Discovery of impurities existing state in carbide slag by chemical dissociation

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Abstract

The existing states of impurities in carbide slag were investigated which can be a good guide for impurity removal by physical methods. The calcium phase and the impurities wrap each other made it hard to research impurities. Therefore an acid chemical dissociation method was firstly proposed via plotting Eh–pH-diagram of the Ca(OH)₂, CaCO₃, MgSiO₃, Al₂SiO₅, Fe₃O₄ and H⁺ system. The optimum dissociation condition (pH = 4.0) was deduced from Eh–pH-diagram and verified by X-ray diffraction, X-ray fluorescence spectrum and morphology analysis. Morphological and elemental chemical analyses of the dissociated residues revealed the existence of Si in the form of SiO₂, Fe and C existed as isolated particles of Fe₃O₄ and carbon respectively. Al and Mg were existed in the form of silicates such as Al₂SiO₅ and MgSiO₃. Si, Al and Mg always appeared together in the carbide slag, providing a possibility for their integral removal.

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1. Introduction

Carbide slag is industrial waste generated by calcium carbide hydrolysis when producing acetylene (C₂H₂), which is the raw material of polyvinyl chloride (PVC). (Eq. (1))

\[
\text{CaC}_2(s) + 2\text{H}_2\text{O}(l) \rightarrow \text{C}_2\text{H}_2(g) + \text{Ca(OH)}_2(s) + 64\text{kcal}
\]

(Ramasamy et al., 2002).

It was reported that 1.5–1.9 t of carbide slag was obtained when producing 1.0 t of PVC (Cheng et al., 2009). The high alkaline slag (pH ≥ 12) could result in environmental destruction such as land occupation and water pollution (Lei et al., 2011; Tub and Caulk, 2001; Hologado et al., 1992). Therefore, the management and disposal of carbide slag require special caution. In view of this, the comprehensive utilization of carbide slag has become an urgent issue for the sustainable development of acetylene industry using the calcium carbide method (Liu, 2005; H. Wang et al., 2007). Due to the presence of impurities (Zhi, 2007) in carbide slag, the complex pretreatment process and low value-added product are two critical problems for industry, which lead to the utilization rate less than 10% (Ding and Tang, 2007; Lin et al., 2006). Whether the impurities are efficiently removed or not is a significant issue.

Recycling carbide slag has aroused wide interest, accordingly, some physical separation methods, which have an advantage of lower cost, have been proposed for the removal of these specific impurities. The ways of physical pretreatment, such as the water washing, coarse screening and filtration drying, are not enough to remove the impurities in carbide slag completely (Tian and Lai, 2010; S. Wang et al., 2007). The reason of the low separation efficiency, to the best of our knowledge, may be the lack of study on the distribution characteristics, chemical composition and phase characteristics of impurities in carbide slag. Based on these researches, it is necessary to investigate the existing state of the impurities in carbide slag, which can be a good guide for impurity removal in carbide slag by physical methods, also for clarifying the separation mechanism.

We cannot analyze the distribution of impurities in carbide slag directly, mainly because calcium-based material and the impurities wrap each other. Moreover, CaCO₃ coated on the outermost layer of carbide slag particles made the research of impurities harder due to its chemical stability. Ca(OH)₂ and CaCO₃ in carbide slag should be removed in order to eliminate interference. As Ca(OH)₂ and CaCO₃ are acid-soluble, chemical dissociation was the most conducive way to study the existing state of impurities in carbide slag. However, it is difficult to determine the appropriate acidic conditions of chemical dissociation. Because on the one hand, a strong acidic condition will make a part of the impurities dissolve, and the original existence state of the impurities will changed. On the other hand, we cannot achieve the aim of the dissociation analysis through weak acidic conditions.

Therefore in this work, the multiple carbide slag was successfully dissociated. A detailed analysis of the existing state of the impurities

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2. Experimental

2.1. Materials

Carbide slag was collected from the Inner Mongolia, China. The chemical components of the carbide slag are shown in Table 1.

