCO_3$, $ZnSiO_3$, $Zn_4Si_2O_7(OH)_2{\cdot}H_2O$, and so on. Leaching of zinc from $ZnCO_3$ and $ZnSiO_3$ in the ammonium-ammonia leaching system is difficult [11–13]. How to improve the zinc recovery from complicated zinc ores? Mineral phase transformation is a good choice. Zhang et al. [5] studied the mineral phase transformation during roasting, and they found that the $ZnCO_3$ phase transformed to the ZnO phase at a temperature of 673 K, which was considered to be the reason for the improvement of zinc leaching recovery. Moreover, the leaching of zinc from roasted zinc leaching residue [14], the leaching of vanadium from roasted stone coal [15], the leaching of nickel from roasted laterite [16] and the leaching of phosphorus from roasted iron ore [17] were studied by other scientists, and mineral phase transformation turned out to be an effective method to process the complicated ores.

In this work, the effects of roasting temperatures on the zinc recovery from the complicated zinc ores were studied, and the mineral phase transformation during roasting was analyzed. In addition, the parameters that can influence the leaching rate of zinc such as the total concentration of ammonia, the liquid to solid ratio, the stirring speeds and the leaching time on zinc leaching behaviors were researched on the basis of a series of experiments. The aim of this work was to develop a new hydrometallurgical technology which can provide a green method to leach zinc from complicated zinc ores.

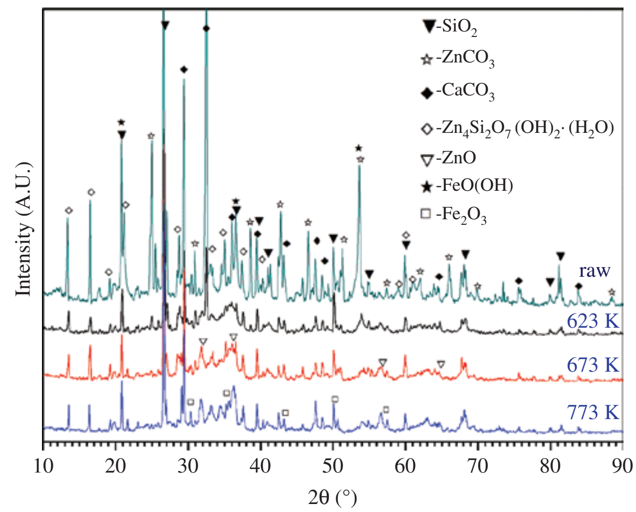

Figure 1: X-ray diffraction (XRD) patterns of complicated zinc ore before and after being roasted at various temperatures.

2 Materials and methods

2.1 Materials

The complicated zinc ores used in this study were provided by the Jinding Zinc Industry Ltd. in Yunnan Province of China. The ore was crushed and ground to a powder of <75 μm with a jaw crusher and a wet ball mill, and its chemical composition is listed in Table 1. The X-ray diffraction (Rigaku D/max-3B powder X-ray diffractometer equipped with Cu Ka radiation, 40 kV, 20 mA, Japan) spectra of the ores before and after roasting at various temperatures are shown in Figure 1, which shows that the major components in the ore are hemimorphite ($Zn_4Si_2O_7[OH]_2{\cdot}H_2O$), smithsonite ($ZnCO_3$), and gangue, such as calcite ($CaCO_3$) and quartz (SiO_2). All reagents used in this study were chemically pure, and deionized water was used for preparing leaching solutions. The ammonia-ammonium chloride solution used in this study was mixed using ammonia (Tianjin Jin Hui Tai Asia chemical limited company, Tianjin, China) and ammonium chloride (Shanghai Sinopharm Group, Shanghai, China) solution with the molecule ratio of 1:1.

2.2 Experimental procedure

With the unroasted ores, the leaching experiments were conducted in a 300 ml conical glass beaker equipped with a magnetic stirrer, and the experiment conditions were as follows: temperature of 298 K, reaction time of 60 min, stirring speed of 300 rpm and liquid to solid ratio of 3:1. The effects of the total ammonia concentration (from 3 mol/l to 8 mol/l) on zinc leaching recovery were studied. After being dried at 398 K for 3 h, the phase compositions of the leaching residues were detected, and the reason for the low zinc leaching recovery from the unroasted ore was analyzed.