2.2. Experimental procedure

The carbide slag was dried at 100 °C for 12 h. 10 g carbide slag was added to 90 ml deionized water in a 500 ml beaker, which was stirred at a constant temperature water bath. The stirring speed was 300 r/min, and the temperature was 25 °C. The pH value was adjusted by adding 1.0 mol/l hydrochloric acid. Peristaltic pump was used to control the drop acceleration until the pH value reached the set value slowly. And then the dropping rate was kept to maintain a constant pH value and the range change of pH was less than 0.3 in the reaction system. The pH value was adjusted by adding HCl while avoiding the impurities to be dissolved. When pH = 4.0 (Fig. 4), the diffraction intensity of SiO2, Al2SiO5, MgSiO3 and Fe3O4 with their homologous ion. It is clear that the intersection region happen to correspond with 4.0 ± 1.0 on the abscissa. That is to say, if pH = 4.0 was taken as chemical dissociation condition, CaCO3 happened to be reacted with HCl while Al2SiO5, MgSiO3 and Fe3O4 could be avoided dissolution.

Based on the optimum chemical dissociation condition derived by the theory, the dissociation conditions of the original sample, pH = 2.0, pH = 4.0, pH = 6.0 and pH = 8.0 were selected as contrast experiments, and the filter residue was collected for analysis. The diffraction intensity of SiO2, Al2SiO5, MgSiO3 and Fe3O4 phases increased with the decrease of the pH value. The diffraction intensity of Ca(OH)2 and CaCO3 went through an opposite trend (Fig. 4). The relative element mass percentages of Ca increased with the decrease of the pH value (Fig. 5). This can be explained by the degree of SiO2, Al2SiO5, MgSiO3 and Fe3O4 exposure enlarged with the enhancement of acidity. When pH = 4.0 (Fig. 4), the diffraction peaks of CaCO3 disappeared compared with pH = 6.0 and pH = 8.0. The relative content percentage of Al, Fe and Mg reached the maximum when pH = 4.0 (Fig. 5). CaCO3 particles have a sudden mutation in the morphology analysis and there was rarely small amount of Ca(OH)2 coated on the surface of the slag in order to protect the MgSiO3, Al2SiO5, Fe3O4 impurities from dissolving. HSC chemical thermodynamics software (Huang, 1989a,b) was used to draw the comprehensive Eh–pH-diagram of the Ca(OH)2, CaCO3, MgSiO3, Al2SiO5, Fe3O4 and H+ system. The boundary line of each material thermodynamically predominance area within the system formed an intersection area (Fig. 3). The Eh–pH-diagram was built at 25 °C using Ca as the main element. The molality of Si, Al, Fe and Mg were 0.539 M, 0.148 M, 0.032 M and 0.020 M respectively, and the pressure is 1.0 bar. In the comprehensive Eh–pH-diagram, shaded area shows the stable region intersection of CaCO3, MgSiO3, Al2SiO5 and Fe3O4 with their homologous ion. It is clear that the intersection region happen to correspond with 4.0 ± 1.0 on the abscissa. That is to say, if pH = 4.0 was taken as chemical dissociation condition, CaCO3 happened to be reacted with HCl while Al2SiO5, MgSiO3 and Fe3O4 could be avoided dissolution.

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Table 1

<table>
<thead>
<tr>
<th>Component</th>
<th>Chemical contents of carbide slag (wt %)</th>
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<tbody>
<tr>
<td></td>
<td>CaO</td>
</tr>
<tr>
<td>CaO</td>
<td>54.20</td>
</tr>
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</table>

3. Results and discussion

3.1. Thermodynamic mechanism of chemical dissociation

The chemical dissociation process is schematically shown in Fig. 2. An optimal chemical dissociation condition was needed to remove only the Ca(OH)2 and CaCO3 coated on the surface of the slag in order to protect the MgSiO3, Al2SiO5, Fe3O4 impurities from dissolving. HSC chemical thermodynamics software (Huang, 1989a,b) was used to draw the comprehensive Eh–pH-diagram of the Ca(OH)2, CaCO3, MgSiO3, Al2SiO5, Fe3O4 and H+ system. The boundary line of each material thermodynamically predominance area within the system formed an intersection area (Fig. 3). The Eh–pH-diagram was built at 25 °C using Ca as the main element. The molality of Si, Al, Fe and Mg were 0.539 M, 0.148 M, 0.032 M and 0.020 M respectively, and the pressure is 1.0 bar. In the comprehensive Eh–pH-diagram, shaded area shows the stable region intersection of CaCO3, MgSiO3, Al2SiO5 and Fe3O4 with their homologous ion. It is clear that the intersection region happen to correspond with 4.0 ± 1.0 on the abscissa. That is to say, if pH = 4.0 was taken as chemical dissociation condition, CaCO3 happened to be reacted with HCl while Al2SiO5, MgSiO3 and Fe3O4 could be avoided dissolution.

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that some of impurities dissolved either. The relative content percentage of Ca had minimum content and Si had maximum content in the dissociation condition of pH = 2.0 from XRF results (Fig. 5). It suggested that the original chemical speciation of the Al2SiO5, MgSiO3 and Fe3O4 was destroyed by over dissociation.

To sum up, the HCl solution of pH = 4.0 was the optimal dissociation condition which made the impurities fully exposed from carbide slag and Al2SiO5, MgSiO3 and Fe3O4 were retained at the possible maximum.

3.2. Existing state of impurities in carbide slag

Before dissociation, the impurities could not be observed obviously from the morphology in the original sample. The carbide slag was composed of many uneven Ca(OH)2 and CaCO3 particles. Some distributed with small size particle while others reunited into large particles (Fig. 7). The major phases detected by XRD were Ca(OH)2 and CaCO3. Chemical components shown the content of Ca(OH)2 and CaCO3 were nearly more than 50%. However, each of the impurities was less than 5% (Figs. 4 and 5). It was indicated that a large amount of CaCO3 was contained from XRD and TG results (Figs. 4 and 8). This was mainly because the carbide slag had been stacked in the air so long that the Ca(OH)2 in it was reacted with CO2 in the air (Shih et al., 1999). CaCO3 coated on the outermost layer of carbide slag particles made the research of impurities harder due to its chemical stability. There are two peaks before dissociation compared with the particle size distribution after dissociation (Fig. 9). The change of particle size distribution further verified that we cannot analyze the distribution of impurities in carbide slag directly before chemical dissociation for the interference of Ca(OH)2 and CaCO3.

After dissociation, most Ca(OH)2 and CaCO3 were took off. The line scan of ED results showed that the mole ratio of Si/O was approximately equal to 1:2 (Fig. 10). Combined with phase analysis (Fig. 4), it was confirmed that Si existed in the form of SiO2 (100–150 μm). There were still some other elements on the surface of the silica-based particles except for Si. SiO2 particles acted as a carrier for other small particles of impurities such as Al and Mg. It was further illustrated that Si (27.62%), Al (6.082%) and Mg (0.827%) always appeared together in carbide slag by the surface scan analysis (Figs. 6 and 11). Combined with the phase analysis results (Fig. 4), Al and Mg in carbide slag existed in the form of silicates such as Al2SiO5 and MgSiO3 rather than metal oxide as described in the literature (Bai and Deng, 2004). The source of these impurities may come from feedstock of the production of limestone and coke ash (El-Naas et al., 1998).

Fe existed with a particle of about 30 μm alone which has a content of 1.929% in carbide slag (Figs. 5 and 12). It was particularly different from Al and Mg which existed by relying on SiO2. The mole ratio of Fe/O was...
approximately equal to 0.485 (Fig. 13). Combined with phase analysis (Fig. 4), Fe existed in the form of Fe$_3$O$_4$ in carbide slag.

The content of carbide impurity was 1.34% (Table 1), and C was generated by the process of the calcium carbide method in which contained some carbon impurities. The process can be showed in the reaction:

$$\text{CaO} + 3\text{C} \rightarrow \text{CaC}_2 + \text{CO}_\uparrow$$

(Pourbaix, 1966).

The C particles had a clear boundary with other material in carbide slag and the main composition was carbon combined with the EDS analysis results (Fig. 14).