The ores were calcined at different temperatures (623 K, 673 K, 723 K, 773 K and 823 K) in a muffle furnace for 30 min before the leaching processes, and the mineral phase transformation during roasting was analyzed. Moreover, the effects of roasting temperatures on zinc leaching recoveries were studied under the following experiment conditions: temperature of 298 K, reaction time of 60 min, stirring speed of 300 rpm, liquid to solid ratio of 3:1 and total ammonia concentration of 5 mol/l. The authors found that the zinc leaching recovery from the ores roasted at 673 K was the best, as shown in Section 3.2. Next, the effects of total ammonia concentrations (from 3 mol/l to 8 mol/l), liquid to solid ratios (from 3:1 to 15:1), desired stirring speeds (from 300 rpm to 900 rpm) and leaching time (from 30 min to 150 min) on zinc leaching recoveries of the ores calcined at 673 K for 30 min were investigated, and the leaching parameters were optimized.

After the leaching experiments, the pulps were filtrated, and the leaching residues were washed with water three times. Then, the zinc ion concentration in the lixivium was detected, and the leaching rate of Zn was calculated according to the following equation:

$$\eta_{Zn} = \frac{C_{Zn} \times V}{m \times W_{Zn}} \times 100\%$$

where C_{Zn}, V, m and W_{Zn} represent the Zn concentration of lixivium (g/l), the volume of lixivium (l), the weight of the zinc oxide ore (g) and the Zn content in the zinc ores (%), respectively.

Table 1: Chemical composition of the zinc oxide ores (wt.%).

Zn	Pb	Fe	Si	Ca	S
15.3	3.68	13.24	13.67	4.86	0.89

3 Results and discussion

3.1 Leaching experiment of unroasted ores

The effects of different total ammonia concentrations (from 3 mol/l to 8 mol/l) on the zinc recovery from unroasted ores are displayed in Figure 2, and the experiment conditions are shown in Section 2.2. The results showed that the zinc leaching rate of the unroasted ores increases with the increase of the total ammonia concentration. The optimal leaching rate of the complicated zinc ores is only 58.9% when the total ammonia concentration is 8 mol/l. In order to reveal the reason for the low zinc recovery, the residue of the complicated zinc ores after being leached in the solution with a total ammonia concentration of 8 mol/l was analyzed by X-ray diffraction (XRD), and the XRD pattern of the residue and that of raw ore are shown in Figure 3. Clearly, the peaks of $ZnCO_3$ can be found in the leaching residue, which illustrates that $ZnCO_3$ is difficult to be leached, and the result is in accord with the research results of Ju et al. [11] and Zhao and Robert [13]. This is the main reason for the low leaching rate of the unroasted ores under the condition of various total ammonia concentrations.

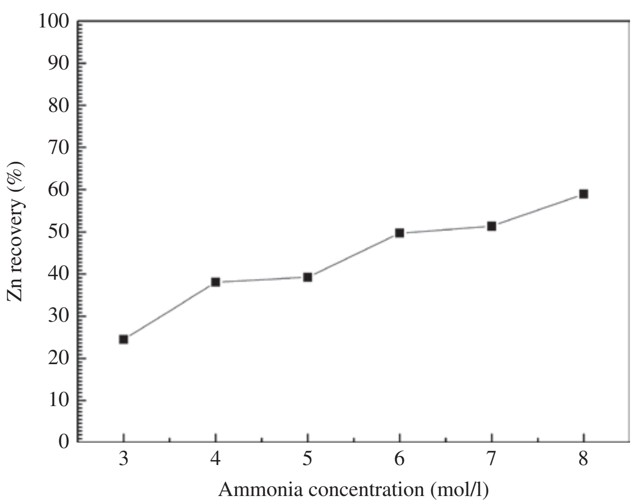

Figure 2: Effects of total ammonia concentrations on zinc recoveries of unroasted ores.

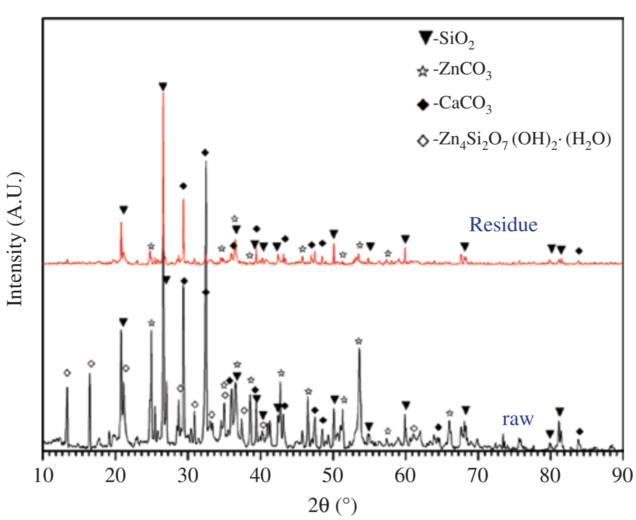

Figure 3: X-ray diffraction (XRD) patterns of complicated zinc ores before and after being leached in the solution with a total ammonia concentration of 8 mol/l.

3.2 Effect of calcination temperature

The effects of calcination temperatures on zinc recovery from complicated zinc ores were studied at the following experiment conditions: leaching temperature of 298 K, reaction time of 60 min, stirring speed of 300 rpm, liquid to solid ratio of 3:1 and total ammonia concentration of 5 mol/l. Figure 4 shows that the zinc leaching rate of the ore roasted at 673 K for 30 min can reach 67.0%, while that of the unroasted ores is only 39.2% under the same leaching conditions. It is obvious that the roasting operation can significantly improve the zinc leaching recovery from the ores. The best roasting temperature was 673 K, which is much lower than that being used in the zinc industry (about 1073 K). As a result, fewer energy sources will be consumed during roasting, and the technical route as shown in this work is green.

To reveal the mechanism of the increase of the Zn leaching rate, the phases of the complicated zinc ores calcined at different temperature (623 K, 673 K and 773 K) and the leaching residue of the ores roasted at 673 K were characterized by XRD. The XRD patterns of raw ores roasted at various temperatures are shown in Figure 1, and the XRD pattern of leaching residue roasted at 673 K is shown in Figure 5. From Figure 1, we find that the peaks of $ZnCO_3$ phase disappear from the XRD spectrum of the ore roasted

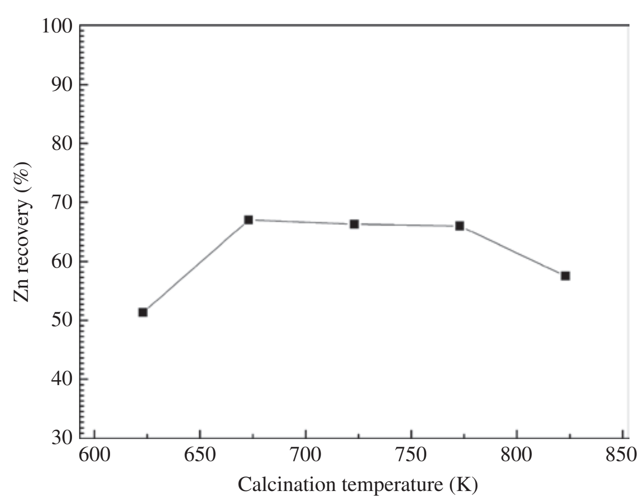

Figure 4: Zinc leaching recoveries of ores roasted at different temperatures.

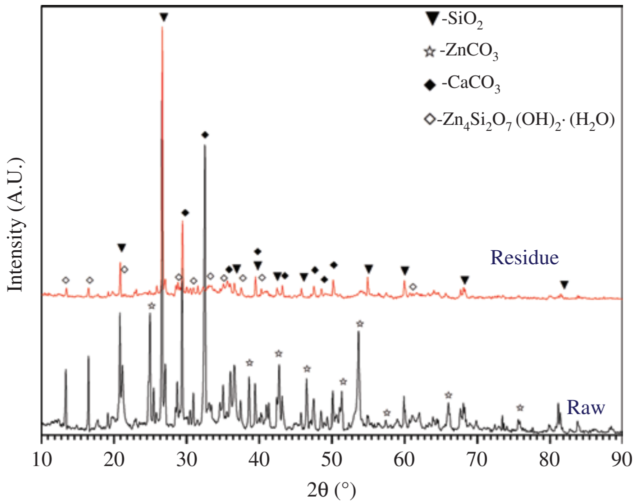

Figure 5: X-ray diffraction (XRD) patterns of leaching residue roasted at 673 K and the raw ore.

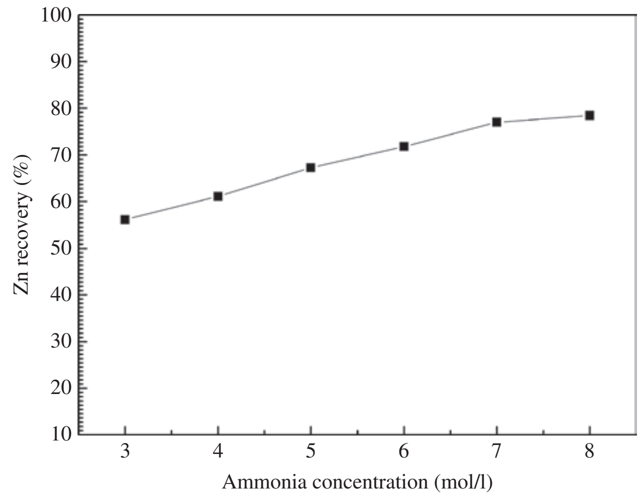

Figure 6: Effects of different ammonia concentrations on the zinc recoveries of the roasted ores.