To sum up, by precise deconstruction analysis, there were no chemical bonds among Ca(OH)$_2$, CaCO$_3$ and the impurities (MgSiO$_3$, Al$_2$SiO$_5$, Fe$_3$O$_4$ and C). The reason they wrap each other by physical bond mainly because of two aspects. On the one hand, the good water retention caused strong molecular surface tensions to make the particles reunited together (Wu et al., 2009). On the other hand, once carbide slag powder particles were squeezed, the contact area between particles increased which make particles relative movement harder for the huge specific surface area of carbide slag (Dong et al., 2008). It means that a way of the physical method may be used to strengthen the shearing action between Ca(OH)$_2$, CaCO$_3$ particles and the impurities (MgSiO$_3$, Al$_2$SiO$_5$, Fe$_3$O$_4$ and C). What’s more, compared the particle size distribution before and after dissociation (Fig. 8). The volume percentage in the range of particle size ($\leq$ 13 $\mu$m) was reduced after dissociation. This result was not only further instructed that pH = 4.0 was the optical dissociation condition which made the

**Fig. 5.** Relative element mass percentages of residues in different dissociation conditions.

**Fig. 6.** Optical microscope images of morphology difference of residues in different dissociation conditions.

**Fig. 7.** SEM image of the carbide slag before chemical dissociation.
Ca(OH)$_2$ and CaCO$_3$ particles. The conclusions imply that it is possible to be a good guide for impurity removal in carbide slag by physical existing state in carbide slag was conducted in this paper which can achieve the purpose of separation by centrifugal sedimentation.

4. Conclusions

A method of chemical dissociation especially for carbide slag was firstly proposed and a precise deconstruction analysis of impurities existing state in carbide slag was conducted in this paper which can be a good guide for impurity removal in carbide slag by physical methods. The conclusions can be drawn as follows:

(1) A comprehensive Eh–pH-diagram of the Ca(OH)$_2$, CaCO$_3$, MgSiO$_3$, Al$_2$SiO$_5$, Fe$_2$O$_4$ and H$^+$ system was proposed via plotting Eh–pH diagram by thermodynamic data.

(2) A predominance intersection area was formed by thermodynamically stable region when pH value was 4.0 ± 1.0. Within the scope of predominance diagram, calcium-based material happened to be reacted with HCl while avoiding the impurities to be dissolved.

(3) Si existed in the form of SiO$_2$ (100–150 μm); Al and Mg existed in the form of silicates such as Al$_2$SiO$_5$ and MgSiO$_3$ which depended on small SiO$_2$ particles. Si, Al and Mg always appeared together in the carbide slag. Fe and C existed as isolated particles of Fe$_2$O$_4$ (about 30 μm) and C (30–60 μm) respectively.

(4) By the precise deconstruction analysis, the junction state of Ca(OH)$_2$, CaCO$_3$ and the impurities (MgSiO$_3$, Al$_2$SiO$_5$, Fe$_2$O$_4$ and C) were physical bonds other than chemical bonds. These imply that a way of centrifugal sedimentation may be suited to strengthen the shearing action between Ca(OH)$_2$, CaCO$_3$ particles and the impurities and achieve the purpose of separation. What’s more, the co-existence of Si, Al and Mg had significant effects on impurity integral removal.

Acknowledgements

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References


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<th>Ca</th>
<th>Si</th>
<th>Al</th>
<th>Fe</th>
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<td>49.96</td>
<td>0.76</td>
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<td>0.33</td>
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<td>28.26</td>
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<td>0.12</td>
<td>0.3</td>
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**Fig. 10.** SEM image and EDS analysis of Si.

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<tr>
<th>Element</th>
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<th>Ca</th>
<th>Si</th>
<th>Al</th>
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<tr>
<td>Weight%</td>
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<td>37.24</td>
<td>2.53</td>
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<td>35.66</td>
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<td>2.02</td>
<td>1.24</td>
<td>0.3</td>
<td>0.65</td>
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**Fig. 11.** SEM images and EDS analysis of Si, Al, and Fe.
### Element C O Ca Si Al Fe Cl Mg

<table>
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<tr>
<th>Weight%</th>
<th>51.31</th>
<th>25.58</th>
<th>1.62</th>
<th>2.28</th>
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**Fig. 12.** SEM images and EDS analysis of Fe.

### Element O Si Al Fe

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<tr>
<td>Atomic%</td>
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<td>0.37</td>
<td>32.48</td>
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**Fig. 13.** SEM images and EDS analysis of Fe.
### Table 1: Elemental Analysis of C, O, and Si

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<th>Element</th>
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<th>Si</th>
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<td>Weight%</td>
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<td>Atomic%</td>
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*Fig. 14. SEM images and EDS analysis of C.*