at 673 K, and this phenomenon indicates that phase transformation happens at this temperature. From the XRD spectrum of leaching residue of the roasted ore, as shown in Figure 5, only some weak peaks of $ZnCO_3$ can be found, and this phenomenon can explain the improved zinc leaching recovery from the roasted ores. The zinc leaching recovery from the ores roasted at 673 K for 30 min is the best, and the roasting temperature of 673 K was chosen as a constant parameter in subsequent experiments.

3.3 Effect of ammonia concentration

The effects of the total ammonia concentrations (from 3 mol/l to 8 mol/l) on the Zn recovery from ores roasted at 673 K for 30 min were studied out at the following conditions: leaching temperature of 298 K, reaction time of 60 min, stirring speed of 300 rpm and liquid to solid ratio of 3:1. The leaching rates of the roasted ores leached in the solutions with different ammonia concentrations are shown in Figure 6, and it is obvious that the leaching rate of Zn rises sharply from 56.1% to 78.4% with the increase of total ammonia concentration. We find that the ammonia concentration plays an important role in the Zn leaching process.

However, with the ammonia concentration increasing from 6 mol/l to 8 mol/l, the Zn leaching rate rises from 71.8% to 78.4%, and the increase in margin is limited. In addition, with the increase of ammonia concentration, more ammonia will flash off from the leaching liquid and a higher cost should be expended. Therefore, an ammonia concentration of 6 mol/l was chosen as a constant parameter in the subsequent experiments.

3.4 Effect of liquid to solid ratio

The effects of liquid to solid ratio on the zinc leaching rate of the roasted ores were studied at the experiment conditions as follows: leaching temperature of 298 K, reaction time of 60 min, stirring speed of 300 rpm and ammonia concentration of 6 mol/l. The results of the liquid to solid ratios (from 3:1 to 15:1) on the zinc recoveries of the roasted ores are shown in Figure 7. When the liquid to solid ratio was 3:1, the zinc recovery from the roasted ores was only 71.8%. When the liquid to solid ratio is 15:1, the zinc recovery can reache 80.7%. It is worth noting that the zinc recovery increases slowly when the liquid to solid ratio exceeds

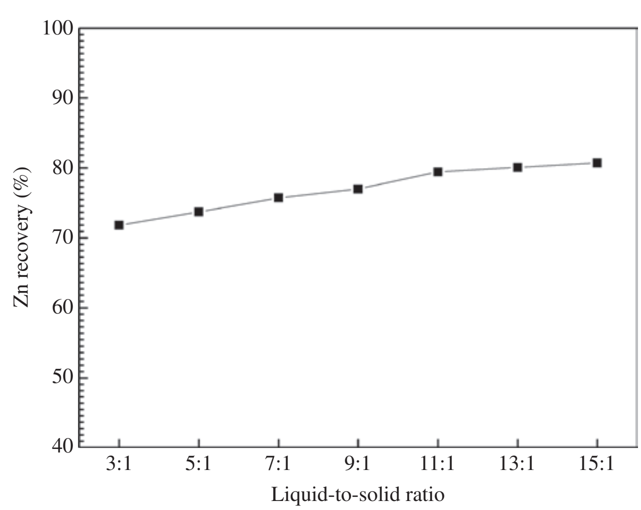

Figure 7: Effects of liquid to solid ratios on zinc recoveries of the roasted ores.

11:1. This is because C_{Zn} decreases with the increase of the liquid to solid ratio, and the impetus of the mass transportation (C_{Zn}^{S}-C_{Zn}) (C_{Zn}^{S} is the saturation of Zn in the leaching solution) improves [18]. Nevertheless, the higher liquid to solid ratio will lead to dilution of the lixivium, and this damages the next procedure (extraction) in the zinc production. Therefore, the liquid to solid ratio of 11:1 is chosen as a constant parameter in subsequent experiments.

3.5 Effect of stirring speeds

The effects of the stirring speed on zinc recovery from the roasted ores were evaluated using various stirring speeds, and the experiment conditions were as follows: leaching temperature of 298 K, reaction time of 60 min, total ammonia concentration of 6 mol/l and liquid to solid ratio of 11:1. Figure 8 shows the effects of different stirring speeds on the zinc recovery from the calcined ores, and it can be seen that the Zn leaching rate increases from 79.4% to 84.7% when the stirring speed rises from 300 rpm to 500 rpm. However, the Zn leaching rate remains at the level of 84.7% when the stirring speed exceeds 500 rpm. Thus, the stirring speed of 500 rpm is chosen as a constant parameter in subsequent experiments.

3.6 Effect of leaching time

The effects of leaching time on the zinc recovery from the roasted ores were investigated under the following conditions: leaching temperature of 298 K, stirring speed of 500 rpm, total ammonia concentration of 6 mol/l and liquid to solid ratio of 11:1. The leaching rate data are shown in Figure 9, and it can be found that the Zn recovery from the calcined zinc ores rises from 76.7% to 84.7% when the leaching holding time increases from 10 min to 60 min. Compared to the zinc leaching recovery from unroasted ores (49.7%, ammonia concentration 6 mol/l), the roasting pretreatment and the optimized process parameters can increase the leaching recovery from zinc by 70.4%, and after 60 min, the leaching rate of Zn remains at the level of 85.0%.

4 Conclusions

(1) The $ZnCO_3$ phase cannot be easily leached in the ammonia solution, and this is the reason for the low leaching rate of the complicated zinc ores.

(2) With roasting pretreatment to the complicated zinc ores at a temperature of 673 K for 30 min, the $ZnCO_3$ can completely decompose into ZnO. As a result, the zinc leaching rate of the roasted ores was improved.

(3) The zinc leaching recovery from the ores roasted at a temperature of 673 K can reach 84.7% under the following optimized experiment conditions: leaching temperature of 298 K, stirring speed of 500 rpm, total ammonia concentration of 6 mol/l, liquid to solid ratio of 11:1 and leaching time of 60 min. The roasting pretreatment and the optimized process parameters can increase the leaching recovery from zinc by 70.4% compared with that of the unroasted ores (49.7%, ammonia concentration 6 mol/l).

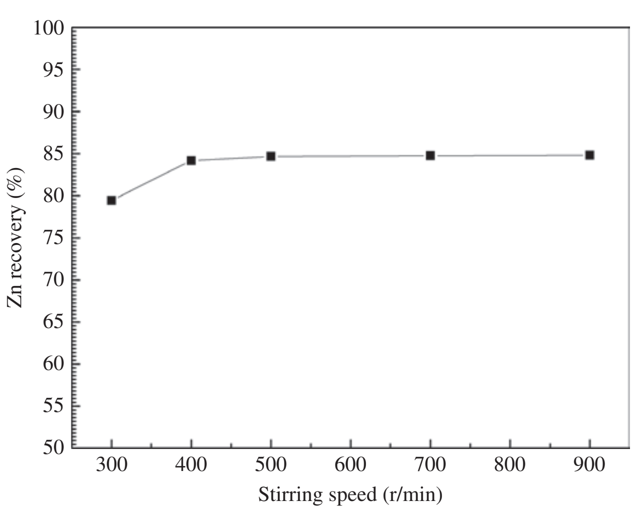

Figure 8: Effects of different stirring speeds on the zinc recoveries of the roasted ores.

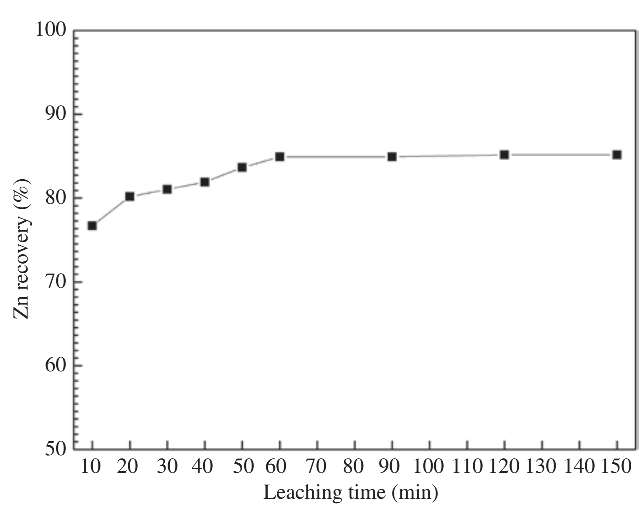

Figure 9: Effects of leaching time on zinc recoveries of the roasted ores.

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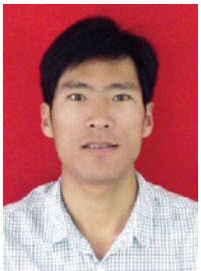

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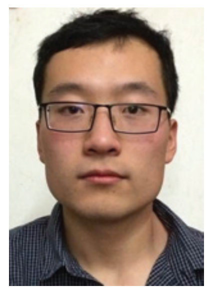

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